Investigating gas adsorption, PSM and molecular-level structure in MOFs

Shoushun Chen
The University of Western Ontario

Supervisor
Yining Huang
The University of Western Ontario

Graduate Program in Chemistry
A thesis submitted in partial fulfillment of the requirements for the degree in Doctor of Philosophy
© Shoushun Chen 2018

Follow this and additional works at: https://ir.lib.uwo.ca/etd

Recommended Citation
https://ir.lib.uwo.ca/etd/5822

This Dissertation/Thesis is brought to you for free and open access by Scholarship@Western. It has been accepted for inclusion in Electronic Thesis and Dissertation Repository by an authorized administrator of Scholarship@Western. For more information, please contact wlswadmin@uwo.ca.
Abstract

Metal-organic frameworks are hybrid organic-inorganic solids that have many important applications including gas storage, separations, heterogeneous catalysis, drug delivery, electrochemical storage and conversion. Although they have various applications, the gas adsorption mechanism, local structures and molecular-level features (which are important to understanding and improving the specific performance of MOFs) are often ambiguous. In this work, a combination of multiple techniques including solid-state NMR (SSNMR), single crystal XRD (SCXRD) and computational methods is employed to investigate gas adsorption mechanism and molecular-level structure in several MOFs. Equally important is the design of functionalized MOFs with a variety of functional groups, since the modified MOFs can gain enhanced and/or new performance in many applications. Therefore, this thesis is also focused on modifying MOFs by introducing various non-framework metal ions and organic functional groups via post-synthetic modification (PSM).

Chapter 1 is a brief introduction of MOFs and SSNMR. In Chapters 2 and 3, gas adsorption mechanism in MOFs Pb-, Cd-SDB (SDB: 4,4′-sulfonyldibenzoate) and Cu(INAIP) (5-(isonicotinamido) isophthalate) were investigated by a combination of SSNMR and SCXRD. In addition, based on the SCXRD of gas loaded Cu(INAIP), computational methods were used to elucidate the host-guest interaction. In Chapter 4, 14 different non-framework metal ions have been loaded into MOF MIL-121 via its free carboxylic acid groups. The materials have been extensively characterized. Several metal loaded MIL-121 variants show enhanced gas adsorption and excellent catalytic performance. In Chapter 5, we found that hierarchical pores can be created in the microporous MIL-121 via controlled linker thermolysis. The MOFs with both micropores and mesopores were characterized by a combination of gas adsorption test, scanning electron microscope (SEM) and multinuclear SSNMR. In Chapter 6, the hierarchical MIL-121 obtained in Chapter 5 has been used for grafting several organic molecules and Pt salts by PSM. In chapter 7, $^{43}$Ca SSNMR and quantum chemical calculations are used to probe the local structure of calcium metal centers within several Ca-MOFs.
Keywords

Metal–organic frameworks, gas adsorption, single crystal XRD, solid-state NMR, post-synthetic modification.
Co-Authorship Statement

This thesis contains materials from previously published manuscripts and Shoushun Chen initiated all the studies described in Chapters 2-7. Chapter 2 is based on the published article co-authored by Shoushun Chen, Bryan E.G. Lucier, Paul D. Boyle, and Yining Huang (Chem. Mater., 2016, 28, 5829-5846.) The samples were prepared by Shoushun Chen. Experiments were performed by Shoushun Chen, Bryan E.G. Lucier and Paul D. Boyle. Shoushun Chen wrote the first draft of the manuscript which was revised by Bryan E.G Lucier and Yining Huang.

Chapter 3 is based on the published communication co-authored by Mansheng Chen, Shoushun Chen, Wei Chen, Bryan E.G. Lucier, Yue Zhang, Anmin Zheng and Yining Huang, (Chem. Mater., 2018, 30, 3613–3617). The single crystal samples were prepared and solved by Mansheng Chen. NMR experiments were performed by Shoushun Chen and Yue Zhang. Wei Chen did the theoretical calculation. The first draft of the manuscript was written by Shoushun Chen and revised by Bryan E. Lucier, Anmin Zheng and Y. Huang.

Chapter 4 is based on the published article co-authored by Shoushun Chen, Bryan E.G. Lucier, Wilson Luo, Xinkai Xie, Kun Feng, Hendrick Chan, Victor V. Terskikh, Xuhui Sun, Tsun-Kong Sham, Mark S. Workentin and Yining Huang (ACS Appl. Mater. Interfaces, 2018, just accepted, DOI: 10.1021/acsami.8b08496). Samples were prepared by Shoushun Chen. NMR experiments were performed by Shoushun Chen, Bryan E.G. Lucier and V. V. Terskikh. X-ray experiments were performed by Hendrick Chan. Gas adsorption tests were carried by Shoushun Chen and Xinkai Xie. Kun Feng did the TEM tests and Wilson Luo was responsible for the catalyst part. The first draft of the manuscript was written by Shoushun Chen and every author contributed in editing the manuscript.

For chapter 5, samples were prepared by Shoushun Chen. NMR experiments were performed by Shoushun Chen and Bryan E.G. Lucier. Dr. Victor V. Terskikh is also credited for some SSNMR spectra presented in Chapter 5. The manuscript was written by Shoushun Chen and revised by Ying-Tung Wong and Yining Huang.

For chapter 6, samples were prepared by Shoushun Chen. NMR experiments were performed by Shoushun Chen and Bryan E. G. Lucier. Prof. Xueliang Sun and Zhongxin Song were
responsible for the collection and analysis of the electrochemical data. They also provided a
draft of the catalysis results that was incorporated into the manuscript. The first draft of
manuscript was written by Shoushun Chen and revised by Ying-Tung Wong and Yining
Huang.

Chapter 7 is based on the published communication co-authored by Shoushun Chen, Bryan
E.G. Lucier, Mansheng Chen, Victor V. Terskikh, and Yining Huang (Chem. Eur. J., 2018, 24,
8732-8736). Samples were prepared by Shoushun Chen and Mansheng Chen. Gas adsorption
tests and PXRD were performed by Shoushun Chen. Dr. Victor V. Terskikh was responsible
for the collection of SSNMR spectra and DFT calculations. The manuscript was written by
Shoushun Chen and revised by Bryan E. G. Lucier and Yining Huang.
Acknowledgements

First of all, I want to give my deepest gratitude to my advisor, Prof. Yining Huang, for not only accepting me as his student at Western University, but also being a great mentor. In the past five years, he gave me tremendous help in my studying and lab work which helped shape and stimulate my interest in scientific research. Without his help and patience, none of my achievements or this dissertation would have been possible.

I also wish to thank Prof. Lars Konermann, Prof. David W. Shoesmith for serving in my committee and for their advice on my first and third year reports. I would like to thank Dr. Johanna M. Blacquiere for her suggestions on my first year report. I also want to take this chance to thank Prof. Yang Song, Prof. John F. Corrigan, Prof. Tsun-Kong Sham, Prof. James A. Wisner for their inspiring courses, which were very valuable for my research. I would like to thank Dr. Victor V. Terskikh and Dr. Mathew Willans for their help in SSNMR experiments. Dr. Paul Boyle and Aneta Borecki have offered assistance with x-ray data collection in many instances and I really appreciate their help. I also want to thank Prof. Xueliang Sun (Department of Engineering), Prof. Mark S. Workentin, Prof. Xuhui Sun (Soochow University) and Prof. Mike Zaworotko (University of Limerick) for offering their guidance in my research.

I want to thank the past and current members in our research group: Dr. Jun Xu, Dr. Wei Wang, Dr. Haiyan Mao, Dr. Farhana Gul-E-Noor, Dr. Yue Hu, Dr. Yue Zhang, Dr. Tetyana Levchenko, Yuanjun Lu, Xuzhao Zhao, Shan Jiang, Zitong Wang, Peng He, Jiacheng Guo, Dr. Mansheng Chen, Dr. Ying Guo, Vinicius Martins, Ying-Tung Wong, Kyungseop Lee, Bligh Desveaux, Bawei Wu, Hendrick Chan and Maxwell Goldman. I want to give my special thank to our postdoc Dr. Bryan E. G. Lucier. We have worked together in this lab for four years and he was extremely helpful for my NMR experiments and preparing manuscripts. He is also a great friend and we have spent so many wonderful times in the grad club and playing golf.

Lastly, I would like to thank all the members in my family for supporting me for all these years. My family is from a small village in China. My parents have never left China, but still encouraged me to pursue my studies in Canada. Without their love and support, I would not be here, let alone finish this degree. I just want to say I love them forever.
# Table of Contents

Abstract .................................................................................................................................................... i  
Co-Authorship Statement ....................................................................................................................... iii  
Acknowledgments .................................................................................................................................... v  
Table of Contents .................................................................................................................................. vi  
List of Tables ............................................................................................................................................ ix  
List of Figures .......................................................................................................................................... x  
List of Abbreviations ............................................................................................................................... xvi  
Chapter 1 .................................................................................................................................................. 1  
  1 Background .......................................................................................................................................... 1  
    1.1 Introduction of MOFs ....................................................................................................................... 1  
    1.2 Application of MOFs in gas adsorption and separation ................................................................. 7  
    1.3 Introducing extra functional groups and metal ions into MOFs by post-synthetic modification (PSM) .................................................................................................................................................. 11  
    1.4 Solid state nuclear magnetic resonance (SSNMR) study in MOFs ................................................. 14  
    1.5 Outline of the thesis ....................................................................................................................... 20  
    1.6 References ..................................................................................................................................... 22  
Chapter 2 .................................................................................................................................................. 25  
  2 Understanding the Fascinating Origins of CO$_2$ Adsorption and Dynamics in SDB-based MOFs .............................................................................................................................. 25  
    2.1 Introduction ..................................................................................................................................... 25  
    2.2 Results and discussion ..................................................................................................................... 28  
    2.3 Conclusion ..................................................................................................................................... 54  
    2.4 References ..................................................................................................................................... 54  
    2.5 Appendix ....................................................................................................................................... 59  
Chapter 3 .................................................................................................................................................. 75
Analyzing Gas Adsorption in an Amide-Functionalized Metal Organic Framework: Are the Carbonyl or Amine Groups Responsible? .......................................................... 75

3.1 Introduction ............................................................................................................. 75

3.2 Results and discussion ............................................................................................ 77

3.3 Conclusion ............................................................................................................... 85

3.4 References .............................................................................................................. 85

3.5 Appendix ............................................................................................................... 86

Chapter 4 ......................................................................................................................... 103

4 Loading Across the Periodic Table: Introducing Fourteen Different Metal Ions to Enhance MOF Performance .............................................................................. 103

4.1 Introduction ............................................................................................................. 103

4.2 Results and discussion ............................................................................................ 106

4.3 Conclusion ............................................................................................................... 118

4.4 References .............................................................................................................. 119

4.5 Appendix ............................................................................................................... 122

Chapter 5 ......................................................................................................................... 159

5 Understanding Thermally Triggered Hierarchical Pores in Metal-organic Frameworks .................................................................................................................... 159

5.1 Introduction ............................................................................................................. 159

5.2 Results and discussion ............................................................................................ 161

5.3 Conclusion ............................................................................................................... 173

5.4 References .............................................................................................................. 173

5.5 Appendix ............................................................................................................... 174

Chapter 6 ......................................................................................................................... 182

6 Post-synthetic Modification via Anhydride Groups in a Hierarchical Metal-organic Framework: A Novel Efficient “Anchor” ........................................................................ 182

6.1 Introduction ............................................................................................................. 182

6.2 Results and discussion ............................................................................................ 184
6.3 Conclusion .............................................................................. 194
6.4 References ............................................................................ 194
6.5 Appendix ............................................................................. 195

Chapter 7 ..................................................................................... 205

7 Probing Calcium-Based Metal-Organic Frameworks via Natural Abundance $^{43}$Ca Solid-State NMR ........................................................................ 205

7.1 Introduction ........................................................................... 205
7.2 Results and discussion .......................................................... 207
7.3 Conclusion ........................................................................... 212
7.4 References ........................................................................... 213
7.5 Appendix ............................................................................. 214

Chapter 8 ..................................................................................... 230

8 Summary and Future Work ....................................................... 230

8.1 Summary ............................................................................. 230
8.2 Future work ........................................................................ 232

Appendices: Copyright Permission ............................................ 234
Curriculum Vitae .......................................................................... 238
List of Tables

Table 1-1 The compositions in flue gas from a coal-fired power plant................................. 10
Table 1-2 The 20 MOFs with the highest selectivity for CO₂ over N₂................................. 11
Table 1-3 Magnitudes of nuclear interactions in liquids and solids ................................. 15
Table 2-1 The apparent, or observed, ¹³C NMR parameters of adsorbed ¹³CO₂ in SDB-based MOFs at different temperatures. .......................................................................................................................... 30
Table 2-2 The CO₂ motional data obtained from EXPRESS simulations of ¹³C VT SSNMR spectra. .................................................................................................................................................. 32
Table 2-3 ²⁰⁷Pb NMR parameters of various PbSDB samples as obtained from simulations of static WURST-CPMG experiments................................................................. 41
Table 2-4 ¹¹¹Cd NMR parameters of activated and CO₂-loaded CdSDB, as obtained from static VT ¹H-¹¹¹Cd CP-echo experiments......................................................................................... 41
Table 5-1 The porosity parameters in thermally treated MIL-121 based on N₂ gas adsorption. ............................................................................................................................................. 163
Table 7-1 Experimental and calculated ⁴³Ca MAS NMR parameters for calcium based MOFs. .............................................................................................................................................. 208
Table 7-2 The experimentally observed and calculated differences in δ_{iso}(⁴³Ca) between different MOF forms.................................................................................................................. 209
List of Figures

Figure 1-1 (a) An illustration of the assembly process of MOFs. (b) The number of reported new MOFs in the Cambridge Structural Database (CSD) since 1972........................................... 2

Figure 1-2 (a) The ditopic carboxylate linkers used to construct IR MOFs and the crystal structure of IRMOF-1-16. (b) The ditopic carboxylate linkers used to expand and/or functionalize UiO-66, the local structure of UIO-66, as well as the crystal structure of UiO-66/67/68 ........................................................................................................................................ 4

Figure 1-3 (a) The template assistant synthesis of hierarchical MOFs. (b) Hierarchical MOFs created by introducing “defects” via chemical labile linkers................................................. 5

Figure 1-4 The crystal structures of HKUST-1, PCN-6’ and MOF-399. ......................... 6

Figure 1-5 (a) The SBU, organic linker and crystal structure of MIL-101. (b) The formation of OMS in MIL-101........................................................................................................................................ 7

Figure 1-6 The ligand, cages and local structure of UMCM-2 (a) and NU-100 (b)........... 8

Figure 1-7 (a) Crystal structure of MOF-74. (b) The local environment of the adsorbed CO\textsubscript{2} and OMSs in MOF-74. ........................................................................................................ 9

Figure 1-8 The PSM method in comparison with direct synthesis and post-synthetic exchange (PSE)........................................................................................................................................ 12

Figure 1-9 (a) The introduction of Pd inside UiO-66. (b) Loading Ir and Pd into bpy-UiO-67.. ........................................................................................................................................ 13

Figure 1-10 Illustration of the Zeeman interaction for a spin-\textit{l}/2 nucleus. ...................... 16

Figure 1-11 (a) The second rank tensor of chemical shielding described in its PAS; (b) the Herzfeld-Berger conventions................................................................................................. 17

Figure 1-12 Simulated $^{13}$C spectra (9.4 T) with different $\delta_{\text{iso}}$, $\Omega$ and $\kappa$. ................. 18

Figure 1-13 $^2$H SSNMR spectra (9.4 T, $\delta_{\text{iso}} = 0$ ppm) with different $C_Q$ and $\eta_Q$ values........ 19
Figure 1-14 (a) Schematic illustration of CO$_2$ local wobbling. (b) The dynamic simulation of CO$_2$ local wobbling ........................................................ ........................................................... 20

Figure 2-1 The experimental static $^{13}$C VT SSNMR spectra of PbSDB loaded with saturated $^{13}$CO$_2$ are shown at left in (a), and the corresponding spectral simulations to extract apparent NMR parameters are shown at right in (b).......................................................... 29

Figure 2-2 In (a), simulated $^{13}$C SSNMR spectra incorporating both the wobbling and hopping motions are shown above experimental spectra, along with the threefold wobbling angles ($\alpha$) and twofold hopping angles ($\beta$) determined at each temperature. In (b), the two motion model of CO$_2$ dynamics in PbSDB is depicted .......................................................... 31

Figure 2-3 (a) The extended lattice of the CO$_2$-loaded PbSDB crystal structure is depicted, as viewed along the crystallographic a axis. The local structure about the CO$_2$ “$\pi$-pocket” adsorption site is shown in (b). In (c) and (d), two adjacent symmetry-equivalent adsorbed CO$_2$ molecules are shown from different perspectives. (e), the proposed two-motion model for CO$_2$ dynamics in PbSDB is illustrated .......................................................... 33

Figure 2-4 Experimental static $^{13}$C VT SSNMR spectra of CO$_2$-saturated CdSDB are shown in (a), accompanied by the analytically simulated spectra to extract observed NMR parameters in (b).......................................................................................... 36

Figure 2-5 The simulated $^{13}$C SSNMR spectra associated with adsorption site 1 in CdSDB are shown as the purple spectra, along with motional simulations to obtain the extracted threefold wobbling angles ($\alpha$) and twofold hopping angles ($\beta$) at each temperature............. 37

Figure 2-6 The static $^{207}$Pb and $^{111}$Cd SSNMR spectra of PbSDB and CdSDB in various conditions are depicted........................................................................................................ 39

Figure 2-7 The extended crystal structure of CdSDB loaded with saturated CO$_2$, as seen along the c axis, is shown in (a). In (b), the local positions of adsorbed CO$_2$ molecules in CdSDB are shown. The local environment about C1A is depicted in (c) along with its missing symmetry equivalent site. In (d), the distances between C1B/C1A and adjacent cadmium atoms are shown........................................................................................................ 45
Figure 2-8 ¹H-¹³C CP/MAS NMR experiments on activated (a) PbSDB and (b) CdSDB at a spinning frequency of 14 kHz.

Figure 2-9 The extended crystal structure of CdSDB and PbSDB loaded with saturated CO₂ are shown in (a) and (b), respectively. The local structure of CO₂ molecules adsorbed at site 1 in CdSDB and at the only adsorption site within PbSDB are shown in (c) and (d). The green “V” shape drawn above the phenyl rings of the SDB linker in (c), (d), and (f) highlights the V-shaped “π-pocket” associated with CO₂ adsorption in these systems. The carbon atoms associated with both unique CO₂ adsorption sites in CdSDB are shown in (g), and the sole CO₂ adsorption site along with its equivalent neighboring CO₂ adsorption site are shown in (h).

Figure 2-10 The extended crystal lattice of CdSDB loaded with unsaturated CO₂ is depicted in (a), as viewed along the c axis. The locations of the symmetry-equivalent carbon atoms associated with CO₂ adsorbed in CdSDB are shown in (b).

Figure 3-1 The extended lattice of the CO₂-loaded Cu(INAIP) SCXRD structure is shown in (a), with hydrogen omitted for clarity. In (b), the local environment about CO₂ is depicted. The experimental and simulated static ¹³C VT SSNMR spectra of adsorbed ¹³CO₂ are illustrated in (c), accompanied by the geometry-optimized local environment in (d). An electron density plot including CO₂ and the amide group is shown in (e), and the electron density graph for CO₂ and H13 of the MOF is given in (f).

Figure 3-2 The SCXRD structure of C₂H₂-loaded Cu(INAIP) is shown in (a) and (b), with hydrogen omitted for clarity. The computationally optimized C₂H₂ local environment is given in (c). In (d), electron density plots of C₂H₂ and O3/O1 of the carboxylate groups (I) along with C₂H₂ and O5 of the amide (II) are shown. Experimental (blue) and simulated (red) ²H VT NMR spectra of C₂D₂-loaded Cu(INAIP) are found in (e), along with simulated contributions from free C₂D₂ gas (light blue) and both hydrogen sites in C₂H₂ (purple and green traces).

Figure 3-3 The long-range SCXRD structure of CH₄-loaded Cu(INAIP) with hydrogen omitted is shown in (a), along with the adsorbed CH₄ local structure in (b). The DFT-optimized CH₄ local environment are illustrated in (c). An electron density plot including
CH$_4$ and O5(amide)/H7 is shown in (d), accompanied by an electron density plot about CH$_4$ and O2 of the carboxylate groups in (e). The static $^2$H VT SSNMR spectra of CH$_4$-loaded Cu(INAIP) are shown in (f).

Figure 4-1 $^1$H–$^{13}$C CP/MAS SSNMR spectra of MIL-121 and Na/Ag/Ca/Zn/Mn/Co-MIL-121 are illustrated in Figure 4-1a; the corresponding $^1$H MAS SSNMR spectra of these samples are provided in Figure 4-1b.

Figure 4-2 a): The $^{43}$Ca MAS NMR spectrum of Ca-MIL-121 and simulated MAS spectrum of the guest metal source Ca(OH)$_2$ are shown. b): The static $^{207}$Pb WURST-CPMG NMR spectra of Pb-MIL-121 and the guest metal source Pb(OAc)$_2$·3H$_2$O are illustrated. In c), $^1$H–$^{111}$Cd CP/MAS NMR spectra of Cd-MIL-121 and the guest metal source Cd(OAc)$_2$·2H$_2$O are depicted. The 21.1 T $^{39}$K MAS NMR spectrum of K-MIL-121 and the simulated MAS spectrum of the guest metal source K$_2$CO$_3$ are provided in d). In e), the 21.1 T $^{25}$Mg MAS SSNMR spectrum of Mg-MIL-121 is shown, along with a MAS spectral simulation of the metal source Mg(OAc)$_2$. The $^{67}$Zn static NMR spectrum of Zn-MIL-121 and simulated spectra of the guest metal source Zn(OAc)$_2$·2H$_2$O and non-hydrated Zn(OAc)$_2$ are given in f). The static $^{139}$La WURST-CPMG NMR spectrum of La-MIL-121 and the guest metal source La(OAc)$_3$·1.5H$_2$O along with simulated spectrum of non-hydrated La(OAc)$_2$ are illustrated in g). In h), the static $^{115}$In SSNMR spectra of In-MIL-121 and guest metal source In(OAc)$_3$ are shown. The silver K-edge EXAFS of Ag-MIL-121 and metal source AgOAc are depicted in i), along with an XPS analysis of Ag NPs@MIL-12 in j).

Figure 4-3 In (a), the adsorption-desorption isotherms for H$_2$ in MIL-121 and metal-loaded MIL-121 variants are shown, as obtained at 77 K for pressures under 10 bar. The adsorption isotherms for CO$_2$ in MIL-121 and metal-loaded MIL-121 variants at 273 K under 1 atm are illustrated in (b). Finally, in (c), the adsorption-desorption isotherms for N$_2$ in MIL-121 and metal-loaded MIL-121 variants at 77 K under 1 bar are depicted.

Figure 4-4 a) and b): The TEM images of Ag NPs@MIL-121 (1.80 wt%) are shown. c): A series of UV-vis absorption spectra are provided of the reduction of 4-NP by NaBH$_4$ in the presence of Ag/100@MIL-121 (1.80 wt%) as catalyst. d): A plot of ln (C$_t$/C$_n$) of 4-NP versus time for the catalyst.
Figure 5-1 (a) Crystal structure of MIL-121 built from octahedral Al chains and BTEC linkers. (b, c) N$_2$ adsorption isotherms and pore size distribution of thermally treated MIL-121 samples. (d) PXRD patterns of Meth-MIL-121 and thermally treated MIL-121 samples. (e) CO$_2$ adsorption isotherms in thermally treated MIL-121 samples at 273 K under 1 atm are illustrated......................... 162

Figure 5-2 SEM images of Meth-MIL-121 and thermally treated samples are shown: (a, b) Meth-MIL-121, (c, d) MIL-121-440ºC-16H, (e, f) MIL-121-440ºC-48H....................... 165

Figure 5-3 $^1$H--$^{13}$C CP/MAS SSNMR spectra of thermally treated MIL-121 samples are illustrated in (a). (b) The corresponding $^1$H MAS SSNMR spectra of these samples.............. 167

Figure 5-4 The $^{27}$Al MAS NMR spectra of Meth-MIL-121 and the thermally treated MIL-121 are shown in (a). (b) In situ $^{13}$C VT SSNMR experimental spectra of $^{13}$CO$_2$-loaded thermally treated MIL-121................................................................. 168

Figure 5-5 Schematic illustration of porosity transition in MIL-121. ......................... 172

Figure 6-1 (a) An illustration of esterification between alcohols and anhydride groups of the HMIL-121. $^1$H--$^{13}$C CP/MAS and $^1$H MAS SSNMR spectra of MIL-121, HMIL-121 and MeO-HMIL-121 are shown in (b) and (c). ................................................................. 185

Figure 6-2 (a) The $^{195}$Pt WURST-CPMG experimental and simulated spectra of Pt(NH$_3$)$_4$(OH)$_2$ and Pt-HMIL-121 at 9.4 T; (b) The XPS analysis of Pt-HMIL-121; (c) The proposed mechanism of incorporation of the Pt species inside HMIL-121.................. 187

Figure 6-3 (a) SEM images of Pt-HMIL-121; (b, c, d) Pt-HMIL-121-900 samples at different scales. Scale bar: 5 μm in (a, b), 500 nm in (b) and 100 nm in (d)......................... 190

Figure 6-4 TEM and HRTEM images of Pt-HMIL-121-900. STEM element maps of C and Pt for Pt-HMIL-121-900 at 100 nm are given in (c) and (d), respectively............... 192

Figure 6-5 (a) ORR curves for the electrocatalysts of 7.0%Pt-HMIL-121-900, HMIL-121-900, and 40.0%Pt/C catalysts. (b) The mass activity at 0.9 V for 7.0%Pt-HMIL-121-900 and commercial 40%Pt/C catalysts. ................................................................. 193
Figure 7-1 $^{43}$Ca MAS NMR spectra (solid lines) and simulations (broken red lines) of three CaBDC phases are shown in (a), (b) and (c), along with those of (d) CaPDC-H$_2$O and (e) CaPDC-DMF.

Figure 7-2 The experimental (solid lines) and simulated (red broken lines) $^{43}$Ca MAS NMR spectra of (a) as made CaSDB, (b) activated CaSDB, (c) as made CaBTC and (d) activated CaBTC.
List of Abbreviations

3D    three-dimensional
3QMAS triple-quantum magic-angle spinning
BDC   1, 4-benzenedicarboxylate
BET   Brunauer-Emmett-Teller
BTC   trimesic acid
BTEC  1,2,4,5-Benzenetetracarboxylic acid
CP    cross-polarization
CPMAS cross-polarization magic-angle spinning
CS    chemical shielding
CSA   chemical shielding anisotropy
CSD   Cambridge structural database
dabco 1,4-Diazabicyclo[2.2.2]octane
DFT   density functional theory
DMF   N,N-dimethylformamide
DOBDC 2,5-dioxido-1,4-benzenedicarboxylate
EFG   electric field gradient
EXAFS Extended X-ray Absorption Fine structure
EXPRESS exchange program for relaxing spin systems
FID   free induction decay
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>FT</td>
<td>Fourier transformation</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier-transform infrared spectroscopy</td>
</tr>
<tr>
<td>FWHH</td>
<td>full-width at half-height</td>
</tr>
<tr>
<td>GIPAW</td>
<td>Gauge Including Projector Augmented Wave</td>
</tr>
<tr>
<td>GTO</td>
<td>Gaussian-type orbital</td>
</tr>
<tr>
<td>H$_2$PDC</td>
<td>2,5-pyridinedicarboxylic acid</td>
</tr>
<tr>
<td>HB</td>
<td>Herzfeld-Berger</td>
</tr>
<tr>
<td>HETCOR</td>
<td>hetero-nuclear correlation</td>
</tr>
<tr>
<td>HKUST</td>
<td>Hong Kong University of Science and Technology</td>
</tr>
<tr>
<td>HRTEM</td>
<td>high resolution transmission electron microscopy</td>
</tr>
<tr>
<td>ICP-MS</td>
<td>inductively coupled plasma mass spectrometry</td>
</tr>
<tr>
<td>ICP-OES</td>
<td>inductively coupled plasma optical emission spectrometry</td>
</tr>
<tr>
<td>INAIP$^{2-}$</td>
<td>5-(isonicotinamido) isophthalate</td>
</tr>
<tr>
<td>INS</td>
<td>inelastic neutron spectroscopy</td>
</tr>
<tr>
<td>IRMOF</td>
<td>isoreticular metal–organic framework</td>
</tr>
<tr>
<td>MAS</td>
<td>magic-angle spinning</td>
</tr>
<tr>
<td>MIL</td>
<td>material from Institut Lavoisier</td>
</tr>
<tr>
<td>MOF</td>
<td>metal–organic framework</td>
</tr>
<tr>
<td>MQ</td>
<td>multiple quantum</td>
</tr>
<tr>
<td>N.A.</td>
<td>natural abundance</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>------------------------------------</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>NPD</td>
<td>neutron powder diffraction</td>
</tr>
<tr>
<td>NPs</td>
<td>nanoparticles</td>
</tr>
<tr>
<td>ORR</td>
<td>oxygen reduction reaction</td>
</tr>
<tr>
<td>ORTEP</td>
<td>oak ridge thermal ellipsoid plot</td>
</tr>
<tr>
<td>OMS</td>
<td>open metal site</td>
</tr>
<tr>
<td>PAS</td>
<td>principle axis system</td>
</tr>
<tr>
<td>PCN</td>
<td>porous coordination network</td>
</tr>
<tr>
<td>ppm</td>
<td>parts per million</td>
</tr>
<tr>
<td>PSM</td>
<td>post-synthetic modification</td>
</tr>
<tr>
<td>PXRD</td>
<td>powder X-ray diffraction</td>
</tr>
<tr>
<td>QCPMG</td>
<td>quadrupolar Carr-Purcell-Meiboom-Gill pulse sequence</td>
</tr>
<tr>
<td>QI</td>
<td>quadrupolar interaction</td>
</tr>
<tr>
<td>rf</td>
<td>radio frequency</td>
</tr>
<tr>
<td>RH</td>
<td>relatively humidity</td>
</tr>
<tr>
<td>RHE</td>
<td>reversible hydrogen electrode</td>
</tr>
<tr>
<td>SBU</td>
<td>second building unit</td>
</tr>
<tr>
<td>SCXRD</td>
<td>single crystal X-ray diffraction</td>
</tr>
<tr>
<td>SDB</td>
<td>4,4′-sulfonyldibenzoic acid</td>
</tr>
<tr>
<td>S/N</td>
<td>signal-to-noise ratio</td>
</tr>
<tr>
<td>Acronym</td>
<td>Definition</td>
</tr>
<tr>
<td>---------</td>
<td>------------</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscopy</td>
</tr>
<tr>
<td>SSNMR</td>
<td>solid-state nuclear magnetic resonance</td>
</tr>
<tr>
<td>SW</td>
<td>spectral width</td>
</tr>
<tr>
<td>STP</td>
<td>standard temperature and pressure</td>
</tr>
<tr>
<td>TEA</td>
<td>triethylamine</td>
</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
</tr>
<tr>
<td>TGA</td>
<td>thermogravimetric analysis</td>
</tr>
<tr>
<td>TMS</td>
<td>tetramethylsilane</td>
</tr>
<tr>
<td>UiO</td>
<td>University of Oslo</td>
</tr>
<tr>
<td>UMCM</td>
<td>University of Michigan Crystalline Material</td>
</tr>
<tr>
<td>VT</td>
<td>variable-temperature</td>
</tr>
<tr>
<td>WURST</td>
<td>wideband uniform-rate smooth truncation</td>
</tr>
<tr>
<td>XANES</td>
<td>X-ray Absorption Near Edge structure</td>
</tr>
<tr>
<td>XAS</td>
<td>X-ray Absorption spectroscopy</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
</tbody>
</table>
Chapter 1

1 Background

1.1 Introduction of MOFs

MOFs are crystalline materials with infinite but uniform framework structures built from organic linkers and inorganic metal cations (Figure 1-1a).\textsuperscript{1-2} Since MOFs with permanent porosity were reported in late 1990s, numerous MOFs have been synthesized with various metal ions and organic linkers, resulting in the largest branch of porous materials.\textsuperscript{3} MOFs have ultrahigh porosity (up to 90% free volume), extremely high internal surface areas (more than 10 000 m\textsuperscript{2}/g), and extraordinary compositional and structural variety.\textsuperscript{4,5} In contrast, other porous materials such as zeolites and activated carbons can only reach surface areas of ca. 1000 m\textsuperscript{2}/g and 3500 m\textsuperscript{2}/g, respectively.\textsuperscript{4} In 2015, the total number of reported MOFs has surpassed 40 000+ (Figure 1-1b) while the number of reported zeolites structures is less than 300.\textsuperscript{4,6-7} Due to the above mentioned remarkable properties, MOFs have realized many promising applications including gas storage,\textsuperscript{8-9} separations,\textsuperscript{10-13} heterogeneous catalysis,\textsuperscript{14-16} drug delivery,\textsuperscript{17-18} biomedical imaging\textsuperscript{19-20} and chemical sensors,\textsuperscript{21-23} leading to a dramatically increase in the number of published papers and fast expanding scope in MOF research.

MOFs are highly crystalline materials with covalently extended structures, which can be obtained by various synthesis methods. The most common way is the solvothermal method, in which a mixture of reaction reagents and solvent is placed in closed vessels and heated at a temperature under autogenous pressure above the boiling point of the solvent.\textsuperscript{24} In recent years, many other methods including microwave heating, electrochemical, mechanochemical, and ultrasonic methods have been employed.\textsuperscript{24-25} Regardless of the method used, carboxylate-based MOFs can be assembled through deprotonation of the organic carboxylic acid in order to react with metal ions to form metal–oxygen bonds. With the help of deprotonation reagent like triethylamine (TEA), some well-known MOFs such as MOF-5, HKUST-1 can be synthesized at room temperature, instead of using solvothermal method.\textsuperscript{26} By carefully controlling the crystallization process, it is possible
to harvest large MOF single crystals of millimeter sizes. Thus the accurate crystal structures can be determined via single-crystal X-ray diffraction (SCXRD).

Figure 1-1 (a) An illustration of the assembly process of MOFs (i.e. Al-MIL-53). (b) The number of reported new MOFs in the Cambridge Structural Database (CSD) since 1972. (Ref. 27)

The relatively strong metal-oxygen bonds enable MOFs with prominent architectural and thermal stabilities.\(^{28}\) The robust structures of MOFs allow one to substitute the organic building blocks with similar linkers without changing the underlying topology of the MOF.\(^{3}\) The substitution with longer organic linkers or linkers with various functional groups in MOFs gives rise to larger storage space and/or optimized physical and chemical
properties. For example, MOF-5 has a cubic six-connected three-dimensional net and contains the simplest ligand, 1,4-benzenedicarboxylate (BDC), among its isoreticular (IR)-MOF family (Figure 1-2a). There are 16 members in this IR-MOF family with the same underlying topology as MOF-5 (also termed as IRMOF-1). Compared to IRMOF-1, the unit cell edge of IRMOF-16 is doubled and its volume is increased by a factor of 8, leading to a free volume as large as 91.1% of the crystal. UiO-66 is a well-known Zr based MOF due to its remarkable stability to thermal treatment and harsh conditions including strong acid or base solution. UiO-66 is a MOF with a cubic close packed structure containing octahedral cages and it can also be easily expanded or functionalized using expanded linkers (Figure 1-2b).

Another way to enlarge the pore size of MOFs is to create hierarchical pores (i.e. mesopores) inside the MOF without the collapse of the whole MOF structure. Two main strategies are developed to achieve hierarchical MOFs: template assistant synthesis and fabricating “defects”. Figure 1-3a shows how to create mesopore inside a MOF by template assistant synthesis. First of all, a template which is sensitive to certain conditions such as calcination or acid treatment is introduced during the MOF synthesis. The template will crystalize with the MOF and can be removed afterwards by specific ways such as acid etching or thermal treatment, leaving the cavities behind and creating hierarchical pores inside the host. Introducing “defects” inside the MOF is a recent popular approach to build mesopores in MOFs (Figure 1-3b). Labile chemical bonds or linkers which are easy to cleave under some treatments are deliberately introduced into a chemically robust MOF. Mesopore can then be formed after the labile chemical bonds or linkers are sabotaged (Figure 1-3b). The hierarchical MOFs can be used to encapsulate large molecules or species such as drugs, enzymes or proteins which are inaccessible to a normal micropore MOFs, expanding MOF applications to the adsorption of large molecules.
Figure 1-2 (a) The ditopic carboxylate linkers used to construct IR MOFs and the crystal structure of IRMOF-1-16. (Ref. 29) (b) The ditopic carboxylate linkers used to expand and/or functionalize UiO-66, the local structure of UiO-66, as well as the crystal structure of UiO-66/67/68 (Ref. 30-31)
Figure 1-3 (a) The template assistant synthesis of hierarchical MOFs (ref. 34). (b) Hierarchical MOFs created by introducing “defects” via chemical labile linkers (ref. 35).

Metal atoms play a pivotal role in constructing the structure of MOFs via connecting the organic linkers. The metal and its coordinated oxygens form metal clusters or infinite chains known as secondary building unit (SBU). The metal based SBU dictates the geometry around the metal ions, providing a specific way of building the extended MOF frameworks and preventing random connections to form other unwanted structures. For example, a well-known MOF, HKUST-1 has a copper paddle wheel SBU (Figure 1-4) with a formula of Cu$_2$(CO$_2$)$_4$. After replacing the trimesic acid ligands (BTC) in HKUST-1 by ligands TATB and BBC, PCN-6’ and MOF-399 with larger pore size are obtained and they have the same topology as HKUST-1 (Figure 1-4).
Figure 1-4 The crystal structures of HKUST-1, PCN-6’, and MOF-399. TATB (4,4’,4”-(1,3,5-triazine-2,4,6-triyl)tribenzoate) are ligands for PCN-6’ and BBC (4,4’,4”(benzene-1,3,5-triyl-tris(benzene-4,1-diyl))tribenzoate) are ligands for MOF-339 (ref: 7).

Metal centers in MOFs are also closely related to the applications of MOFs including guest adsorption, catalysis, sensing and luminescence. A typical example is the open metal site (OMS) which is generated by the removal of the coordinated solvents from the metal centers by heating and/or evacuation. The formation of an OMS in MOFs can increase the surface areas (unit: m²/g) due to the decreased mass of MOFs and also enhance the gas adsorption capabilities including H₂, CO₂, O₂ and CH₄ through the strong interaction between the OMSs and adsorbed gas molecules. The OMS in MOFs also can serve as strong Lewis acidic site, providing promising catalytic activity in various reactions. MIL-101 is a mesoporous MOF with potential OMSs decorating inside the cages-like pores (Figure 1-5a). After removing the coordinated water, the exposed Cr OMS (Figure 5b)
shows high catalytic activity in the cyanosilylation of benzaldehyde, sulphoxidation of thioethers with \( \text{H}_2\text{O}_2 \) and benzylic oxidation of tetralin.\textsuperscript{39}

**Figure 1-5** (a) The SBU, organic linker and crystal structure of MIL-101. (b) The formation of OMS in MIL-101. (ref: 39-40)

### 1.2 Application of MOFs in gas adsorption and separation

Due to their high surface areas and chemically tunable structures, MOFs are regarded as very promising sorbents for gas adsorption and separation. The steadily decreasing fossil fuel deposits and increasing global warming caused by emission of carbon dioxide lead to the search for clean energy carriers such as hydrogen gas and the development of carbon capture technology that can effectively reduce \( \text{CO}_2 \) from atmosphere.\textsuperscript{41-42}

The concept of “Hydrogen Economy” has attracted much attention in the past decades due to its great advantages compared to the current fossil fuel economy, including high energy density (almost tripled than gasoline per mass unit), carbon free, and water as the only
To realize “Hydrogen Economy”, hydrogen storage is one of the key technologies that need to be developed. MOF-5 is the first MOF tested for H$_2$ storage, which was reported in 2003.\textsuperscript{43} It adsorbed up to 4.5 wt\% H$_2$ at 78 K and 10 bar, revealing the excellent potential of MOFs in hydrogen adsorption applications. The subsequent study shows that MOFs with increased surface area lead to enhanced H$_2$ storage: UMCM-2 (Brunauer–Emmett–Teller surface areas (BET): 5200 m$^2$/g) has stored 6.9 wt\% at 77 K and 46 bar and NU-100 (BET: 6143 m$^2$/g) exhibits hydrogen adsorption as high as 9.0 wt\% at 77 K and 56 bar (Figure 1-6).\textsuperscript{44} Despite of these tremendous progresses in H$_2$ storage, the H$_2$ adsorption in MOFs is usually carried out at low temperatures, which still cannot reach the target for H$_2$ storage given by the US Department of Energy, requiring 5.5 wt\% and 40 g/L at −40 to 60°C below 100 bar.\textsuperscript{45}

![Figure 1-6](image)

**Figure 1-6** The ligand, cages and local structure of UMCM-2 (a, ref:46) and NU-100 (b, ref: 47).

The global warming arising from CO$_2$ greenhouse effect has become one of the largest challenges for human beings in the 21st century. Unfortunately, CO$_2$ emission is still
dramatically increasing since the global population is expanding and the development of economy and industry is still largely based on consuming of fossil fuel.\textsuperscript{42, 48} The CO$_2$ capture using MOFs for storage is promising due to the high surface areas as well as their tunability in structural and chemical properties, allowing one to adjust the pore size and interaction between the framework and adsorbed CO$_2$.\textsuperscript{49-51} In 2005, Yaghi et al.\textsuperscript{8} reported that the MOF-177 can adsorb CO$_2$ as high as 320 cm$^3$(STP)/cm$^3$ (147 wt% or 33.5 mml/g) at ambient temperature and 42 bar, surpassing all the other porous materials at that time, including benchmark materials such as zeolites 13X and activated carbon MAXSORB. The record of CO$_2$ adsorption at room temperature (298 K) and 1 bar is held by Mg-MOF-74,\textsuperscript{48} which gives a high value of 8.7 mmol/g due to the strong interaction between its OMSs and the adsorbed CO$_2$ (Figure 1-7).

\textbf{Figure 1-7}  (a) Crystal structure of MOF-74 (ref: 52). (b) The local environment of the adsorbed CO$_2$ and OMSs in MOF-74. (ref: 53)
The capture of CO$_2$ always competes with other gas molecules like N$_2$ and O$_2$ during the adsorption. The ubiquitous water vapor presents another challenge for CO$_2$ capture since many MOFs are unstable to moisture and lose most of their gas adsorption capacities in humid environments.$^{54-55}$ A typical post-combustion flue gas composition for a coal-fired power plant is given in Table 1-1, which clearly requires that MOFs must have high selectivity in CO$_2$ adsorption over other gases in the presence of water vapor. The flue gas from the power plant contains mainly N$_2$ (~75%), making it critical for MOFs to selectively adsorb CO$_2$ over N$_2$ in order to separate CO$_2$ from the gas stream. Compared to N$_2$, CO$_2$ has a different kinetic diameter (CO$_2$: 3.30 Å vs. N$_2$: 3.64 Å) and quadrupole moment value (CO$_2$: 43 x 10$^{-27}$esu$^{-1}$cm$^{-1}$ vs. N$_2$: 15.2 x 10$^{-27}$esu$^{-1}$cm$^{-1}$). Many MOFs have shown high adsorption selectivity for CO$_2$ over N$_2$, which can be achieved by delicately adjusting the pore size and/or optimizing the interaction between the framework and the quadrupole moment of CO$_2$.$^{56-60}$ The reported 20 MOFs with high selectivity of CO$_2$ over N$_2$ or CH$_4$ are given in Table 1-2, among which the Qc-5-Cu-sql-β yields a selectivity value as high as 40000 in CO$_2$/N$_2$.$^{61}$ To improve the CO$_2$ adsorption performance of MOFs in the presence of water, functional groups such as amine have been introduced into MOFs. After

**Table 1-1 The compositions in flue gas from a coal-fired power plant. (ref: 42)**

<table>
<thead>
<tr>
<th>molecule</th>
<th>concentration (by volume)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$</td>
<td>73–77%</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>15–16%</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>5–7%</td>
</tr>
<tr>
<td>O$_2$</td>
<td>3–4%</td>
</tr>
<tr>
<td>SO$_2$</td>
<td>800 ppm</td>
</tr>
<tr>
<td>SO$_3$</td>
<td>10 ppm</td>
</tr>
<tr>
<td>NO$_x$</td>
<td>500 ppm</td>
</tr>
<tr>
<td>HCl</td>
<td>100 ppm</td>
</tr>
<tr>
<td>CO</td>
<td>20 ppm</td>
</tr>
<tr>
<td>hydrocarbons</td>
<td>10 ppm</td>
</tr>
<tr>
<td>Hg</td>
<td>1 ppb</td>
</tr>
</tbody>
</table>
functionalized by primary amine groups, the MOF IRMOF-74-III’s CO$_2$ adsorption capacity under 65% relatively humidity (RH) is almost the same as that under dry CO$_2$.\textsuperscript{62}

Table 1-2 The 20 MOFs with the highest selectivity for CO$_2$ over N$_2$.\textsuperscript{(ref: 61)}

<table>
<thead>
<tr>
<th>MOF</th>
<th>Surface area ($\text{m}^2\text{g}^{-1}$)</th>
<th>CO$_2$ uptake (mmol g$^{-1}$)</th>
<th>Selectivity CO$_2$/N$_2$</th>
<th>Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Qc-5-Cu-sql-β</td>
<td>222</td>
<td>N/A</td>
<td>N/A</td>
<td>293</td>
</tr>
<tr>
<td>SIFSLX-3-Cu</td>
<td>300</td>
<td>2.34</td>
<td>N/A</td>
<td>298</td>
</tr>
<tr>
<td>SIFSLX-3-Zn</td>
<td>250</td>
<td>N/A</td>
<td>5.41</td>
<td>298</td>
</tr>
<tr>
<td>SIFSLX-2-Cu-i</td>
<td>735</td>
<td>N/A</td>
<td>5.41</td>
<td>298</td>
</tr>
<tr>
<td>PEI-MIL-101-125</td>
<td>382.9</td>
<td>3.85</td>
<td>770</td>
<td>298</td>
</tr>
<tr>
<td>PEI-MIL-101-100</td>
<td>608.4</td>
<td>2.40</td>
<td>600</td>
<td>298</td>
</tr>
<tr>
<td>mmen-CuBTTr</td>
<td>870</td>
<td>4.20</td>
<td>600</td>
<td>298</td>
</tr>
<tr>
<td>UTSA-16</td>
<td>328</td>
<td>2.37</td>
<td>314.7</td>
<td>296</td>
</tr>
<tr>
<td>Zn$_2$(bpdc)$_2$(bpee)</td>
<td>N/A</td>
<td>N/A</td>
<td>294</td>
<td>298</td>
</tr>
<tr>
<td>MAF-66</td>
<td>1014</td>
<td>4.41</td>
<td>298</td>
<td></td>
</tr>
<tr>
<td>mmen-Mg$_2$(dobpdc)</td>
<td>70</td>
<td>4.36</td>
<td>298</td>
<td></td>
</tr>
<tr>
<td>Mg-MOF-74</td>
<td>1800</td>
<td>5.28</td>
<td>148.1</td>
<td>313</td>
</tr>
<tr>
<td>SNU-M10</td>
<td>505</td>
<td>2.10</td>
<td>98</td>
<td>298</td>
</tr>
<tr>
<td>HPIP@ZnPC-2</td>
<td>709</td>
<td>3.36</td>
<td>98</td>
<td>298</td>
</tr>
<tr>
<td>Zn-MOF-74</td>
<td>1176</td>
<td>1.67</td>
<td>87.7</td>
<td>296</td>
</tr>
<tr>
<td>bio-MOF-11</td>
<td>1040</td>
<td>N/A</td>
<td>75</td>
<td>298</td>
</tr>
<tr>
<td>Cu-TDPAT</td>
<td>1938</td>
<td>N/A</td>
<td>57.8</td>
<td>296</td>
</tr>
<tr>
<td>UiO-66(Zr)-(COOH)$_2$</td>
<td>415</td>
<td>N/A</td>
<td>56</td>
<td>303</td>
</tr>
<tr>
<td>BUT-11</td>
<td>1310</td>
<td>N/A</td>
<td>31.5</td>
<td>298</td>
</tr>
<tr>
<td>Ni-MOF-74</td>
<td>1312</td>
<td>4.86</td>
<td>30</td>
<td>298</td>
</tr>
</tbody>
</table>

1.3 Introducing extra functional groups and metal ions into MOFs by post-synthetic modification (PSM)

The chemical properties of MOFs can be tuned by employing ligands with various functional groups, resulting in optimized gas adsorption. Another important approach is to introduce extra functional groups and metal ions into MOFs by post-synthetic modification (PSM).\textsuperscript{63-64} PSM means modification of MOFs is carried out on the MOFs which are already synthesized. Compared to other synthetic approaches, PSM can be very effective and prevent both the parent MOF and incorporate functional groups or metal moiety from being damaged during the introducing process (Figure 1-8).\textsuperscript{65}
The chemical properties of MOFs can be largely altered after the extra functional groups or metals have been introduced. After introducing lithium ions to MIL-53(Al)-OH through decorating the pendant hydroxy groups, the resulting MOF with lithium alkoxide shows a larger H\(_2\) storage capacity (1.7 wt\%) under 1 bar and 77K compared to the unmodified parent MOF (0.5 wt\%). MOFs UiO-66 and UiO-67 are the most common MOFs for introducing extra metals due to their high chemical stabilities. Their structural topologies remain unchanged after replacing the ligands in parent MOFs and/or subsequent metal inserting via PSM. In Figure 1-9, two samples are given to show how extra metals are introduced into UiO-66/67 by PSM. In a study from Cohen group, the ligand 2,3-dimercaptoterephthalic acid (tcat-H\(_2\)bdc) was used to replace parts of the BDC organic linkers in UiO-66 by ligand exchanged (Figure 1-9a) due to the difficulty of direct synthesis.
of tcat-H₂bdc based UiO-66. The ligand exchanged UiO-66-TCAT was further metalated with Pd(OAc)₂ via the strong binding interaction between thiocatechol groups and heavy metals. The resulting UiO-66-PdTCAT shows high catalyst activity in regioselective functionalization of sp² C-H bond.⁶⁷ Wenbin Lin et al.⁶⁸ reported another way of introducing noble metals Pd and Ir inside UiO-67. First, 2,2'-bipyridine-5,5'-dicarboxylic acid based UiO-67 was successfully synthesized (Figure 1-9b). The 2,2'-bipyridyl-derived bpy-Uio-67 was then metalated with [Ir(COD)(OMe)]₂ and [Pd(CH₃CN)₄][BF₄]₂, respectively, yielding Ir and Pd functionalized bpy-Uio-Ir and bpy-Uio-Pd (Figure 1-9b).⁶⁸ The bpy-Uio-Ir shows high catalytic activity in both the borylation of aromatic C–H bonds and ortho-silylation of benzylicsilyl ethers, and bpy-Uio-Pd is good at catalyzing the dehydrogenation of substituted cyclohexenes to Phenols.

![Diagram of Pd and Ir functionalization in UiO-66 and bpy-Uio-67](image)

**Figure 1-9** (a) The introduction of Pd inside UiO-66. (ref: 67). (b) Loading Ir and Pd into bpy-Uio-67. (ref: 68).
1.4 Solid state nuclear magnetic resonance (SSNMR) study in MOFs

As mentioned above, the MOF’s applications are closely related with its structure. Naturally, structural characterization plays a critical role in understanding MOFs and the associated performances. SCXRD is the main tool to elucidate the crystal structure if a suitable size single crystal is available. Unfortunately, due to the difficulty in obtaining suitable single crystals for X-ray diffraction, many MOFs structures were determined from more limited powder XRD data. Furthermore, SCXRD only provides time averaged long-range order structures and cannot provide dynamic information. To address these issues, various methods such as FTIR (Fourier-transform Infrared), EXAFS (Extended X-ray Absorption Fine Structure), and XANES (X-ray Absorption Near Edge Structure) spectroscopy have been employed to investigate the structure of MOFs. In addition to them, SSNMR spectroscopy is regarded as an important complementary method to X-ray diffraction as it probes both short-range ordering and local structure of MOFs. Indeed, SSNMR spectroscopy can provide various detailed information on MOFs including the organic linkers, metal centers, dynamics of the adsorbed guest and host–guest interaction. For example, $^{13}$C and $^1$H SSNMR spectroscopy can be used to interrogate the organic linkers and the attached multiple functional groups as well as monitor the adsorption of guest species. Since the metal ions in MOFs play a key role in the frameworks, it is of importance to apply SSNMR spectroscopy to gain direct information about the local geometry around metal center and the metal-guest interaction. In situ variable-temperature (VT) SSNMR spectroscopy can be used to acquire information regarding gas molecule adsorption and host-gas interactions. Dynamic information including specific types, rates, and routes of guest motions can be obtained via the simulation based on the in situ VT SSNMR experimental spectra.

Since SSNMR spectroscopy is one of the main characterization techniques used in this thesis, some basic knowledge of it will be briefly introduced. NMR spectroscopy was first described and measured in molecular beams by Isidor Rab in 1938. In 1946, Felix Bloch and Edward Mills Purcell expanded NMR spectroscopy for applications on liquids and solids, and they shared the Nobel Prize in Physics in 1952. Since then, NMR spectroscopy
has been an important technique in studying materials, which is widely used in areas such as chemistry, biology, and physics. However, SSNMR spectroscopy wasn’t as popular as its liquid phase analogue at the beginning due to the low resolution. In the past decades, the development of technologies including MAS (magic angle spinning), MQ (multiple quantum) NMR, CP (cross polarization) and the appearance of spectrometers with ultrahigh magnetic fields like 18.7 T and above enable scientists to obtain high resolution SSNMR spectra and boost its application in many research fields.

The NMR experiments on the nuclei of interest is directly connected with its nuclear spin angular momentum ($I$), or “spin”, which is an intrinsic property. For nuclei with $I = 0$ such as $^{12}$C, $^{16}$O, and $^{32}$S, they are NMR silent since they have no angular momentum. Luckily, most of the elements in the periodic table have active isotopes with nonzero $I$ even though sometimes corresponding isotope enrichment is needed due to the low natural abundance.

A typical NMR experiment require three steps: first the nuclear spin system (i.e. the target sample) is placed in an external magnetic field ($B_0$), then a pulse of radio frequency (rf) radiation is applied on the spin system, resulting a second rf field ($B_1$) which is used to cause “perturbation”; the $B_1$ field is then removed and the spin system will induce a voltage change in the coil of NMR probe, leading to a free induction decay (FID) that can be recorded and processed. The FID is a time domain signal containing frequency information and can be transferred into a frequency based spectrum by Fourier transformation (FT). The resulted intensity vs frequency plots are the most common NMR spectra.

**Table 1-3** Magnitudes of nuclear interactions in liquids and solids

<table>
<thead>
<tr>
<th>Nuclear interactions</th>
<th>Magnitude in liquids (Hz)</th>
<th>Magnitude in solids (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeeman interaction</td>
<td>$10^7$–$10^9$</td>
<td>$10^7$–$10^9$</td>
</tr>
<tr>
<td>dipolar interaction</td>
<td>0</td>
<td>$10^3$–$10^5$</td>
</tr>
<tr>
<td>chemical shielding</td>
<td>$\sigma_{iso}$</td>
<td>$10^2$–$10^5$</td>
</tr>
<tr>
<td>Scalar/J-coupling</td>
<td>$10^0$–$10^3$</td>
<td>$10^6$–$10^3$</td>
</tr>
<tr>
<td>Quadrupolar interaction</td>
<td>0</td>
<td>$10^3$–$10^7$</td>
</tr>
</tbody>
</table>

The nuclear spin system undergoes many interactions when $B_0$ is applied, including Zeeman interaction, dipolar interaction, chemical shielding interaction, scalar/J-coupling interaction and quadrupolar interaction. The magnitudes of the mentioned interactions are given in Table 1-3. Due to the rapid random molecular tumbling in solution, the dipolar
interaction and quadrupolar interaction are averaged to zero and chemical shielding is averaged into its isotropic value, $\sigma_{\text{iso}}$. As a result, solution NMR spectra are featured with very sharp peaks while, in contrast, the SSNMR spectra can have much broad resonances since all mentioned interactions are present in solids.

**Zeeman interaction**

Zeeman interaction is due to the interaction between $B_0$ and a nuclear spin. For a nucleus with spin I, there are $2I+1$ possible energy levels that are degenerate in the absence of external magnetic field (i.e. the nuclear spin states all have same energy). Once there is an external magnetic field $B_0$, due to the interaction between the magnetic moment of the nuclear spins and $B_0$, the spin states will split and become non-equivalent, yielding $2I+1$ possible energy levels which can be distinguished by magnetic quantum number $m_I$ ($m_I = -I, -I + 1, -I + 2, \ldots, I - 2, I - 1, I$, Figure 1-10). Thus, the Zeeman interaction results in energy gap between adjacent energy levels, which are proportional to the gyromagnetic ratio $\gamma$ and the strength of $B_0$. The equation of energy gap is also given in Figure 1-10, where the $\nu$ stands for Larmor frequency and $h$ is the Planck’s constant.

![Figure 1-10 Illustration of the Zeeman interaction for a spin-$l/2$ nucleus.](image)

**Chemical shielding and quadrupolar interaction**

In addition to Zeeman interaction, chemical shielding and quadrupolar interaction are another two important interactions that can affect SSNMR spectra. Due to the interaction between $B_0$ and the electronic cloud of the nucleus, extra local magnetic fields are also induced on the nucleus, which will affect the actual magnetic field experienced by the
nucleus. This effect is called chemical shielding, which will either strengthen or reduce the applied magnetic field that is experienced by the nucleus.

The chemical shielding can be described by a $3 \times 3$ second-rank tensor in its principal axis system (PAS, Figure 1-11a). The chemical shielding tensor has three principal components, $\sigma_{11}$, $\sigma_{22}$ and $\sigma_{33}$ ($\sigma_{11} \leq \sigma_{22} \leq \sigma_{33}$). To report chemical shielding, they are usually converted to Herzfeld-Berger conventions. The relationship between chemical shielding tensor and Herzfeld-Berger conventions are listed in Figure 1-11b, in which the $\sigma_{\text{iso}}$ is isotropic chemical shielding tensor; $\delta_{\text{iso}}$ is isotropic chemical shift, which equals the average of the three principle chemical shift components. The $\delta_{\text{iso}}$ is equivalent to the chemical shift value obtained in a solution sample. $\Omega$ is span, which measures the width of resonance powder pattern and $\kappa$ is skew with a value range from +1 to -1, which is used to describe the shape of the resonance. When the value of $\kappa$ equals to +1 or -1, it suggests that the nucleus observed has an axially symmetric environment since two of the three principle components ($\sigma_{11}$, $\sigma_{22}$ and $\sigma_{33}$) become equivalent. The effects of $\delta_{\text{iso}}$, $\Omega$ and $\kappa$ on the $^{13}\text{C}$ line shape are given as an example and illustrated in Figure 1-12.

$$\sigma = \begin{pmatrix} \sigma_{11} & 0 & 0 \\ 0 & \sigma_{22} & 0 \\ 0 & 0 & \sigma_{33} \end{pmatrix}$$

![Figure 1-11](image)

**Figure 1-11** (a) The second rank tensor of chemical shielding described in its PAS; (b) the Herzfeld-Berger conventions.
Quadrupolar interaction is another important interaction that can give rise to broad SSNMR spectra. When the nuclear spin quantum number of a nucleus is greater than 1/2, its electrical charge distribution becomes non-spherical, yielding a nuclear quadrupole moment \( Q \) that interacts with the electric field gradient (EFG) in the molecule. This interaction between quadrupole moment with EFG is termed as quadrupolar interaction (QI) and the corresponding nucleus is called quadrupolar nucleus. The EFG can also be described by a second-rank tensor which is similar to the above mentioned chemical shielding. The three principal components of EFG in PAS are \( V_{xx}, V_{yy} \) and \( V_{zz} \) with the order of \(|V_{xx}| < |V_{yy}| < |V_{zz}|\). Quadrupolar coupling constant \( C_Q \) and the asymmetry \( \eta_Q \) are the two reported parameters to describe the QI. Their definitions are given as follow (e: elementary charge):

\[
C_Q = eQV_{zz}/\hbar \quad \text{and} \quad \eta_Q = (V_{xx} - V_{yy})/V_{zz}
\]
C_Q is used to evaluate the strength of QI while η_Q indicates the axial symmetry of the EFG tensors. When the C_Q value is close to 0, it suggests that the local environment of the quadrupolar nucleus resembles high spherical symmetry (such as cubic or octahedral). The η_Q has a value range from 0 to 1. The value of 0 represents an axially symmetric environment of the nucleus and 1 stands for an axially asymmetric local electronic environment. The influence of C_Q and η_Q on $^2$H SSNMR spectra is illustrated in Figure 1-13.

**Figure 1-13** $^2$H SSNMR spectra (9.4 T, δ_iso = 0 ppm) with different C_Q and η_Q values.

**Spectral Simulations:**

There are two types of spectral simulations involved in this thesis: analytical simulation and dynamic simulation. Analytical simulation is to use softwares such as WSolids\textsuperscript{69} or DmFit\textsuperscript{70-71} to simulate experimental SSNMR spectra and extract the observed NMR parameters, including δ_iso, Ω, κ, C_Q and η_Q. During the analytical simulation, all errors in NMR parameters were estimated by varying the parameter of interest in both directions from the best-fit value. The dynamic simulation mainly relies on the software EXPRESS...
(Exchange Program for Relaxing Spin Systems) to generate the calculated spectra. The calculated spectra are adjusted by considering the dynamic of the guest including the types of motions and the motional rates and angles. The corresponding dynamic information of the guest can be obtained once the calculated spectra match well with the analytically simulated spectra. The local wobbling of CO₂ along a fixed axis is given as an example (Figure 1-14a). The line shape of the calculated $^{13}$C NMR spectra of CO₂ changes when the wobbling angles are altered (Figure 1-14b).

![Figure 1-14](attachment:image.png)

**Figure 1-14** (a) Schematic illustration of CO₂ local wobbling. (b) The dynamic simulation of CO₂ local wobbling. (ref: 53)

### 1.5 Outline of the thesis

The main objectives of this thesis are to investigate several aspects of MOFs, including gas adsorption mechanism, the introduction of extra metal ions by PSM, the formation of hierarchical structure, new functional group for PSM study and metal centers in various calcium-based MOFs. The thesis is organized in the following way: Chapter 2 describes the CO₂ adsorption in two 4,4’-sulfonyldibenzonic acid (SDB) based MOFs, PbSDB and CaSDB, via a combination study of SCXRD and SSNMR. The adsorption sites, gas dynamic and the guest-framework interaction have been clearly revealed by these two methods. Following Chapter 2, small gas molecules including CO₂, C₂H₂ and CH₄
adsorption in an amide functionalized Cu(INAIP) [INAIP$^{2-} = 5$-(isonicotinamido) isophthalate] MOF are discussed in Chapter 3. Amide functional groups have been introduced into MOFs due to their strong affinity to small gas molecules, but the corresponding gas adsorption mechanisms remain unclear and the exact guest binding sites are under dispute. We employed a combination of SCXRD, SSNMR, and computational methods on the gas-loaded Cu(INAIP), which unambiguously revealed the binding model for each gas. In Chapter 4, a green and simple method has been used to introduce 14 different metal ions inside the MIL-121 MOF. The local structure of dopants and the relationship between the introduced metals and MOF have been comprehensively studied by multinuclear NMR and X-ray adsorption spectroscopy. In addition, we found that the MOFs with introduced metals show enhanced gas adsorption towards H$_2$ and CO$_2$. Ag nanoparticles loaded MIL-121 exhibit remarkably high catalytic activity for a model reaction involving the reduction of 4-nitrophenol. In Chapter 5, a thermal triggered hierarchical structure has been discovered in MIL-121. The surface area and pore size and/or volume of MIL-121 can be directly improved and a greatly enhanced CO$_2$ adsorption capacity in the corresponding hierarchical MOF is achieved. A combination of gas adsorption, scanning electron microscopy (SEM) and SSNMR spectroscopy has been used to investigate the porosity transition and a detailed mechanism for the formation of hierarchical structure has been established. We also discovered that the residual anhydride groups in the hierarchical MIL-121 shows excellent activity in bonding with various functional groups. In Chapter 6, a detailed study on employing anhydride groups in MIL-121 as “anchor” sites for PSM is described. Organic species including alcohols, aminos, thiols and noble metal Pt based compounds have been successfully incorporate into hierarchical MIL-121 via the residue anhydride groups. In Chapter 7, natural abundance $^{43}$Ca SSNMR spectroscopy has been employed to investigate the metal centers of nine different Ca MOFs that are structurally related. $^{43}$Ca SSNMR spectroscopy is extremely challenging to perform, particularly in density-diluted systems such as MOFs, but we show that it is now becoming more accessible at high magnetic field. Chapter 8 is the final chapter, which contains a brief summary of the thesis as well as some description of future works.
1.6 References


Chapter 2

2 Understanding the Fascinating Origins of CO$_2$ Adsorption and Dynamics in SDB-based MOFs

2.1 Introduction

Increasing atmospheric levels of the greenhouse gas CO$_2$\textsuperscript{1-2} and concomitant global warming poses a grave danger to many species on Earth.\textsuperscript{3-7} The formidable challenge of stabilizing and eventually reducing atmospheric CO$_2$ levels must be urgently addressed. Metal-organic frameworks (MOFs) are a promising class of materials for CO$_2$ capture and storage due to their porous nature, extremely large surface areas, affinity for guest molecules, and variety of tunable properties.\textsuperscript{8-9} Specific combinations of metal ions with organic linkers gives rise to MOFs which possess permanent porosity and can feature one-, two-, or three-dimensional crystalline channels.\textsuperscript{10-11} The nearly limitless variations of different metals and linkers have led to the preparation and study of many MOFs over the past two decades,\textsuperscript{10} with potential applications in fields such as gas storage,\textsuperscript{12-15} gas and liquid separations,\textsuperscript{16-18} catalysis,\textsuperscript{19-20} chemical sensors,\textsuperscript{21-23} and drug delivery.\textsuperscript{24-26} In particular, there are numerous MOFs that are capable of CO$_2$ adsorption and capture.\textsuperscript{9,27-29} At the present time, MOFs cannot selectively adsorb sufficient quantities of CO$_2$ to be employed in automobiles and industry under practical conditions;\textsuperscript{30} however, many exciting avenues are being explored to address specific obstacles. To improve CO$_2$ capacity and selective adsorption over other small gases like N$_2$, CH$_4$, and O$_2$, researchers have found success using strategies such as incorporation of coordinatively-unsaturated open metal sites (OMSs),\textsuperscript{17,31-35} use of organic linkers featuring basic nitrogen-containing organic groups,\textsuperscript{36-41} and the introduction of strongly polarizing functional groups onto the linkers.\textsuperscript{42-45} Although these methods often increase the MOF-CO$_2$ binding strength, they are associated with additional challenges. Many MOFs, including those containing OMSs, are typically very sensitive to the presence of water vapor, which restricts many practical applications due to the ubiquity of humid environments.\textsuperscript{46-50} For example, MOF-74 incorporates OMSs and has exhibited a remarkable ability for CO$_2$ capture; however, the M-MOF-74 series of MOFs (M = Zn, Co, Ni and Mg) loses most of its affinity for CO$_2$
after exposure to humid environments due to preferential coordination of water molecules at guest binding sites.\textsuperscript{51-54} While the introduction of basic nitrogen-containing organic groups or other polarizing functional groups can increase CO\textsubscript{2} adsorption capabilities in MOFs,\textsuperscript{31, 36-37, 55} these procedures significantly increase the financial and labor costs of MOF synthesis, and reduce the commercial competitiveness of these materials compared to other porous media.\textsuperscript{56-57}

Recently, several MOFs based on the semi-rigid, V-shaped H\textsubscript{2}SDB ligand (4,4'-sulfonyldibenzoic acid, Appendix: Figure 2-A1) have been reported.\textsuperscript{58-60} These systems have demonstrated high CO\textsubscript{2}/N\textsubscript{2} selectivities even in humid environments,\textsuperscript{61-62} which is promising for practical applications. The four known H\textsubscript{2}SBD-based MOFs (CaSDB,\textsuperscript{58-59}, CdSDB,\textsuperscript{62} ZnSDB,\textsuperscript{63} and PbSDB\textsuperscript{64}) all lack the OMSs or polarizing functional groups thought necessary for selective CO\textsubscript{2} adsorption, indicating that a unique CO\textsubscript{2} adsorption mechanism is present. The CO\textsubscript{2} adsorption location and mechanism in any given MOF is strongly dependent on topological details and may also be influenced by the incorporated metal atoms, hence, detailed long- and short-range structural characterization is necessary to understand the interaction between CO\textsubscript{2} and the MOF binding sites.

An in-depth study of CO\textsubscript{2} adsorption in these SDB-based MOFs is essential to understand the exact guest locations, occupancies, dynamics, and binding strengths, in addition to the influences of the metal center and MOF topology on CO\textsubscript{2} adsorption. The CO\textsubscript{2} binding sites and adsorption mechanisms within PbSDB and CdSDB (Figure 2-A2) are currently unknown. PbSDB was the first reported porous SDB-based MOF\textsuperscript{64} and is of special interest since a majority of Pb-based MOFs are non-porous.\textsuperscript{65} Although it is known that PbSDB has no uptake of N\textsubscript{2} at 1 atm of pressure, CO\textsubscript{2} adsorption has not been studied, and this MOF may also exhibit selective adsorption of CO\textsubscript{2} over N\textsubscript{2}. CdSDB was recently reported\textsuperscript{62} and was shown to possess a high CO\textsubscript{2}/N\textsubscript{2} selectivity, along with the ability to adsorb CO\textsubscript{2} in conditions of 30% humidity. Both PbSDB and CdSDB incorporate the V-shaped SDB ligand and feature one-dimensional channels, however, the metal center and coordination number has a profound influence on MOF topology: PbSDB features 7-coordinate Pb and linear channels, while the 6-coordinate Cd atoms in CdSDB and corresponding changes in topology impart a sinusoidal shape to the MOF channels (Figure 2-A2). Since these MOFs
share the same ligand but are based on different metals and display unique topologies, this is an excellent opportunity to examine the specific structural factors influencing CO$_2$ adsorption in this system, and also to elucidate, compare, and contrast the locations and dynamic behavior of CO$_2$ guests.

Obtaining a comprehensive understanding of MOFs and their guests through a single characterization technique is elusive, if not impossible. An alternative approach is to perform X-ray diffraction (XRD) experiments and solid-state NMR (SSNMR) spectroscopy, using both of these powerful complementary solid characterization methods to investigate systems in great detail.$^{66-67}$. Single crystal XRD (SCXRD) is a very useful technique for determining the long-range periodic crystal structure and differentiating between individual forms or phases of MOFs.$^{68}$ In ideal conditions, SCXRD can determine the crystal structure and pinpoint the exact locations and site occupancies of guest molecules in MOFs. Unfortunately, conditions are not always ideal: SCXRD studies of guest-loaded MOFs are littered with challenges, including the growth of a high quality single crystal, preservation of crystal quality through the relatively harsh MOF activation process (*i.e.*, solvent exchange, heating, vacuum), and loading sufficient amounts of guest molecules.$^{69-73}$ In addition, SCXRD only provides a time-averaged crystal structure; guest motion often leads to crystallographic disorder and uncertain site occupancies, limiting both the utility of the information and the depth of conclusions that can be obtained.$^{68, 73}$ To minimize the problems associated with guest dynamics, SCXRD is commonly performed at low experimental temperatures, however, this restricts the amount of motional information that can be extracted (*i.e.*, static guests at low temperatures necessarily yield no motional information).

SSNMR can provide detailed information on guest dynamics and is a sensitive probe of short-range structure and crystallinity, serving as an excellent complement to SCXRD.$^{66-67}$ SSNMR has been shown to yield key information regarding the framework structure,$^{74-76}$ guest dynamics,$^{77-78}$ and host–guest interactions$^{79-80}$ in many MOFs. $^{13}$C and $^1$H SSNMR can be used to confirm the identity of the organic linkers and the presence of key functional groups upon modification of the linkers, and can monitor the adsorption of guest species.$^{80-83}$ The metal ions within MOFs play a crucial role in structure-property relationships and
are often NMR-active; accordingly, SSNMR of the metal centers provides rich information regarding the local geometry and coordination of the metal center, and can intimately probe metal-guest interactions.\textsuperscript{74, 82, 84-85} \textit{In situ} variable-temperature (VT) SSNMR experiments can identify the specific types, rates, and routes of guest motion,\textsuperscript{78, 86-89} especially when there is detailed \textit{a priori} knowledge of the MOF structure available from SCXRD experiments. The elegant combination of SSNMR and SCXRD is critical for investigating CO\textsubscript{2} adsorption mechanisms, relating CO\textsubscript{2} storage capacity to dynamics, discovering structural features conducive to CO\textsubscript{2} adsorption, and ultimately designing better MOF-based CO\textsubscript{2} absorbents.

Herein, we describe a detailed SSNMR and SCXRD study of CO\textsubscript{2} adsorption in PbSDB\textsuperscript{64} and CdSDB.\textsuperscript{62} The specific CO\textsubscript{2} adsorption sites and the guest CO\textsubscript{2} molecules themselves were accurately located using SCXRD methods. \textit{In situ} VT \textsuperscript{13}C SSNMR techniques have been successfully employed to reveal detailed information regarding the dynamics of CO\textsubscript{2} guests in both of these SDB-based MOFs.\textsuperscript{207}Pb and \textsuperscript{111}Cd VT SSNMR techniques targeting the metal centers reveal clear difference in CO\textsubscript{2} guest locations and metal-guest interactions, which are connected to the unique Cd/PbSDB MOF structures and topologies. This study demonstrates that small alterations in MOF topology between two closely related systems can profoundly affect guest adsorption, and the knowledge of guest CO\textsubscript{2} motion gained in this work has clear practical implications for adapting today and tomorrow’s MOFs for enhanced CO\textsubscript{2} adsorption and storage.

### 2.2 Results and discussion

\textit{In situ} \textsuperscript{13}C SSNMR of PbSDB saturated with \textsuperscript{13}CO\textsubscript{2}.

To understand the dynamics of saturated CO\textsubscript{2} adsorbed within PbSDB, \textit{in situ} \textsuperscript{13}C VT SSNMR experiments at temperatures ranging from 413 to 183 K were performed; the resulting experimental and analytically simulated spectra are illustrated in Figure 2-1. Since \textsuperscript{13}C is only ca. 0.96% naturally abundant,\textsuperscript{90} and given that 99% isotopically labeled \textsuperscript{13}CO\textsubscript{2} gas was used, all of the observed \textsuperscript{13}C resonances originate solely from \textsuperscript{13}CO\textsubscript{2} molecules rather than the framework.
Figure 2-1 The experimental static $^{13}$C VT SSNMR spectra of PbSDB loaded with saturated $^{13}$CO$_2$ are shown at left in (a), and the corresponding spectral simulations to extract apparent NMR parameters are shown at right in (b).

Experimental $^{13}$C SSNMR spectra obtained at temperatures from 413 to 293 K feature two distinct resonances, (Figure 2-1a), as confirmed by analytical simulations (Figure 2-1b). The sharp, intense central resonance located at ca. 124 ppm originates from gaseous, mobile CO$_2$, while the underlying $^{13}$C powder pattern is broadened by a considerable amount of chemical shift anisotropy (CSA) due to decreased CO$_2$ mobility. The broad, temperature-dependent powder pattern undoubtedly corresponds to $^{13}$CO$_2$ adsorbed within the MOF; similarly broad $^{13}$C SSNMR powder patterns that change with temperature have been observed for CO$_2$ adsorbed in other MOFs.  78, 86-87, 91

At temperatures below 293 K, the sharp $^{13}$C resonance corresponding to gaseous CO$_2$ is no longer visible, while the broad underlying powder pattern is clearly evident, implying that a majority of CO$_2$ is adsorbed within the MOF. The broad powder pattern increases in width as temperature decreases, reflecting a further reduction in adsorbed CO$_2$ mobility, and confirming that a significant adsorptive interaction exists between CO$_2$ and PbSDB.
At 183 K, the broad and well-defined single powder pattern is the sole spectral feature, indicating that only one CO$_2$ adsorption site exists in PbSDB under these conditions and that no free CO$_2$ remains. This finding is particularly interesting as there are no OMSs or polarizing functional groups in PbSDB, hinting that some other MOF feature gives rise to this adsorptive interaction.

Table 2-1 The apparent, or observed, $^{13}$C NMR parameters of adsorbed $^{13}$CO$_2$ in SDB-based MOFs at different temperatures.

<table>
<thead>
<tr>
<th>MOF</th>
<th>Adsorption site</th>
<th>Temperature (K)</th>
<th>$\delta$iso (ppm)</th>
<th>$\Omega$ (ppm)</th>
<th>$\kappa$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbSDB</td>
<td>1</td>
<td>413</td>
<td>124(2)</td>
<td>101(2)</td>
<td>0.73(2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>383</td>
<td>124(2)</td>
<td>103(2)</td>
<td>0.70(3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>353</td>
<td>124(2)</td>
<td>105(2)</td>
<td>0.65(2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>323</td>
<td>124(2)</td>
<td>110(2)</td>
<td>0.60(2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>293</td>
<td>124(2)</td>
<td>115(3)</td>
<td>0.55(2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>243</td>
<td>124(2)</td>
<td>115(2)</td>
<td>0.45(2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>213</td>
<td>124(2)</td>
<td>118(2)</td>
<td>0.35(2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>183</td>
<td>124(2)</td>
<td>125(3)</td>
<td>0.30(3)</td>
</tr>
<tr>
<td>CdSDB</td>
<td>1</td>
<td>413</td>
<td>124(1)</td>
<td>90(2)</td>
<td>0.18(9)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>383</td>
<td>124(1)</td>
<td>101(2)</td>
<td>0.22(5)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>353</td>
<td>124(1)</td>
<td>103(2)</td>
<td>0.26(3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>323</td>
<td>124(1)</td>
<td>106(2)</td>
<td>0.29(2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>293</td>
<td>124(1)</td>
<td>112(1)</td>
<td>0.33(1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>243</td>
<td>124(1)</td>
<td>114(1)</td>
<td>0.43(1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>213</td>
<td>124(1)</td>
<td>114(1)</td>
<td>0.43(1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>183</td>
<td>124(1)</td>
<td>116(1)</td>
<td>0.48(1)</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>413</td>
<td>110(4)</td>
<td>117(3)</td>
<td>-1.00(7)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>383</td>
<td>110(4)</td>
<td>123(3)</td>
<td>-1.00(7)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>353</td>
<td>110(3)</td>
<td>131(2)</td>
<td>-1.00(6)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>323</td>
<td>110(2)</td>
<td>138(2)</td>
<td>-1.00(3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>293</td>
<td>108(2)</td>
<td>143(2)</td>
<td>-1.00(2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>243</td>
<td>105(1)</td>
<td>156(2)</td>
<td>-1.00(2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>213</td>
<td>101(1)</td>
<td>167(2)</td>
<td>-0.95(2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>183</td>
<td>90(1)</td>
<td>175(2)</td>
<td>-0.95(2)</td>
</tr>
</tbody>
</table>

The span ($\Omega$) value (i.e., powder pattern breadth) of adsorbed CO$_2$ in PbSDB increases from 101(2) ppm at 413 K to 125(3) ppm at 183 K (Table 2-1); these span values are non-zero but less than half that of static CO$_2$ (335 ppm).\textsuperscript{92} The moderate span exhibited by CO$_2$ in PbSDB indicates that guest molecules are not static, nor completely mobile; the apparent $^{13}$C span value and CSA is significantly reduced by systematic CO$_2$ motion about the
adsorption site in PbSDB. As temperature decreases, the $^{13}$C skew value ($\kappa$) decreases, suggesting that CO$_2$ dynamics and perhaps the MOF-CO$_2$ interaction strength are altered.

Figure 2-2 In (a), simulated $^{13}$C SSNMR spectra incorporating both the wobbling and hopping motions are shown above experimental spectra, along with the threefold wobbling angles ($\alpha$) and twofold hopping angles ($\beta$) determined at each temperature; both motions occur at a rate $\geq 10^7$ Hz. The * symbol denotes the resonance arising from free, unbound CO$_2$. In (b), the two motion model of CO$_2$ dynamics in PbSDB is depicted, which incorporates both local wobbling through an angle of $\alpha$, and non-localized twofold hopping through an equivalent angle $\beta$ between two symmetry-equivalent sites.

To gain a deeper understanding of CO$_2$ motion in PbSDB, the EXPRESS software package$^{93}$ was used to simulate experimental $^{13}$C SSNMR spectra and determine the types of dynamic motion present, along with their rates and associated motional angles. The simulations fit experimental data well (Figure 2-2a) and reveal that CO$_2$ undergoes two types of distinct motion in PbSDB: a localized rotation upon the adsorption site modeled by a threefold ($C_3$) rotation or “wobbling,” as well as a twofold ($C_2$) non-localized hopping between symmetry-equivalent adsorption sites (Figure 2-2b); CO$_2$ has been found to
exhibit similar types of motion in other MOFs.\textsuperscript{78, 86-87, 91} We define the rotational angle between CO\textsubscript{2} and the C\textsubscript{3} wobbling axis as \(\alpha\), while the equivalent rotational angle for C\textsubscript{2} hopping about the rotational axis is denoted by \(\beta\). It should be noted that the threefold wobbling is a model for a local rotation of CO\textsubscript{2} through a continuum of orientations on the adsorption site defined by \(\alpha\), and all wobbling rotational symmetry \(\geq C_3\) gives rise to the same powder pattern.

**Table 2-2** The CO\textsubscript{2} motional data obtained from EXPRESS\textsuperscript{93} simulations of \textsuperscript{13}C VT SSNMR spectra. The rate of all motions is \(\geq 10^7\) Hz.

<table>
<thead>
<tr>
<th>MOF</th>
<th>Temperature (K)</th>
<th>(\alpha) (C\textsubscript{3} Wobbling angle, (^\circ))</th>
<th>(\beta) (C\textsubscript{2} Hopping angle, (^\circ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbSDB</td>
<td>383</td>
<td>39(1)</td>
<td>19(1)</td>
</tr>
<tr>
<td></td>
<td>353</td>
<td>39(1)</td>
<td>22(1)</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>38(1)</td>
<td>23(1)</td>
</tr>
<tr>
<td></td>
<td>293</td>
<td>38(1)</td>
<td>25(1)</td>
</tr>
<tr>
<td></td>
<td>243</td>
<td>36(1)</td>
<td>28(1)</td>
</tr>
<tr>
<td></td>
<td>213</td>
<td>36(1)</td>
<td>29(1)</td>
</tr>
<tr>
<td></td>
<td>183</td>
<td>35(1)</td>
<td>29(1)</td>
</tr>
<tr>
<td>CdSDB(^a)</td>
<td>413</td>
<td>48(4)</td>
<td>33(3)</td>
</tr>
<tr>
<td></td>
<td>383</td>
<td>40(2)</td>
<td>32(2)</td>
</tr>
<tr>
<td></td>
<td>353</td>
<td>38(1)</td>
<td>31(2)</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>37(1)</td>
<td>31(2)</td>
</tr>
<tr>
<td></td>
<td>293</td>
<td>37(1)</td>
<td>29(1)</td>
</tr>
<tr>
<td></td>
<td>243</td>
<td>35(1)</td>
<td>29(1)</td>
</tr>
<tr>
<td></td>
<td>213</td>
<td>33(1)</td>
<td>29(1)</td>
</tr>
<tr>
<td></td>
<td>183</td>
<td>32(1)</td>
<td>28(1)</td>
</tr>
</tbody>
</table>

\(^a\) This is motional data for CO\textsubscript{2} at adsorption site 1; simulations of experimental data for CO\textsubscript{2} at adsorption site 2 did not yield reliable motional data (see discussion in text).

The motional angles at each temperature are tabulated in Table 2-2. The motional rate of CO\textsubscript{2} is in the fast motion regime (\textit{i.e.}, \(\geq 10^7\) Hz) at all temperatures. As the temperature increases from 183 to 383 K, the value of \(\alpha\) increases slightly from 35(1)\(^a\) to 39(1)\(^a\), indicating that CO\textsubscript{2} wobbles through a larger angle and samples a larger volume of space when more thermal energy is available to compete with the adsorptive interaction. In contrast, the twofold hopping angle \(\beta\) decreases from 29(1)\(^a\) at 183 K to 19(1)\(^a\) at 383 K, which is likely due to a change in the orientation of CO\textsubscript{2} molecules with respect to the C\textsubscript{2}
rotational axis as the experimental temperature is altered; a similar reduction in hopping angles with increased temperature was observed for guests in the MIL-53\textsuperscript{91} and MOF-74 frameworks.\textsuperscript{78, 88}

**SCXRD of PbSDB saturated with CO\textsubscript{2}**

![Diagram](image)

**Figure 2-3** (a) The extended lattice of the CO\textsubscript{2}-loaded PbSDB crystal structure is depicted, as viewed along the crystallographic $a$ axis. The local structure about the CO\textsubscript{2} “$\pi$-pocket” adsorption site is shown in (b). In (c) and (d), two adjacent symmetry-equivalent adsorbed CO\textsubscript{2} molecules are shown from different perspectives. Lastly, in (e), the proposed two-motion model for CO\textsubscript{2} dynamics in PbSDB is illustrated, with CO\textsubscript{2} locally wobbling and non-locally hopping between adjacent equivalent adsorption sites. Carbon is colored grey, oxygen is red, lead is purple, sulfur is yellow, and the carbon atoms corresponding to CO\textsubscript{2} guests are green.

\textsuperscript{13}C SSNMR spectra and corresponding simulations have revealed the nature of CO\textsubscript{2}
dynamics in PbSDB, however, the exact location of the adsorption site remains unclear. Accordingly, SCXRD was used to obtain the crystal structure of CO$_2$-saturated PbSDB at 110 K. The structure of activated PbSDB was used as a starting model and the guest CO$_2$ atomic positions were subsequently obtained from a difference Fourier map. The long-range crystal lattice of CO$_2$-saturated PbSDB is shown in Figure 2-3a: all CO$_2$ molecules are located at well-defined positions inside the one-dimensional channels that run along the crystallographic $a$ axis, and none of the CO$_2$ molecules exhibit positional disorder at 110 K. The CO$_2$ geometry is linear ($\angle$O-C-O = 179.96$^\circ$), and the normalized occupancy for the CO$_2$ molecule was refined to a value of 0.45. Within each channel and unit cell of the PbSDB MOF, only one crystallographically independent CO$_2$ molecule is observed, as denoted by the carbon atom C1A and corresponding CO$_2$ molecule in Figure 2-3b; this is in good agreement with the single unique CO$_2$ species indicated from the sole powder pattern in $^{13}$C SSNMR spectra.

The CO$_2$ carbon atom is located in the area bordered by the V-shaped SDB linker, adsorbed at an equivalent distance (3.550 Å) from both SDB phenyl rings (Figure 2-3b). A study of the related CaSDB MOF suggested that the V-shaped “$\pi$-pocket” geometry formed by the SDB linkers (Figure 2-A3) is associated with CO$_2$ uptake, since it facilitates attractive interactions between the molecular quadrupole moment of CO$_2$ and the delocalized $\pi$ aromatic system of the phenyl rings. The CO$_2$ adsorption sites and binding mechanisms within other SDB-based MOFs have not yet been determined, however, PbSDB incorporates the same SDB linker as CaSDB and shares similar features, including the presence of a V-shaped $\pi$-pocket. Our SCXRD experiments clearly show that adsorbed CO$_2$ resides in the middle of the SDB-based $\pi$-pocket structure within PbSDB.

Although SCXRD gives a static picture of the time-averaged atomic positions, the ORTEP depiction of the CO$_2$ adsorption site (Figure 2-A4) reveals that the CO$_2$ molecule is associated with large thermal ellipsoids, confirming that the localized CO$_2$ wobbling motion still occurs at 110 K. The twofold hopping motion of CO$_2$ can be explained by examining the positions of two neighboring symmetry-equivalent CO$_2$ molecules along the longitudinal direction of an individual PbSDB channel (Figure 2-3c,d). The distance between the carbon atoms of these adjacent CO$_2$ molecules is 3.144 Å, which is short
enough to permit twofold hopping of CO$_2$ molecules between both positions; yet because the two CO$_2$ adsorption sites and molecules are symmetry-equivalent, only a single broad $^{13}$C SSNMR powder is observed. The combined CO$_2$ motional and positional information from SSNMR and SCXRD experiments is illustrated in Figure 2-3e. Based on the success of this experimental approach for elucidating the position and dynamics of CO$_2$ adsorbed in PbSDB, a similar strategy was utilized to examine CO$_2$-loaded CdSDB.

**In situ $^{13}$C SSNMR and guest dynamics in CO$_2$-saturated CdSDB.**

Much like PbSDB, CdSDB also lacks the OMSs or polarizing functional groups thought to be key for gas adsorption. One would assume that the CO$_2$ adsorption site in CdSDB should resemble the adsorption site in PbSDB and give rise to a single $^{13}$C SSNMR powder pattern; however, Figure 2-4a reveals that two distinct broad powder patterns corresponding to adsorbed CO$_2$ are present in the $^{13}$C VT SSNMR spectra of CO$_2$-loaded CdSDB, in addition to the sharp third $^{13}$C resonance belonging to mobile, non-adsorbed CO$_2$. The analytical simulations in Figure 2-4b confirm that two CO$_2$ adsorption sites are present in CdSDB, denoted as adsorption sites 1 and 2, which must differ in local geometry and/or CO$_2$ binding affinity due to their distinct $^{13}$C NMR parameters (Table 2-1). The observed $^{13}$C NMR parameters of both powder patterns undergo clear changes as temperature is reduced, implying that CO$_2$ guests adsorbed at both sites are undergoing motion on the NMR timescale.

There are striking similarities in both visual appearance and apparent $^{13}$C NMR parameters between CO$_2$ adsorbed at adsorption site 1 in CdSDB and that of CO$_2$ adsorbed at the sole adsorption site in PbSDB (Table 2-1), strongly suggesting that these adsorption sites share a common location: the V-shaped π-pocket of the SDB ligand. In contrast, CO$_2$ at adsorption site 2 in CdSDB corresponds to a unique powder pattern and different $^{13}$C NMR parameters, implying that this resonance arises from CO$_2$ adsorbed at a different location in the MOF. The $^{13}$C powder pattern linked to adsorption site 2 is considerably broader than the powder pattern of adsorption site 1 ($\Omega = 143(2)$ versus $112(1)$ ppm at 293 K), implying that CO$_2$ molecules at adsorption site 2 may experience reduced motion and a relatively stronger binding interaction with the MOF (Table 2-1, Figure 2-A5).
Figure 2-4 Experimental static $^{13}\text{C}$ VT SSNMR spectra of CO$_2$-saturated CdSDB are shown in (a), accompanied by the analytically simulated spectra to extract observed NMR parameters in (b). The * label denotes the resonance corresponding to free gaseous CO$_2$.

Adsorption site 2 is the more populated of the two at high experimental temperatures, but interestingly, more CO$_2$ is located at adsorption site 1 at temperatures below 293 K (Figure 2-A6). Since $^{13}\text{C}$ NMR parameters indicate reduced CO$_2$ motion and a presumably stronger MOF-CO$_2$ interaction at adsorption site 2, the increased CO$_2$ population at adsorption site 1 at low temperatures suggests that site 1 must be significantly more accessible to CO$_2$ guests. The low accessibility of site 2 may originate from a number of factors, such as disordered or distorted local geometry about the adsorption site.
Figure 2-5 The simulated $^{13}$C SSNMR spectra associated with adsorption site 1 in CdSDB are shown as the purple spectra, along with motional simulations to obtain the extracted threefold wobbling angles ($\alpha$) and twofold hopping angles ($\beta$) at each temperature depicted by the dashed red lines.

The $^{13}$C VT SSNMR spectra of CO$_2$-saturated CdSDB were simulated to extract CO$_2$ motional information. CO$_2$ molecules at adsorption site 1 in CdSDB, which is presumably in the SDB $\pi$-pocket, exhibit the same type of wobbling and hopping motions as CO$_2$ adsorbed at the $\pi$-pocket in PbSDB (Figure 2-5 and Table 2-2), as modeled by a fast (i.e., motional rate $\geq 10^7$ Hz) threefold ($C_3$) rotation and twofold ($C_2$) hopping, respectively. At site 1 in CdSDB, wobbling angles ($\alpha$) decrease from 48(4)$^\circ$ at 413 K to 32(1)$^\circ$ at 183 K, while $\alpha$ values are similar and likewise decrease from 40(1)$^\circ$ to 36(1)$^\circ$ in PbSDB, owing to the similar SDB $\pi$-pocket environments between these adsorption sites. The hopping angles ($\beta$) are similar between adsorption site 1 in CdSDB and in PbSDB, but the trends diverge: at site 1 in CdSDB, $\beta$ decreases from 33(3)$^\circ$ at 413 K to 28(1)$^\circ$ at 183 K, while
across this temperature range in PbSDB, $\beta$ increases from 24(1)$^\circ$ to 30(1)$^\circ$. The most likely explanation is that temperature-induced changes in CO$_2$ orientation occur in order to maximize attractive interactions with adsorption site 1, leading to a gradual alteration of hopping angles with temperature; the differences in MOF topology and local adsorption site geometry between PbSDB and CdSDB may also have some significant influence on CO$_2$ hopping angles.

CO$_2$ adsorbed at site 2 in CdSDB gives rise to a distinct $^{13}$C SSNMR powder pattern and NMR parameters that unfortunately could not be properly simulated to extract dynamic information. We were unable to obtain a satisfactory practical and meaningful model to describe CO$_2$ dynamics at adsorption site 2 despite many attempts involving alternate motional simulations along with numerous different angles and rates of motion. Additional attempts to fit the powder pattern of adsorption site 2 using motional simulations based on the parameters of CO$_2$ adsorbed at site 1 also repeatedly failed. Taken together, the sum of $^{13}$C NMR parameters and decidedly unique CO$_2$ dynamics strongly indicates that adsorption site 2 in CdSDB is fundamentally different in local environment and adsorption affinity versus the $\pi$-pocket structure located at site 1 and in PbSDB. Furthermore, the $^{13}$C powder pattern of CO$_2$ at adsorption site 2 is broader than that of CO$_2$ at adsorption site 1, indicating that CO$_2$ is bound more strongly and is less mobile at adsorption site 2. Unfortunately, $^{13}$C SSNMR experiments alone cannot conclusively locate CO$_2$, describe its associated motions, and examine the local geometry about adsorption site 2 in CdSDB. In order to further investigate CO$_2$ adsorption in PbSDB and CdSDB, $^{207}$Pb and $^{111}$Cd SSNMR experiments were performed on various forms of these MOFs.

$^{207}$Pb and $^{111}$Cd SSNMR experiments on PbSDB and CdSDB.
Figure 2-6 The static $^{207}$Pb and $^{111}$Cd SSNMR spectra of PbSDB and CdSDB in various conditions are depicted. In (a), the $^{207}$Pb WURST-CPMG SSNMR spectra of PbSDB loaded with various guests are shown. “PbSDB with 0.5 CO$_2$” means that the molar ratio of CO$_2$ guests to Pb is 0.5. In (b), the experimental and simulated spectra of as-made PbSDB and activated PbSDB are illustrated. The static VT $^1$H-$^{111}$Cd CP-echo SSNMR spectra of as-made, activated, and CO$_2$-loaded CdSDB (CO$_2$: metal molar ratio of 0.2) are
the broad spectra depicted in (c). The room temperature $^1$H-$^{111}$Cd CP/MAS spectra of as-made and activated CdSDB are also included in (c) as the relatively narrower lineshapes shown in the second and fourth traces from the top, respectively, with the $\delta_{\text{iso}}$($^{111}$Cd) value labeled and spinning sidebands marked by an asterisk (*). A simulation of the static $^1$H-$^{111}$Cd room temperature SSNMR spectrum of CdSDB loaded with 0.2 CO$_2$ is also included in (c), with simulations of individual powder patterns in purple (termed “CdL”) and green (known as CdR), along with the overall simulation in dashed red lines.

SSNMR is often employed to study the local metal environment, metal-linker coordination, and metal-guest interactions in MOFs.$^{74, 80, 84, 95-98}$ $^{207}$Pb and $^{111}$Cd SSNMR experiments were carried out on PbSDB and CdSDB MOFs under various conditions, with the resulting spectra and simulations shown in Figure 2-6, Figure 2-A7, and Figure 2-A8, and accompanying NMR parameters summarized in Tables 2-3 and 2-4.

All $^{207}$Pb SSNMR spectra were acquired under static conditions using the WURST-CPMG pulse sequence, which yields spectra composed of a series of spikelets that trace out the overall manifold of the $^{207}$Pb powder pattern. The $^{207}$Pb SSNMR spectrum of as-made PbSDB (Figure 2-6a) is of an irregular shape, and simulations (Figure 2-6b) confirm the presence of two individual powder patterns of similar breadth but opposing $\kappa$ values (Table 2-3). After activation, only the $\kappa = +1$ $^{207}$Pb powder pattern remains, indicative of a single unique Pb site and in agreement with the crystal structure of PbSDB (Figure 2-A2). Therefore, in the $^{207}$Pb SSNMR spectrum of as-made PbSDB, the second powder pattern corresponding to $\kappa = -1$ must arise from Pb centers that are proximate to, or otherwise influenced by, residual solvent molecules from synthesis. The presence of residual solvent molecules in as-made PbSDB has a surprisingly profound impact on the axial symmetry of the $^{207}$Pb CS tensor, as evidenced by the change in $\kappa$ from one form of axial symmetry ($\kappa = +1, \delta_{11} = \delta_{22}$) to the other ($\kappa = -1, \delta_{22} = \delta_{33}$). There is also a significant change of ca. 360 ppm in $\delta_{\text{iso}}$. Given the apparent sensitivity of the $^{207}$Pb CS tensor to the presence of guest molecules, PbSDB samples loaded with a variety of solvents and CO$_2$ were examined via $^{207}$Pb SSNMR to further probe host-guest interactions, and to investigate the origins of the second $^{207}$Pb powder pattern in as-made PbSDB.
Table 2-3 ²⁰⁷Pb NMR parameters of various PbSDB samples as obtained from simulations of static WURST-CPMG experiments.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Resonance 1</th>
<th>δ&lt;sub&gt;iso&lt;/sub&gt; (ppm)</th>
<th>Ω (ppm)</th>
<th>κ</th>
</tr>
</thead>
<tbody>
<tr>
<td>As made</td>
<td></td>
<td>-2057(13)</td>
<td>1158(45)</td>
<td>0.91(4)</td>
</tr>
<tr>
<td>Activated</td>
<td></td>
<td>-2067(15)</td>
<td>1155(35)</td>
<td>1.00(2)</td>
</tr>
<tr>
<td>Loaded with 5% water</td>
<td></td>
<td>-2067(15)</td>
<td>1178(30)</td>
<td>0.92(3)</td>
</tr>
<tr>
<td>Loaded with 5% methanol</td>
<td></td>
<td>-2067(17)</td>
<td>1178(40)</td>
<td>0.92(4)</td>
</tr>
<tr>
<td>Loaded with 5% DMF</td>
<td></td>
<td>-2067(20)</td>
<td>1178(40)</td>
<td>0.92(2)</td>
</tr>
<tr>
<td>Loaded with 0.5 CO₂ (293 K)</td>
<td></td>
<td>-2077(15)</td>
<td>1170(35)</td>
<td>0.95(5)</td>
</tr>
</tbody>
</table>

Table 2-4 ¹¹¹Cd NMR parameters of activated and CO₂-loaded CdSDB, as obtained from static VT ¹H-¹¹¹Cd CP-echo experiments. “Cd₇” and “Cd₈” refer to the “left” (high-frequency) and “right” (low-frequency) cadmium NMR powder patterns.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature (° K)</th>
<th>Resonance</th>
<th>δ&lt;sub&gt;iso&lt;/sub&gt; (ppm)</th>
<th>Ω (ppm)</th>
<th>κ</th>
</tr>
</thead>
<tbody>
<tr>
<td>As made</td>
<td>293</td>
<td>Cd₈</td>
<td>-53(1)</td>
<td>242(7)</td>
<td>-0.23(4)</td>
</tr>
<tr>
<td>Activated</td>
<td>293</td>
<td>Cd₈</td>
<td>-71(3)</td>
<td>233(8)</td>
<td>-0.22(2)</td>
</tr>
<tr>
<td>Activated</td>
<td>153</td>
<td>Cd₈</td>
<td>-66(4)</td>
<td>252(5)</td>
<td>-0.22(3)</td>
</tr>
<tr>
<td>Loaded with 0.2 CO₂</td>
<td>293</td>
<td>Cd₇</td>
<td>-24(4)</td>
<td>199(14)</td>
<td>0.02(7)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cd₈</td>
<td>-78(4)</td>
<td>243(9)</td>
<td>-0.21(3)</td>
</tr>
<tr>
<td>Loaded with 0.2 CO₂</td>
<td>273</td>
<td>Cd₇</td>
<td>-25(3)</td>
<td>199(12)</td>
<td>0.02(4)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cd₈</td>
<td>-78(3)</td>
<td>228(10)</td>
<td>-0.21(3)</td>
</tr>
<tr>
<td>Loaded with 0.2 CO₂</td>
<td>253</td>
<td>Cd₇</td>
<td>-23(4)</td>
<td>199(10)</td>
<td>0.02(5)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cd₈</td>
<td>-78(2)</td>
<td>217(8)</td>
<td>-0.18(2)</td>
</tr>
<tr>
<td>Loaded with 0.2 CO₂</td>
<td>213</td>
<td>Cd₇</td>
<td>-23(4)</td>
<td>192(11)</td>
<td>0.04(4)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cd₈</td>
<td>-74(3)</td>
<td>216(9)</td>
<td>-0.18(2)</td>
</tr>
<tr>
<td>Loaded with 0.2 CO₂</td>
<td>153</td>
<td>Cd₇</td>
<td>-23(3)</td>
<td>192(13)</td>
<td>0.04(6)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cd₈</td>
<td>-74(3)</td>
<td>215(7)</td>
<td>-0.2(2)</td>
</tr>
</tbody>
</table>

Since the solvent used for PbSDB synthesis was a 1:1 mixture of methanol and DMF, the impact of separately loading 5% wt of methanol, DMF, and water into activated PbSDB was examined via ²⁰⁷Pb SSNMR (Figure 2-6a). The water- and methanol-loaded samples of PbSDB each feature a single ²⁰⁷Pb powder pattern which corresponds to nearly the same ²⁰⁷Pb NMR parameters as activated empty PbSDB (Figure 2-A7, Table 2-3), confirming that neither solvent has an appreciable influence on the local environment of Pb. In contrast, DMF-loaded PbSDB yields a ²⁰⁷Pb powder pattern resembling that of as-made PbSDB; this spectrum features a clear increase in spectral intensity in the low-frequency region between ca. -2500 and -3000 ppm that is not particularly well-defined. The lack of a clearly
resolved second powder pattern is likely due to short-range disorder about the solvent-proximate Pb centers, owing to the re-introduction of solvent to the activated MOF. From these $^{207}$Pb SSNMR spectra, it is clear that DMF gives rise to the unique second powder pattern in as-made PbSDB. The SSNMR data indicates that in PbSDB, DMF either coordinates directly to Pb or experiences a strong attractive interaction with Pb.

VT $^{207}$Pb SSNMR was also used to probe the impact of CO$_2$ guests on the local environment of Pb and to investigate the possibility of any Pb-CO$_2$ interactions in PbSDB. The $^{207}$Pb SSNMR spectrum of CO$_2$-loaded PbSDB at 293 K is strikingly similar to the spectrum of empty activated PbSDB (Figure 2-6a), and simulations (Figure 2-A7) indicate that both spectra correspond to approximately the same $^{207}$Pb NMR parameters (Table 2-3). The clear similarities between the $^{207}$Pb NMR parameters of activated and CO$_2$-loaded PbSDB imply that CO$_2$ adsorbed in the SDB π-pocket has a minute or negligible influence on the local Pb environment. Pb does not directly interact with adsorbed CO$_2$ and the local environment about Pb is preserved. No Pb-CO$_2$ adsorptive interactions in these systems have otherwise been documented, in good agreement with our findings.

To determine if CO$_2$ dynamics have any impact on the Pb metal center in PbSDB, VT $^{207}$Pb SSNMR experiments were performed on CO$_2$-loaded PbSDB at 183 K, yielding a powder pattern unchanged from room temperature and corresponding to approximately the same NMR parameters (Figure 2-6a, Figure 2-A7, Table 2-3). The differences in NMR parameters between temperatures are small, within experimental uncertainties, and likely due solely to the well-documented temperature dependence of the $^{207}$Pb chemical shift;$^{99}$ CO$_2$ dynamics thus have no effect on the Pb metal center in PbSDB. To see if the same conclusions held true when a different metal center was incorporated, $^{111}$Cd SSNMR experiments were performed on CdSDB.

The static $^1$H-$^{111}$Cd CP-echo SSNMR spectra of as-made and activated CdSDB at room temperature exhibit similar lineshapes (Figure 2-6c), and simulations suggest the presence of one $^{111}$Cd powder pattern, in accordance with the single crystallographically unique cadmium site in the CdSDB crystal structure.$^{62}$ $^1$H-$^{111}$Cd CP/MAS spectra (Figure 2-6c) clearly confirm the presence of a single resonance at ca. $\delta_{iso} = -52$ ppm in as-made and
activated CdSDB. Static experiments reveal that the $^{111}$Cd CS parameters $\Omega$ and $\kappa$ are similar between as-made and activated CdSDB, suggesting that Cd binding and connectivity is preserved (i.e., no Cd-linker bonds have been made or broken). This data indicates that the local Cd environment is only slightly perturbed by the removal of residual solvent from the MOF pores, likely via minor differences in linker-metal bond lengths and angles or linker orientation. It should be noted that there is some discrepancy in measured $\delta_{\text{iso}}$($^{111}$Cd) values for activated CdSDB between $^1$H-$^{113}$C static CP-echo (-71.3 ppm) and CP/MAS experiments (-52.4 ppm), which may be due to the influence of frictional heating from the spinning sample rotor ($\nu_{\text{rot}} = 10$ kHz, 4 mm rotor). When the temperature is reduced to 153 K, static $^1$H-$^{111}$Cd CP-echo experiments on activated CdSDB reveal $\delta_{\text{iso}}$ has again shifted to -66(4) ppm, supporting the notion of a temperature-dependent $^{111}$Cd chemical shift in this system.

The introduction of CO$_2$ to activated CdSDB at room temperature causes the appearance of a second $^{111}$Cd powder pattern, implying that two distinct local Cd environments are now present (Figure 2-6c). For clarity, these two powder patterns are denoted as Cd$_L$ and Cd$_R$ (left (high-frequency) and right (low-frequency), respectively, see Figure 2-A8). Cd$_R$ and its associated $^{111}$Cd NMR parameters ($\delta_{\text{iso}} = -78(4)$ ppm, $\Omega = 243(9)$ ppm, $\kappa = -0.21(3)$) in CO$_2$-loaded CdSDB at room temperature are strikingly similar to the single powder pattern observed in activated CdSDB ($\delta_{\text{iso}} = -71(3)$ ppm, $\Omega = 233(8)$ ppm, $\kappa = -0.22(2)$), suggesting that these resonances correspond to nearly identical local Cd environments. In contrast, the Cd$_L$ powder pattern is linked to unique $^{111}$Cd CS parameters ($\delta_{\text{iso}} = -24(4)$ ppm, $\Omega = 199(14)$ ppm, $\kappa = 0.02(7)$), and represents a second distinct Cd environment perturbed from that of activated CdSDB and associated with adsorption of CO$_2$ guests.

VT static $^1$H-$^{111}$Cd CP-echo SSNMR experiments were performed on CO$_2$-loaded CdSDB at reduced temperatures to probe the influence of CO$_2$ dynamics on the Cd metal centers. Although $^{111}$Cd NMR parameters associated with both Cd resonances are invariant with reduced temperature aside from a 10 % decrease in $\Omega$(Cd$_R$), the relative intensity of Cd$_L$ versus Cd$_R$ climbs from ca. 0.2 at 293 K to ca. 1.2 at 153 K (Table 2-4, Figures 2-A8 and 2-A9). Since more CO$_2$ is adsorbed within CdSDB at lower temperatures, the evolution in
the Cd\textsubscript{L}/Cd\textsubscript{R} intensity ratio indicates that the population of these Cd environments are
directly linked to the amount of adsorbed CO\textsubscript{2} and permits spectral assignment: Cd\textsubscript{L}
corresponds to Cd centers proximate to adsorbed CO\textsubscript{2} guests in occupied MOF channels,
while Cd\textsubscript{R} is linked to Cd in relatively empty channels that are distant from any CO\textsubscript{2}. The
distinct $^{111}$Cd NMR parameters associated with Cd\textsubscript{L} suggest the presence of minor guest-
induced changes in metal-linker bond angles and/or linker orientations, which would have
a measurable impact on the $^{111}$Cd CS tensor.

On the basis of VT $^{13}$C SSNMR experiments targeting adsorbed CO\textsubscript{2} in CdSDB (vide supra), we have hypothesized that CO\textsubscript{2} adsorption site 1 in CdSDB is similar to the V-
shaped $\pi$-pocket formed by the SDB linkers in PbSDB, while adsorption site 2 in CdSDB
must have a unique geometry and engage in a different CO\textsubscript{2} adsorptive interaction. The
unchanged $^{111}$Cd NMR parameters across temperature variations in CO\textsubscript{2}-loaded CdSDB
indicate that CO\textsubscript{2} dynamics at sites 1 and 2 have very little or no influence on the Cd metal
center, much like in the case of PbSDB. The impact of CO\textsubscript{2} adsorption on $^{111}$Cd SSNMR
spectra and associated NMR parameters implies adsorption site 2 may be located closer to
Cd, but the question remains: assuming that the SDB-based $\pi$-pocket is already occupied
by site 1, where exactly is adsorption site 2 located in CdSDB? Since the position of the
CO\textsubscript{2} adsorption sites in CdSDB are not readily available from our NMR data, SCXRD
experiments were performed.

**SCXRD of CO\textsubscript{2}-saturated CdSDB.**

The first sample examined was CdSDB loaded with saturated CO\textsubscript{2} at a temperature of 110
K, which yielded the crystal structure pictured in Figure 2-7a. All CO\textsubscript{2} molecules are
located inside the sinusoidal channels that propagate along the crystallographic $c$ axis.
There are two unique CO\textsubscript{2} molecules in each pore, represented by their carbon atoms C1A
and C1B (Figure 2-7b) that are located ca. 0.79 Å apart. There are two equivalent C1B sites
and only one C1A site.
Figure 2-7 The extended crystal structure of CdSDB loaded with saturated CO\textsubscript{2}, as seen along the $c$ axis, is shown in (a). In (b), the local positions of adsorbed CO\textsubscript{2} molecules in CdSDB are shown, highlighting the carbon atoms of CO\textsubscript{2} that are associated with two unique adsorption sites C1A and C1B, where C1B has two symmetry-equivalent positions. The local environment about C1A is depicted in (c) along with its missing symmetry equivalent site located ca. 1.6 Å away, as indicated by a dashed red circle. In (d), the distances between C1B/C1A and adjacent cadmium atoms are shown, along with the short distance of 1.318 Å between the two symmetry-equivalent C1B adsorption sites. Note that the distance between C1B and both adjacent cadmium sites is significantly shorter than those of C1A. Oxygen atoms on adsorbed CO\textsubscript{2} are omitted for clarity and the purple phenyl rings in (b), (c), and (d) represent the other possible phenyl ring orientation in these disordered structures (see main text along with Figure 2-A10).

The number of unique CO\textsubscript{2} sites and their respective local environments are in agreement with our $^{13}$C SSNMR data. The C1A site resides in the middle of the $\pi$-pocket structure formed by the SDB linker, and is an equivalent 3.805 Å from both phenyl rings (Figure 2-7c). This crystallographic C1A site corresponds to the CO\textsubscript{2} “adsorption site 1” resonance
observed in $^{13}$C SSNMR spectra of CO$_2$-loaded CdSDB (Figure 2-4). In this case, the
twofold hopping between equivalent C1A sites extracted from SSNMR simulations likely
describes CO$_2$ jumping 5.75 Å down the longitudinal direction of the CdSDB channel (i.e.,
the c axis) between adjacent C1A adsorption sites, similar to the CO$_2$ jumping in PbSDB.

On the basis of the unique second powder pattern in $^{13}$C SSNMR spectra and the influence
of CO$_2$ adsorption on $^{111}$Cd spectra, we postulated that the second CO$_2$ adsorption site in
CdSDB should be located relatively proximate to the Cd metal center. The measured
distance between the nearest cadmium atom and C1B is 6.332 Å, versus a longer distance
of 6.895 Å between C1A and the nearest cadmium center (Figure 2-7d). In a similar trend,
the distance between C1B and the next nearest Cd is 6.379 Å, while the distance between
the next nearest Cd and C1A is 7.007 Å. Therefore, the second CO$_2$ adsorption site
observed in $^{13}$C SSNMR spectra should correspond to the crystallographic site C1B, which
is located relatively closer to Cd.

Although $^{13}$C SSNMR experiments could not establish a motional model for CO$_2$ at
adsorption site 2 (vide supra), SCXRD data yields two important pieces of data. First, the
measured distance between the two equivalent C1B carbon atoms in the same pore is 1.318
Å (Figure 2-7d), which is too close to permit CO$_2$ hopping between adjacent C1B sites;
any CO$_2$ hopping at adsorption site 2 likely involves longitudinal jumping down the
channel between C1B sites (i.e., along the c axis). Second, along with the short C1B-C1B
distance of 1.318 Å, the distance between C1A and the equivalent C1B atoms is a short
0.79 Å; these short distances prohibit simultaneous occupation of all three adsorption sites
in any given MOF channel cross-section.

An interesting question is why there is only a single C1A site indicated from SCXRD data,
yet there are two SDB-based “π-pocket” structures capable of CO$_2$ adsorption in CdSDB
which should presumably give rise to two equivalent C1A sites (Figure 2-7c). We believe
the absence of a second C1A adsorption site in SCXRD experiments is linked to our
observation of disordered phenyl rings on the unique SDB linker that composes the
“bottom” half of the channel perimeter in CdSDB (indicated by SCXRD experiments, see
the purple carbon atoms in Figure 2-7b,c,d). It should be noted that the SDB linkers along
the “top” half of the channel perimeter are not disordered. Disordered SDB phenyl rings were previously reported in CdSDB, but no detailed discussion was offered. The presence of disordered SDB linkers in CdSDB contrasts with the ordered phenyl rings in other SDB-based MOFs including PbSDB, however, disordered phenyls on linker species have been observed in other MOFs and coordination polymers.

**Figure 2-8** $^1$H-$^{13}$C CP/MAS NMR experiments on activated (a) PbSDB and (b) CdSDB at a spinning frequency of 14 kHz. Note the extra $^{13}$C resonances in CdSDB located in the region from 137 – 145 ppm, which correspond to the other orientation of the static disordered phenyl rings.

The SDB phenyl groups contain carbon atoms C1, C2, C3, C4, C5, and C6 (all colored grey in Figure 2-7), and the disorder of the phenyl ring arises from a reorientation or partial flip around the C1-C4 axis, yielding alternate carbon positions C2', C3', C5', and C6' (all colored in purple in Figure 2-7). $^1$H-$^{13}$C CP/MAS NMR experiments (Figure 2-8) confirm that there is static disorder of the phenyl rings in CdSDB: while PbSDB yields two $^{13}$C resonances corresponding to the equivalent C2-C6 and C3-C5 carbon atom pairs of the
SDB phenyl ring, CdSDB yields four $^{13}$C resonances originating from the C2-C6, C3-C5, C2'-C6', and C3'-C5' pairs of SDB carbon atoms. The dihedral angle between the two phenyl planes is ca. 32.2°, and the normalized occupancy was refined to a value of 0.659(6) for the major conformer (depicted in grey). Owing to the disorder in phenyl orientations, there are four different combinations of phenyl ring orientations in the SDB ligand (Figure 2-A10), however, only one combination can form a SDB-based π-pocket$^{61}$ that affords simultaneous CO$_2$ adsorptive interactions with both phenyl rings. Accordingly, CO$_2$ adsorption and the CO$_2$ population at this equivalent location to site 1 is greatly reduced; the resulting low density of CO$_2$ molecules prohibit SCXRD detection of adsorbed guests at the lower π-pocket in the crystal structure (Figure 2-7c), red dashed circle).

Although SCXRD data has shown that CO$_2$ guests adsorbed in PbSDB adopt the typical linear geometry, SCXRD indicates that adsorbed CO$_2$ in CdSDB is bent in a nonlinear conformation. Bent CO$_2$ molecules have been reported in a variety of different MOF systems and topologies,$^{106-109}$ and the underlying details remain under debate.$^{106}$ The bent CO$_2$ configuration derived from SCXRD data is actually a time-averaged picture of CO$_2$ structure, which can be significantly influenced by dynamics and the distribution of possible CO$_2$ positions, and may not necessarily reflect the true CO$_2$ geometry.$^{106,109}$ With these considerations in mind, we believe CO$_2$ remains linear and do not place a high degree of confidence in the bent CO$_2$ geometry observed in CdSDB; only the carbon positions are indicated in corresponding Figures.
Figure 2-9 The extended crystal structure of CdSDB and PbSDB loaded with saturated CO$_2$ are shown in (a) and (b), respectively. The local structure of CO$_2$ molecules adsorbed at site 1 in CdSDB and at the only adsorption site within PbSDB are shown in (c) and (d).
The carbon atoms of CO$_2$ adsorbed in both MOFs are located at equivalent distances from both nearby phenyl groups: for C1A in CdSDB, the distances are 3.805 Å, for C1A in PbSDB, the distances are 3.550 Å. The green “V” shape drawn above the phenyl rings of the SDB linker in (c), (d), and (f) highlights the V-shaped “π-pocket” associated with CO$_2$ adsorption in these systems. The carbon atoms of CO$_2$ found at the two symmetry-equivalent locations associated with adsorption site 2 in CdSDB (denoted C1B) are shown in (e), along with their different distances from the phenyl rings. The arrangement of phenyl groups about the cadmium centers gives rise to another V-shaped π-pocket, as indicated by the blue V shape in (e). In (f), the only π-pocket in PbSDB is pictured; the orientation of the bottom two SDB phenyl rings prevents formation of a second π-pocket structure. The carbon atoms associated with both unique CO$_2$ adsorption sites in CdSDB are shown in (g), and the sole CO$_2$ adsorption site along with its equivalent neighboring CO$_2$ adsorption site are shown in (h). In all instances carbon is colored grey, oxygen is red, cadmium is blue, lead is purple, sulfur is yellow, and carbon atoms corresponding to adsorbed CO$_2$ are green. Oxygen atoms on adsorbed CO$_2$ in CdSDB are omitted for clarification, and the purple phenyl rings in (c), (e), and (g) represent another possible orientation of these disordered phenyl rings (see Figure 2-A10).

There are similar CO$_2$ adsorption sites denoted C1A located at the π-pocket structures in both CdSDB and PbSDB, as shown by the green V shape in Figures 2-9c and 2-9d, which exhibit very similar $^{13}$C NMR powder patterns. In CdSDB there is a second CO$_2$ adsorption site, C1B, that gives rise to a unique $^{13}$C powder pattern and is located at a different position in the channel (Figure 2-9e). A more careful examination of the local geometry about C1B reveals that CO$_2$ molecules located at this adsorption site may interact with a second type of π-pocket that is formed by two phenyl rings from the two separate SDB linkers attached to the cadmium metal centers. This second Cd-based π-pocket (Figure 2-9e, blue V shape) is unique because the CO$_2$ adsorption site is not equidistant from the phenyl rings: one C1B-phenyl distance is ca. 3.774 Å, and other C1B-phenyl distance is ca. 4.100 Å (Figure 2-9e). This second π-pocket does not exist in PbSDB since the phenyl group orientation about Pb makes such an arrangement impossible (Figure 2-9f). In the SDB-based π-pocket, the phenyl rings are in the correct orientation to bind CO$_2$ molecules equidistant from both
rings within a perpendicular plane. In contrast, the geometry about the Cd-based \( \pi \)-pocket is slightly distorted and the associated phenyl rings have deviated (i.e., tilted) away from an ideal orientation, resulting in an off-centered C1B adsorption site of unique local geometry that exhibits different distances to each phenyl ring (Figure 2-9e); this is why CO\(_2\) adsorbed at the C1B site gives rise to a distinct second \(^{13}\)C powder pattern. It should be noted that the disordered phenyl rings of one SDB ligand in CdSDB (vide supra) may restrict CO\(_2\) adsorption at the C1B site in the Cd-based \( \pi \)-pocket to some extent due to unfavorable geometry; however, the successful location of both C1B sites via SCXRD methods clearly demonstrates that CO\(_2\) sufficiently populates both sites, and that phenyl ring disorder only has a minor impact on adsorption at the Cd-based \( \pi \)-pocket in CdSDB.

The nature and coordination of the metal center has a profound influence on linker orientation and CO\(_2\) adsorption sites in these two SDB-based MOFs. Incorporation of the 7-coordinate Pb metal results in a single unique SDB-based CO\(_2\) adsorption site, as the framework topology forces the other unique SDB ligand to adopt a phenyl ring orientation that prevents \( \pi \)-pocket formation at this second SDB linker and at Pb. In contrast, selection of the 6-coordinate Cd center leads to two unique CO\(_2\) adsorption sites, since the MOF topology permits the appropriate SDB phenyl ring orientation to form one unique type of \( \pi \)-pocket in the V-shaped space of the SDB linker and two symmetry-equivalent \( \pi \)-pockets in the V-shaped spaces proximate to Cd. Our combined SCXRD and SSNMR data illustrates the importance of choosing the specific metal and its coordination number for the design and application SDB-based MOFs, since this directly influences MOF topology as well as the number, nature, and location of CO\(_2\) adsorption sites.

**SCXRD of CO\(_2\)-loaded (unsaturated) CdSDB.**

With the locations and origins of adsorption sites in PbSDB and CdSDB now known, the relative adsorption strengths and preferential occupation of adsorption sites in CdSDB can now be explored. \(^{13}\)C SSNMR data has suggested that the C1B site is preferentially occupied over C1A at room temperature. To investigate, low levels of CO\(_2\) were loaded in an unsaturated manner (see details in Appendix) to a single crystal of CdSDB for SCXRD experiments, yielding the structure depicted in Figure 2-10a.
Figure 2-10 The extended crystal lattice of CdSDB loaded with unsaturated CO$_2$ is depicted in (a), as viewed along the $c$ axis. The locations of the symmetry-equivalent carbon atoms associated with CO$_2$ adsorbed in CdSDB are shown in (b). Oxygen atoms on adsorbed CO$_2$ are omitted for clarification, and the purple phenyl rings in (b) represent the other possible orientation of the disordered phenyl rings in CdSDB (see Figure 2-A10).

There are two equivalent C1B CO$_2$ molecules located near their usual Cd-based $\pi$-pocket positions in the pore, while there are no C1A CO$_2$ molecules to be found in either SDB-based $\pi$-pocket structure (Figure 2-10b). It should be noted that although the C1B in this instance remains positioned within the Cd-based $\pi$-pocket, C1B is also located slightly closer to the SDB-based $\pi$-pocket structure versus the C1B position within CO$_2$-saturated CdSDB. The normalized occupancy of C1B CO$_2$ in unsaturated CdSDB was refined to a value of 0.69. These SCXRD experiments clearly show that a majority of CO$_2$ is adsorbed at the C1B adsorption site when CO$_2$ loading levels are low, indicating that CO$_2$ adsorption strength is likely higher at the C1B site in the Cd-based $\pi$-pocket, and binding should be relatively weaker at the SDB-based $\pi$-pocket associated with C1A. Of particular note is that the relatively stronger CO$_2$ adsorption associated with the Cd-based $\pi$-pocket is linked to unequal CO$_2$-phenyl distances, while the weaker adsorption at the SDB-based $\pi$-pocket involves equal CO$_2$-phenyl distances; this raises the potential for further increasing the CO$_2$ binding energy in SDB-based MOFs, and MOFs in general, by modification of specific phenyl ring orientations and distances. Much like the situation of saturated CO$_2$ loaded in CdSDB, the geometry of unsaturated CO$_2$ in CdSDB was also found to be nonlinear in
SCXRD experiments. In addition to the previously discussed reasons (vide supra), another reason for the observation of bent CO\(_2\) in unsaturated CdSDB may be the low electron density of adsorbed CO\(_2\) arising from the relatively low unsaturated guest loading level.

Finally, SCXRD data was thoroughly examined in order to understand the influence of adsorbed CO\(_2\) at adsorption site 2 (C1B) on the Cd local environment and \(^{111}\)Cd NMR parameters. A comparison of activated empty CdSDB and CO\(_2\)-loaded CdSDB SCXRD data (Table 2-A3) reveals that the unit cell parameters and local Cd coordination environment (including bond lengths and angles) are nearly the same in both systems, hinting some other structural change gives rise to the changes in \(^{111}\)Cd NMR parameters. Since each Cd center is bound to three SDB linkers with disordered phenyl rings (six connected SDB linkers in total, see Figure 2-A2), it is possible that adsorbed CO\(_2\) at site 2 (C1B) may influence the two possible orientations of the nearby disordered phenyl groups associated with the Cd-based \(\pi\)–pocket.

In activated CdSDB, SCXRD data indicates that the dihedral angle between the two possible orientations of phenyl rings (Figure 2-A11, Table 2-A4) are identical for both phenyl rings attached to the SDB linker. After loading CO\(_2\) into CdSDB at unsaturated levels, the dihedral angles between the disordered phenyl orientations for both phenyl groups in the same SDB linker now differ by ca. 0.3\(^\circ\), and are also altered from the values in empty activated CdSDB (Table 2-A4), suggesting that CO\(_2\) guests have some influence on phenyl orientation. In CO\(_2\)-saturated CdSDB, the disparity between the measured dihedral angles grows larger to ca. 0.6\(^\circ\). These findings help explain the two observed powder patterns in \(^1\)H-\(^{111}\)Cd CP SSNMR spectra (Figure 2-6c): the presence of guest CO\(_2\) slightly modifies the individual static orientations of the disordered phenyl rings on the SDB ligand, which perturbs the \(^{111}\)Cd NMR parameters and gives rise to the Cd\(_L\) resonance. When more CO\(_2\) is adsorbed in CdSDB (i.e., at lower experimental temperatures), the phenyl ring orientations are modified to a greater degree, creating more Cd\(_L\) environments and causing a further increase in Cd\(_L\) powder pattern intensity. In this case, even small changes in dihedral angles between the static disordered phenyl orientations can be clearly detected from both SCXRD and SSNMR methods.
2.3 Conclusion

A series of SSNMR and SCXRD experiments have been used to understand CO$_2$ adsorption and dynamics in the PbSDB and CdSDB MOFs, which do not feature open metal sites or polarizing functional groups. Multinuclear VT SSNMR experiments revealed the number of CO$_2$ adsorption sites in each MOF and yielded detailed guest motional data, as well as information on the MOF-CO$_2$ adsorptive interaction and the influence of the metal center on CO$_2$ adsorption. CO$_2$ guests undergo a combination of a localized rotation or “wobbling” as well as a non-localized hopping between symmetry-equivalent SDB-based adsorption sites in both MOFs. SCXRD experiments were used to elucidate the exact locations of CO$_2$ adsorption sites and their occupancies, along with the relationship between phenyl ring disorder and guest adsorption. CO$_2$ adsorption occurs at the V-shaped π-pocket in both MOFs, which is located equidistant from both phenyl rings of the bent SDB linker. SSNMR and SCXRD experiments reveal that the second adsorption site in CdSDB is located in another π-pocket formed by phenyl rings about the 6-coordinate Cd metal; in contrast, the distinct connectivity between 7-coordinate Pb and SDB linkers in PbSDB prohibits the phenyl ring geometry necessary for the formation of an additional Pb-based π-pocket and a second CO$_2$ adsorption site. The choice of metal center and coordination number permits controlled incorporation of one or multiple π-pocket structures in a single MOF, which has the potential to increase CO$_2$ adsorption and permit fine-tuning of the guest adsorption strength within future rationally-designed MOFs. Both SSNMR and SCXRD experiments detected uncommon CO$_2$-induced structural changes in CdSDB, which provide yet another avenue to further optimize CO$_2$ adsorption in MOFs. This work is a vivid illustration of how diverse, detailed structural and motional insights are available when utilizing a combination of solid state NMR and SCXRD experiments; pairing these complementary characterization methods is an extremely effective avenue for studying guest adsorption in MOFs.

2.4 References


(75). X. Kong, H. Deng, F. Yan, J. Kim, J. A. Swisher, B. Smit, O. M. Yaghi and J. A.


2.5 Appendix

Section A1: Experimental details.

Sample preparation. PbSDB was prepared according to the reported procedure, which is briefly summarized below. A reagent mixture of 0.165 g Pb(NO$_3$)$_2$ (BDH Chemicals, 99.5%), 0.306 g H$_2$SDB (Sigma-Aldrich, 97%), and 0.123 g LiNO$_3$ (BDH, 99.5%) was prepared in 10 mL of a 1:1 dimethylformamide (DMF, Caledon Laboratories, 99.8%) and methanol (MeOH, Fischer Chemical, 99.9%) solvent blend, and the resulting reagent mixture was placed into a Teflon chamber within a Teflon-lined stainless steel autoclave. The autoclave was then sealed, put into an oven, and heated at a temperature of 160 °C for 2 days. After cooling the autoclave to room temperature and allowing it to sit sealed without agitation for 5 days, colorless needle-shaped crystals were obtained, which were separated by vacuum filtration and washed with MeOH three times.

CdSDB was prepared following the previously reported procedure with some modifications. A mixture of 0.109 g Cd(NO$_3$)$_2$•4H$_2$O (Strem Chemicals, 98%) and 0.104 g H$_2$SDB (Sigma-Aldrich, 97%) was dissolved in a mixture of 7 mL ethanol (EtOH, Fischer Chemical, 95 %) and 3 mL of deionized H$_2$O. Following this, the reagent mixture was
placed in a Teflon chamber within a Teflon-lined stainless steel autoclave, which was then sealed and heated in a 180 °C oven for 2 days. After cooling the autoclave to room temperature and letting it rest without agitation for 48 hours, the product was obtained as colorless rectangular crystals, which were isolated by vacuum filtration and washed with EtOH three times.

**Activation and CO\textsubscript{2} loading of MOFs.** To load Pb/CdSDB with CO\textsubscript{2} and prepare these materials for SSNMR experiments, the following procedure was employed. The MOFs were first packed into the bottom of an L-shaped glass tube attached to a vacuum line, and a small amount of glass wool was used to secure the MOF sample in place. The glass tube was then heated at 180 °C / 453 K under dynamic vacuum (≤ 1 mbar) for ca. 12 hours to activate the MOF (i.e., purge all solvent and excess linker from the MOF channels). A known amount of 13C-labeled 13CO\textsubscript{2} (Sigma-Aldrich, 99% 13C isotope enriched, referred to herein as simply CO\textsubscript{2}) was then introduced into the same empty vacuum line. CO\textsubscript{2} was condensed and trapped in the MOF sample by immersing the glass tube in liquid nitrogen (77 K) and then flame-sealing the L-shaped tube off from the vacuum line. In the case of activated PbSDB loaded with 5% DMF, a set quantity of vaporized DMF was introduced to the vacuum line before flame-sealing the tube from the vacuum line.

**SSNMR measurements.** All SSNMR experiments were performed using a Varian Infinity Plus wide-bore NMR spectrometer, equipped with an Oxford 9.4 T wide-bore magnet (ν\textsubscript{0}(13C) = 100.5 MHz, ν\textsubscript{0}(207Pb) = 83.7 MHz, ν\textsubscript{0}(111Cd) = 84.8 MHz) and a 5 mm HX static Varian/Chemagnetics probe unless otherwise noted. 13C NMR spectra were referenced to the high-frequency resonance of ethanol at 58.05 ppm. Static 13C experiments were performed using the DEPTH-echo pulse sequence for enhanced background signal suppression\cite{4,5}, employing a 90° pulse width of 3.1 µs and a 180° pulse width of 6.2 µs. The recycle delays and number of scans required for 13C SSNMR acquisition of both MOFs at variable temperatures are included in Supporting Information Table 2-A1. Static 207Pb NMR spectra were acquired using the WURST-CPMG pulse sequence\cite{6,11} with a 1H decoupling field of 40 kHz, and were referenced to a saturated solution of Pb(NO\textsubscript{3})\textsubscript{2} at room temperature (δ\textsubscript{0}(207Pb) = -2970 ppm).\cite{12} The calibrated 207Pb recycle delay employed was 10 s, while the spikelet separation in the frequency domain was 2500 Hz, and the
spectral window was 1000 kHz. The static $^{111}$Cd spectra were acquired using a variable-amplitude $^1$H-$^{111}$Cd cross-polarized (CP) echo pulse sequence, and referenced to 0.1 M Cd(ClO$_4$)$_2$ ($\delta^{(111)}$Cd) = 0 ppm).$^{13-14}$ The optimized recycle delay was 3 s, $^1$H 90° pulse was 3 µs, $^{111}$Cd 180° pulse was 5.25 µs, and the $^1$H-$^{111}$Cd CP mixing time was 10 ms. $^1$H-$^{111}$Cd CP-echo experiments also employed a spectral width of 300 kHz, a Hartmann-Hahn matching field of 73 kHz, and a $^1$H decoupling field of 63 kHz. The $^{111}$Cd isotope was chosen for study rather than $^{113}$Cd due to rf interference from nearby radio stations.

$^1$H-$^{13}$C and $^1$H-$^{111}$Cd CP magic angle spinning (CP/MAS) SSNMR experiments were performed on the same Varian Infinity Plus 9.4 T NMR spectrometer, using a 4 mm HXY Varian/Chemagnetics probe and a spectral width of 100 kHz. $^1$H-$^{13}$C CP/MAS experiments were performed at a spinning frequency of 14 kHz, using a contact time of 5 ms and a recycle delay of 3 s. $^1$H-$^{13}$C CP experiments on PbSDB and CdSDB involved the acquisition of 298 and 1684 scans, respectively. $^1$H-$^{111}$Cd CP/MAS experiments were carried out at a spinning frequency of 10 kHz using a contact time of 4 ms and a recycle delay of 1 s. 1204 scans were acquired on the as-made CdSDB sample, while 1072 scans were acquired for activated CdSDB.

**Single crystal XRD.** To begin, a small amount of single crystals were packed into NMR tubes, and activated using the same vacuum line and procedure as employed for activation prior to NMR experiments (vide supra). For MOF samples loaded to saturation with CO$_2$, the glass tube containing the activated sample was exposed to CO$_2$ while immersed in liquid nitrogen for ca. 15 minutes to ensure full saturation; the glass tube containing the CO$_2$-saturated MOF was then flame-sealed from the vacuum line and kept at room temperature. After one week at rest, the glass tubes were broken, and the CO$_2$-saturated samples were immediately coated with paratone oil in order to retain all CO$_2$ within the MOF. An optical microscope was used to select high-quality single-crystals for structural analysis. For CdSDB samples loaded but not saturated with CO$_2$, the glass tube containing activated CdSDB was only exposed to CO$_2$ at liquid nitrogen temperature for 30 s before being flame-sealed from the vacuum line and stored at room temperature for 3 days.

All SCXRD measurements were made on a Bruker Kappa Axis Apex2 diffractometer at a
temperature of 110 K. The frame integration was performed using SAINT.\textsuperscript{18} The resulting raw data was scaled and absorption corrected using a multi-scan averaging of symmetry equivalent data with SADABS.\textsuperscript{19} Structures were solved by using a dual space methodology incorporated in the SHELXT program.\textsuperscript{20} All non-hydrogen framework atoms were obtained from the initial structural solution. The hydrogen atoms were introduced at idealized positions and were allowed to ride on the parent atom. The atomic positions for the CO\textsubscript{2} molecules were obtained from a difference Fourier map. The structural model was fit to the data using a full matrix least-squares method based on F\textsuperscript{2}. The calculated structure factors included corrections for anomalous dispersion from the usual tabulation. The structure was refined using the SHELXL-2014 program from the SHELX suite of crystallographic software.\textsuperscript{21} A detailed summary of the crystallographic data of CO\textsubscript{2}-loaded Pb/CdSDB is given in Table 2-A2.

**Section A2:**

![Figure 2-A1](image_url) The structure of H\textsubscript{2}SDB (4,4'- sulfonyldibenzoic acid).
**Figure 2-A2** At left in (a) and (b), the extended framework of PbSDB and local coordination environment of Pb are shown, respectively. The green spheres in (a) represent the void space accessible to guests within the PbSDB channels. At right in (c), the CdSDB framework is depicted, with purple spheres indicating the vacant space within the one-dimensional channels of this MOF. The local coordination environment of Cd within CdSDB is depicted in (d).

**Figure 2-A3** A schematic view of CO$_2$ adsorbed in the “π-pocket” MOF structural feature that is formed by the V-shaped SDB ligand. The dashed black lines between the phenyl rings and the CO$_2$ molecule symbolize the adsorptive interaction between the molecular quadrupole moment of CO$_2$ and delocalized π aromatic system of both phenyl rings. The distance between the carbon atom of CO$_2$ (“C1C”) and the two phenyl rings is typically identical.
**Figure 2-A4** An ORTEP drawing of PbSDB loaded with CO$_2$. Thermal ellipsoids are drawn at the 50% probability level, and hydrogen atoms were omitted for clarity. Note the large thermal ellipsoids associated with the dynamic CO$_2$ molecule versus the small ellipsoids of the relatively more static MOF atoms.

**Figure 2-A5** A comparison of Ω values associated with $^{13}$CO$_2$ adsorbed at the two unique adsorption sites within CdSDB. Although the span of CO$_2$ adsorbed at both sites decreases when temperature increases, the changes in the span value of CO$_2$ adsorbed at site 2 are more pronounced than those of CO$_2$ adsorbed at site 1.
Figure 2-A6 A comparison of the observed intensity ratio between the $^{13}$C powder patterns versus experimental temperatures in CO$_2$-saturated CdSDB. The ratios are based on analytical simulations of the experimental spectra. Note that adsorption site 2 is more populated at high temperatures, but adsorption site 1 becomes more populated at lower temperatures.
Figure 2-A7 The experimental and simulated static $^{207}$Pb WURST-CPMG SSNMR spectra of CO$_2$-loaded PbSDB (CO$_2$: Pb molar ratio of 0.5) at 293 and 183 K, along with those of PbSDB loaded with 5% water and methanol (by mass) at 293 K. Note that all spectra are nearly identical, suggesting limited or no interactions between Pb and the guest species.
**Figure 2-A8** The experimental and simulated static $^1$H-$^{111}$Cd CP-echo SSNMR spectra of as made CdSDB, activated CdSDB and CO$_2$-loaded CdSDB (CO$_2$: Cd molar ratio of 0.2) at various temperatures. “Cd$_L$” and “Cd$_R$” are the left (high-frequency) and right (low-frequency) $^{111}$Cd powder patterns. The red trace is the simulation of both $^{111}$Cd powder patterns.
Figure 2-A9 The integrated intensity ratio of the Cd$_R$:Cd$_L$ powder patterns versus temperature in CO$_2$-loaded CdSDB (CO$_2$ : Cd molar ratio of 0.2), as obtained from Wsolids simulations of static $^1$H-$^{111}$Cd CP-echo SSNMR experiments.

Figure 2-A10 At top, the V-shaped “π-pocket” formed by the linkers in the two SDB-based MOFs is shown, with the two possible orientations of each phenyl ring depicted in grey and purple. In (a) – (d), the four possible combinations of phenyl ring orientations are depicted. Of these four combinations, only (a) has the correct orientation of phenyl rings capable of forming the ideal “π-pocket” structure necessary for CO$_2$ guest adsorption in this system.
Figure 2-A11 A depiction of dihedral angles between the disordered phenyl rings in CdSDB. In (a), a zoomed-out view of the disordered phenyl rings in one pore is shown, as viewed along the c axis. In (b), a zoomed-in illustration of the dihedral angle formed by the left disordered phenyl rings is shown. In (c), the dihedral angle formed by the right disordered phenyl rings is depicted. The corresponding values of dihedral angles in dehydrated, saturated and unsaturated CO2-loaded CdSDB are given in Table 2-A4. The purple and grey atoms represent the two possible orientations of these disordered phenyl rings.

Figure 2-A12 Simulated and experimental powder XRD patterns of as-made PbSDB.
Figure 2-A13 Simulated and experimental powder XRD patterns of as-made CdSDB.

Figure 2-A14 An ORTEP drawing of saturated CO$_2$-loaded CdSDB is shown, along with the naming and numbering scheme. Ellipsoids are drawn at the 20% probability level, and hydrogen atoms are omitted for clarity. The atoms of the disordered phenyl group are depicted as “hollow” ellipsoids.
Figure 2-A15 An ORTEP drawing of unsaturated CO$_2$-loaded CdSDB is shown, along with the atomic naming and numbering scheme. Ellipsoids are drawn at the 50% probability level, and hydrogen atoms are omitted for clarity. The atoms of the disordered phenyl group are depicted as “hollow” ellipsoids.

Table 2-A1 Static $^{13}$C DEPTH-echo SSNMR experimental parameters.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>PbSDB</th>
<th>CdsDB</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Recycle delay (s)</td>
<td>Number of scans</td>
</tr>
<tr>
<td>413</td>
<td>5</td>
<td>899</td>
</tr>
<tr>
<td>383</td>
<td>5</td>
<td>1219</td>
</tr>
<tr>
<td>353</td>
<td>5</td>
<td>1330</td>
</tr>
<tr>
<td>323</td>
<td>5</td>
<td>755</td>
</tr>
<tr>
<td>293</td>
<td>7</td>
<td>5537</td>
</tr>
<tr>
<td>243</td>
<td>15</td>
<td>238</td>
</tr>
<tr>
<td>213</td>
<td>20</td>
<td>205</td>
</tr>
<tr>
<td>183</td>
<td>20</td>
<td>241</td>
</tr>
</tbody>
</table>
Table 2-A2 A summary of SCXRD data for PbSDB and CdSDB.

<table>
<thead>
<tr>
<th></th>
<th>PbSDB-CO$_2$ (Saturated)</th>
<th>CdSDB (Dehydrated)</th>
<th>CdsDB-CO$_2$ (Unsaturated)</th>
<th>CdsDB-CO$_2$ (Saturated)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C$<em>{14.45}$H$</em>{3.89}$PbS</td>
<td>C$<em>{14}$H$</em>{5}$CdO$_6$S</td>
<td>C$<em>{14.05}$H$</em>{5}$CdO$_6.05$S</td>
<td>C$<em>{14.43}$H$</em>{5}$CdO$_6.80$S</td>
</tr>
<tr>
<td>Formula Weight (g/mol)</td>
<td>531.15</td>
<td>416.66</td>
<td>418.06</td>
<td>434.60</td>
</tr>
<tr>
<td>Crystal System</td>
<td>orthorhombic</td>
<td>monoclinic</td>
<td>monoclinic</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Space Group</td>
<td>P n m a</td>
<td>C 2/c</td>
<td>C 2/c</td>
<td>C 2/c</td>
</tr>
<tr>
<td>Temperature, K</td>
<td>110</td>
<td>110</td>
<td>110</td>
<td>110</td>
</tr>
<tr>
<td>$a$, Å</td>
<td>5.8815(16)</td>
<td>13.376(3)</td>
<td>13.386(4)</td>
<td>13.391(3)</td>
</tr>
<tr>
<td>$b$, Å</td>
<td>13.035(3)</td>
<td>21.481(5)</td>
<td>21.482(5)</td>
<td>21.450(4)</td>
</tr>
<tr>
<td>$c$, Å</td>
<td>19.371(4)</td>
<td>10.1680(17)</td>
<td>10.176(2)</td>
<td>10.1758(15)</td>
</tr>
<tr>
<td>$\alpha^*$</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>$\beta^*$</td>
<td>90</td>
<td>94.756(7)</td>
<td>94.752(8)</td>
<td>94.960(5)</td>
</tr>
<tr>
<td>$\gamma^*$</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>V, Å$^3$</td>
<td>1485.1(6)</td>
<td>2911.6(11)</td>
<td>2916.2(12)</td>
<td>2911.8(9)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>8</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>F(000)</td>
<td>991</td>
<td>1632</td>
<td>1638</td>
<td>1704</td>
</tr>
<tr>
<td>$\rho$ (g/cm$^3$)</td>
<td>2.376</td>
<td>1.901</td>
<td>1.904</td>
<td>1.983</td>
</tr>
<tr>
<td>I, Å, (MoKα)</td>
<td>0.71073</td>
<td>0.71073</td>
<td>0.71073</td>
<td>0.71073</td>
</tr>
<tr>
<td>$m$, (cm$^{-1}$)</td>
<td>11.535</td>
<td>1.669</td>
<td>1.667</td>
<td>1.677</td>
</tr>
<tr>
<td>Max 2q for data collection, °</td>
<td>90.496</td>
<td>95.906</td>
<td>80.874</td>
<td>86.558</td>
</tr>
<tr>
<td>Measured fraction of data</td>
<td>0.996</td>
<td>0.997</td>
<td>0.996</td>
<td>0.997</td>
</tr>
<tr>
<td>Number of reflections measured</td>
<td>59644</td>
<td>103756</td>
<td>66950</td>
<td>84479</td>
</tr>
<tr>
<td>Unique reflections measured</td>
<td>6085</td>
<td>13380</td>
<td>9113</td>
<td>10722</td>
</tr>
<tr>
<td>$R_{merge}$</td>
<td>0.0442</td>
<td>0.0413</td>
<td>0.0613</td>
<td>0.0483</td>
</tr>
<tr>
<td>$R_1$</td>
<td>0.0249</td>
<td>0.0264</td>
<td>0.0376</td>
<td>0.0314</td>
</tr>
<tr>
<td>$wR_2$</td>
<td>0.0404</td>
<td>0.0521</td>
<td>0.0711</td>
<td>0.0591</td>
</tr>
<tr>
<td>$R_1$ (all data)</td>
<td>0.0385</td>
<td>0.0410</td>
<td>0.0653</td>
<td>0.0502</td>
</tr>
<tr>
<td>$wR_2$ (all data)</td>
<td>0.0431</td>
<td>0.0560</td>
<td>0.0782</td>
<td>0.0640</td>
</tr>
<tr>
<td>GOF</td>
<td>1.040</td>
<td>1.033</td>
<td>1.030</td>
<td>1.047</td>
</tr>
</tbody>
</table>

$R_1=\frac{|F_o|-|F_c|}{F_o}$

$wR_2=\frac{\sum w(F_o^2-F_c^2)^2}{\sum (wF_o^4)}^{1/2}$

$GOF=\left[\left(\frac{\sum w(F_o^2-F_c^2)^2}{\sum wF_o^4}\right)\right]^{1/2}$

$\sum w(F_o^2-F_c^2)^2/(\text{No. of reflns. - No. of params.})^{1/2}$
Table 2-A3 The SCXRD and metrical data of activated and CO$_2$-loaded (at saturated and unsaturated levels) CdSDB.

<table>
<thead>
<tr>
<th></th>
<th>Activated CdSDB</th>
<th>CdSDB loaded with saturated CO$_2$</th>
<th>CdSDB loaded with unsaturated CO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C$_{14}$H$_8$CdO$_6$S</td>
<td>C$_{14.43}$H$<em>8$CdO$</em>{6.80}$S</td>
<td>C$_{14.05}$H$<em>8$CdO$</em>{6.05}$S</td>
</tr>
<tr>
<td>Formula Weight (g/mol)</td>
<td>416.66</td>
<td>434.60</td>
<td>418.06</td>
</tr>
<tr>
<td>Space group</td>
<td>C 2/c</td>
<td>C 2/c</td>
<td>C 2/c</td>
</tr>
<tr>
<td>a, Å</td>
<td>13.376(3)</td>
<td>13.391(3)</td>
<td>13.386(4)</td>
</tr>
<tr>
<td>b, Å</td>
<td>21.481(5)</td>
<td>21.450(4)</td>
<td>21.482(5)</td>
</tr>
<tr>
<td>c, Å</td>
<td>10.1680(17)</td>
<td>10.1758(15)</td>
<td>10.176(2)</td>
</tr>
<tr>
<td>α, °</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>β, °</td>
<td>94.756(7)</td>
<td>94.960(5)</td>
<td>94.752(8)</td>
</tr>
<tr>
<td>γ, °</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>V, Å$^3$</td>
<td>2911.6(11)</td>
<td>2911.8(9)</td>
<td>2916.2(12)</td>
</tr>
<tr>
<td>Cd1-O3, Å</td>
<td>2.1868(7)</td>
<td>2.1851(9)</td>
<td>2.1885(12)</td>
</tr>
<tr>
<td>Cd1-O2$^1$, Å</td>
<td>2.2216(7)</td>
<td>2.2228(9)</td>
<td>2.2236(12)</td>
</tr>
<tr>
<td>Cd1-O5, Å</td>
<td>2.2677(7)</td>
<td>2.2666(8)</td>
<td>2.2679(12)</td>
</tr>
<tr>
<td>Cd1-O5$^2$, Å</td>
<td>2.2953(6)</td>
<td>2.2944(8)</td>
<td>2.2969(11)</td>
</tr>
<tr>
<td>Cd1-O6$^4$, Å</td>
<td>2.3445(7)</td>
<td>2.3446(8)</td>
<td>2.3435(12)</td>
</tr>
<tr>
<td>Cd1-O1$^3$, Å</td>
<td>2.5229(7)</td>
<td>2.5276(8)</td>
<td>2.5260(12)</td>
</tr>
<tr>
<td>O3-Cd1-O2$^1$,°</td>
<td>3.4285(6)</td>
<td>3.4301(5)</td>
<td>3.4298(7)</td>
</tr>
<tr>
<td>O3-Cd1-O5$^1$,°</td>
<td>163.07(2)</td>
<td>163.15(3)</td>
<td>163.10(4)</td>
</tr>
<tr>
<td>O2$^1$-Cd1-O5$^1$,°</td>
<td>86.16(3)</td>
<td>85.93(3)</td>
<td>86.06(5)</td>
</tr>
<tr>
<td>O3-Cd1-O5$^2$,°</td>
<td>111.26(3)</td>
<td>111.26(3)</td>
<td>111.22(5)</td>
</tr>
<tr>
<td>O2$^1$-Cd1-O5$^2$,°</td>
<td>144.25(2)</td>
<td>144.08(3)</td>
<td>144.24(4)</td>
</tr>
<tr>
<td>O5-Cd1-O5$^2$,°</td>
<td>76.40(3)</td>
<td>76.46(3)</td>
<td>76.45(4)</td>
</tr>
<tr>
<td>O3-Cd1-O6$^1$,°</td>
<td>81.18(3)</td>
<td>81.22(3)</td>
<td>81.19(5)</td>
</tr>
<tr>
<td>O2$^1$-Cd1-O6$^1$,°</td>
<td>131.91(2)</td>
<td>131.80(3)</td>
<td>131.81(4)</td>
</tr>
<tr>
<td>O5-Cd1-O6$^1$,°</td>
<td>85.89(3)</td>
<td>85.95(3)</td>
<td>85.90(4)</td>
</tr>
<tr>
<td>O5$^2$-Cd1-O6$^1$,°</td>
<td>78.28(3)</td>
<td>78.45(3)</td>
<td>78.34(4)</td>
</tr>
<tr>
<td>O3-Cd1-O1$^3$,°</td>
<td>89.86(3)</td>
<td>90.01(3)</td>
<td>89.92(4)</td>
</tr>
<tr>
<td>O2$^1$-Cd1-O1$^3$,°</td>
<td>78.17(2)</td>
<td>78.04(3)</td>
<td>78.16(4)</td>
</tr>
<tr>
<td>O5-Cd1-O1$^3$,°</td>
<td>106.76(2)</td>
<td>106.51(3)</td>
<td>106.67(4)</td>
</tr>
<tr>
<td>O5$^2$-Cd1-O1$^3$,°</td>
<td>77.42(3)</td>
<td>77.41(3)</td>
<td>77.42(4)</td>
</tr>
<tr>
<td>O6$^1$-Cd1-O1$^8$,°</td>
<td>148.91(2)</td>
<td>149.21(3)</td>
<td>149.04(4)</td>
</tr>
<tr>
<td>O3-Cd1-Cd1$^1$,°</td>
<td>74.735(18)</td>
<td>74.90(2)</td>
<td>74.78(3)</td>
</tr>
<tr>
<td>O2$^1$-Cd1-Cd1$^1$,°</td>
<td>73.499(17)</td>
<td>73.34(2)</td>
<td>73.40(3)</td>
</tr>
<tr>
<td>O5-Cd1-Cd1$^1$,°</td>
<td>89.262(15)</td>
<td>89.158(19)</td>
<td>89.24(3)</td>
</tr>
<tr>
<td>O5$^2$-Cd1-Cd1$^1$,°</td>
<td>135.935(17)</td>
<td>136.14(2)</td>
<td>136.01(3)</td>
</tr>
<tr>
<td>O6$^1$-Cd1-Cd1$^1$,°</td>
<td>59.046(17)</td>
<td>59.12(2)</td>
<td>59.06(3)</td>
</tr>
<tr>
<td>O1$^3$-Cd1-Cd1$^1$,°</td>
<td>146.334(16)</td>
<td>146.20(2)</td>
<td>146.28(3)</td>
</tr>
</tbody>
</table>
Table 2-A4 A listing of the dihedral angles between the left and right disordered phenyl rings about sulfur in CdSDB, as measured from the experimental crystal structures. See Figure 2-A11 for an illustration of the corresponding angles.

<table>
<thead>
<tr>
<th></th>
<th>Left dihedral angle (°)</th>
<th>Right dihedral angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated CdSDB</td>
<td>32.232</td>
<td>32.232</td>
</tr>
<tr>
<td>CdSDB loaded with</td>
<td>31.049</td>
<td>31.653</td>
</tr>
<tr>
<td>saturated CO₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CdSDB loaded with</td>
<td>31.748</td>
<td>32.060</td>
</tr>
<tr>
<td>unsaturated CO₂</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

References

(15). *Journal*, Bruker-AXS, SAINT version 2013.8, 2013, Bruker-AXS, Madison, WI 53711, USA.
Chapter 3

3 Analyzing Gas Adsorption in an Amide-Functionalized Metal Organic Framework: Are the Carbonyl or N-H Groups Responsible?

3.1 Introduction

Metal-organic frameworks (MOFs) have exhibited great promise for use as adsorbents in gas storage and separation, which is typically credited to relatively strong host-guest interactions arising from specific pore sizes and/or shapes, the incorporation of open metal sites (OMSs), or the presence of functional groups that serve as guest binding sites.\(^1\) Identifying specific adsorption sites and understanding the gas binding mechanism is necessary to improve the performance of MOFs as gas sorbents, and should lead to the development of MOFs for targeted gas adsorption.\(^3\)\(^-\)\(^4\) Pendant functional groups like –NH\(_2\)\(^5\) or -OH\(^6\) can be introduced to the MOF linkers to tune specific host-gas interactions. Amides are a popular functional group choice due to their strong affinity for gas molecules such as CO\(_2\), C\(_2\)H\(_2\) and CH\(_4\), leading to a high gas uptake and increased selectivity towards N\(_2\).\(^7\)\(^-\)\(^9\)

The amide group has two potential gas binding sites: the carbonyl (C=O⋯gas) and the amide N-H (NH⋯gas). Theoretical calculations on amide MOFs (Appendix: Table 3-A1) have found that (i) the amide guest binding site is the carbonyl group;\(^10\) and (ii) in a MOF with both OMSs and amides, the electronegative amide carbonyl group increases positive charge on the OMS and no adsorption on the amide occurs.\(^11\) Experiments directly probing gas binding sites in amide MOFs remain rare; there have been only two reports from the same research group, which employed neutron powder diffraction (NPD) and inelastic neutron spectroscopy (INS), and reached conflicting findings\(^12\)\(^-\)\(^13\) which did not support theoretical predictions. No direct interaction between adsorbed CO\(_2\)/CH\(_4\) and amide groups was observed in the MFM-136 MOF,\(^12\) which lacks OMSs, indicating the presence of amide groups does not necessarily increase MOF affinity for gases. A study on MFM-188\(^13\) suggested the OMS and amide are both CO\(_2\) and C\(_2\)H\(_2\) binding sites, with the amide guest adsorption site on the N-H portion. The inconsistent experimental findings and disagreement with computational work indicates the role of amides in MOF gas adsorption
remains poorly understood, which restricts future advances in the design and synthesis of amide functionalized MOFs.

Direct observation of guest binding sites in amide MOFs is difficult due to the close proximity of the N-H and carbonyl sites, which can both serve as binding sites. Single crystal XRD (SCXRD) can be used to pinpoint the binding sites of guests such as N₂, CO₂, CH₄ and Xe. Unfortunately, SCXRD is typically carried out at low temperatures and only provides time-averaged long-range structural data. In addition, accurately locating the light atoms in small gas molecules is difficult, and hydrogen is undetectable. In situ variable-temperature (VT) solid-state NMR (SSNMR) experiments are an ideal complement to SCXRD that can probe gas molecule adsorption and host-guest interactions across a large temperature range (> 250 K). Using the SCXRD structure, computational methods can be used to confirm binding site locations and unravel adsorptive interactions, especially when a cooperative interaction exists, which is difficult to probe experimentally.

Herein, we present a detailed SCXRD, SSNMR and computational study on CO₂, C₂H₂ and CH₄ adsorption in the amide-functionalized porous Cu(INAIP) [INAIP₂⁻ = 5-(isonicotinamido) isophthalate] MOF, which selectively adsorbs CO₂ over N₂ and is stable to activation as well as solvent exposure. Cu(INAIP) has a unique 4-fold interpenetrated (10-3)-b topology in which the Cu(II) site is fully coordinated to carboxylate and pyridyl groups (a detailed diagram of the Cu(INAIP) MOF is shown in Figure 3-A1); the lack of OMSs permits unambiguous examination of guest adsorption on the amide group. Our results indicate that CO₂, C₂H₂ and CH₄ exhibit a cooperative binding model in which the carbonyl group of the amide plays a prominent role.
3.2 Results and discussion

CO\textsubscript{2} adsorption in Cu(INAIP)

**Figure 3-1** The extended lattice of the CO\textsubscript{2}-loaded Cu(INAIP) SCXRD structure is shown in (a), with hydrogen omitted for clarity. In (b), the local environment about CO\textsubscript{2} is depicted. A larger illustration of the MOF is given in Figure 3-A1. The experimental and simulated static \textsuperscript{13}C VT SSNMR spectra of adsorbed \textsuperscript{13}CO\textsubscript{2} are illustrated in (c), accompanied by the geometry-optimized local environment in (d). An electron density plot including CO\textsubscript{2} and the amide group is shown in (e), and the electron density graph for CO\textsubscript{2} and H13 of the MOF is given in (f). (Carbon: gray, oxygen: red, nitrogen: blue, copper: green, and hydrogen: cyan (hydrogen: white in (e/f)).
Single crystals of Cu(INAIP) were prepared hydrothermally and the MOF structure was preserved after the activation process removed all guests, as evidenced by powder XRD and qualitatively by visual inspection (Figures 3-A1 and Figure 3-A18). Empty Cu(INAIP) was then saturated with $^{13}$CO$_2$, C$_2$D$_2$ or CH$_3$D gas ($^{13}$CO$_2$ is herein referred to as simply CO$_2$, C$_2$H$_2$, and CH$_4$, see Appendix for details) and SCXRD was performed. CO$_2$-loaded Cu(INAIP) (Figure 3-1a) features a single unique adsorption location in the 1D channel. The CO$_2$ guests are ordered and exhibit a slightly bent geometry ($\angle$O-C-O = 176.6°). The local environment of adsorbed CO$_2$ (Figure 3-1b) suggests the electropositive CO$_2$ carbon atom interacts with the electronegative MOF carbonyl oxygen atom located 2.911(5) Å away. This is noteworthy because a NPD study on another amide MOF, MOF-188,$^{13}$ indicated CO$_2$ is bound via weak hydrogen bonding to the N-H portion of the amide rather than the carbonyl. In Cu(INAIP), adsorbed CO$_2$ and the N-H portion of the amide are 3.905(35) Å apart, indicating no direct interaction exists (Figure 3-A2). In Cu(INAIP), there are also weak hydrogen bonds between CO$_2$ oxygen atoms and adjacent linker protons (O7(CO$_2$)···H14: 2.660(5) Å, Figure 3-1b), hinting at the presence of a cooperative binding model.

To obtain insight on CO$_2$ adsorbed within Cu(INAIP), in situ $^{13}$C VT SSNMR experiments were performed from 393 to 133 K (Figure 3-1c, Figure 3-A3). $^{13}$C-labeled (99%) $^{13}$CO$_2$ gas was used, and since $^{13}$C is just ca. 0.96 % abundant, all $^{13}$C NMR resonances originate from $^{13}$CO$_2$. The 393 K NMR spectrum features a sharp resonance at ca. 124 ppm arising from a small amount of highly mobile CO$_2$, along with a single broad powder pattern corresponding to adsorbed CO$_2$. The sharp resonance of highly mobile CO$_2$ is absent below 333 K, indicating all CO$_2$ guests are adsorbed. The well-defined single $^{13}$C powder pattern reveals that one unique CO$_2$ adsorption site exists in Cu(INAIP), in agreement with the single independent CO$_2$ observed via SCXRD (Figure 3-1b). The span ($\Omega$) of the powder pattern at all temperatures is less than that of static CO$_2$,$^{20}$ indicating that adsorptive interactions are present which restrict CO$_2$ mobility and/or there is a significant Cu$^{2+}$-CO$_2$ paramagnetic interaction present. The $^{13}$C isotropic chemical shift ($\delta_{\text{iso}}(^{13}\text{C})$) is very sensitive to the paramagnetic interaction in MOFs. MAS experiments have indicated that linker $^{13}$C nuclei are significantly influenced by nearby paramagnetic metals, with $\delta_{\text{iso}}(^{13}\text{C})$
values ranging from ca. -50 to 850 ppm; however, adsorbed and mobile CO$_2$ guests proximate to paramagnetic centers exhibit $\delta_{\text{iso}}$(^{13}\text{C}) values near the accepted diamagnetic system range of 124 – 132 ppm and are typically not significantly influenced by the paramagnetic interaction. Our $^{13}$C MAS NMR spectrum of CO$_2$-loaded Cu(INAIP) (Figure 3-A4) exhibits $\delta_{\text{iso}}$(^{13}\text{C}) = 119(2) ppm at 293 K, indicating the lack of a significant paramagnetic interaction; the spectral broadening in static $^{13}$C VT NMR spectra of $^{13}$CO$_2$-loaded Cu(INAIP) must be mainly due to chemical shift anisotropy partially averaged by CO$_2$ motion, thus simulations of $^{13}$C SSNMR spectra can yield motional data. CO$_2$ guests undergo a localized rotation and a non-localized twofold hopping between adjacent equivalent adsorption sites (Figure 3-A3).

To obtain deeper insight into CO$_2$ adsorption within Cu(INAIP) and accurately place all hydrogen atoms, the SCXRD structure of CO$_2$-loaded Cu(INAIP) (Figure 3-1b) was geometry-optimized using density functional theory (DFT) methods (see details in Appendix). The optimized local environment of adsorbed CO$_2$ molecules (Figure 3-1d) has shortened distances between the CO$_2$ oxygen atoms and the neighboring MOF hydrogen atoms (H14, H5, H12 and H13). To investigate the role of the amide and framework hydrogen in CO$_2$ adsorption, DFT electron density plots were calculated based on the PBE-D method (Figure 3-1e/f, see calculation details in Appendix.) There is sizable electron density overlap between C15(CO$_2$) and O5(amide carbonyl), indicating a significant contribution to CO$_2$ adsorption. However, for observed NMR spectra, this interaction is averaged by the motions of CO$_2$ and may only have a small influence on the $^{13}$C NMR lineshape. In contrast, there is no obvious electron density overlap between the amide N-H site and CO$_2$ (N-H1⋯O7(CO$_2$)) (Figure 3-A5). There is also minor electron density overlap between CO$_2$ oxygen atoms and nearby hydrogen (H14 and H13), suggesting weak CO$_2$-H interactions make a small contribution to adsorption. DFT calculations indicate that there is a single unique CO$_2$ adsorption site located on the carbonyl portion of the amide group in Cu(INAIP). A cooperative binding model exists in which the amide carbonyl makes the primary contribution to CO$_2$ adsorption, while proximate framework hydrogen atoms play a weaker secondary role.
C$_2$H$_2$ adsorption in Cu(INAIP)

Figure 3-2 The SCXRD structure of C$_2$H$_2$-loaded Cu(INAIP) is shown in (a) and (b), with hydrogen omitted for clarity. The computationally optimized C$_2$H$_2$ local environment is given in (c). In (d), electron density plots of C$_2$H$_2$ and O3/O1 of the carboxylate groups (I) along with C$_2$H$_2$ and O5 of the amide (II) are shown. Experimental (blue) and simulated (red) $^2$H VT NMR spectra of C$_2$D$_2$-loaded Cu(INAIP) are found in (e), along with simulated contributions from free C$_2$D$_2$ gas (light blue) and both hydrogen sites in C$_2$H$_2$ (purple and green traces).
The adsorption of C$_2$H$_2$ in Cu(INAIP) was also investigated using SCXRD, SSNMR, and DFT calculations. SCXRD (Figure 3-2a and 3-2b) reveals that one unique C$_2$H$_2$ adsorption site is present with a refined occupancy of 1.00. It appears that C$_2$H$_2$ adsorption relies on hydrogen bonding to the oxygen atoms of the amide group and to the framework carboxylate groups in a cooperative manner. One C$_2$H$_2$ end is close to the amide carbonyl group, forming an O$_5$(amide)⋯H$_{15}$(C$_2$H$_2$) hydrogen bond (2.647(2) Å, Figure 3-2b). The relatively long distance of 3.993(7) Å between the amide amine group and C$_2$H$_2$ (N-H$_1$⋯C$_{15}$(C$_2$H$_2$), Figure 3-A6) indicates only the carbonyl amide group is involved in C$_2$H$_2$ adsorption. The other C$_2$H$_2$ end (H$_{16}$) engages in hydrogen bonding with three MOF carboxylate oxygen atoms (O$_1$, O$_3$ and O$_4$), with H⋯O distances of 2.489(2) Å, 2.972(2) Å and 3.208(2) Å, respectively (Figure 3-2b).

In the DFT-optimized crystal structure of C$_2$H$_2$-loaded Cu(INAIP), the distances between H16 (C$_2$H$_2$) and the nearest carboxylate oxygen atoms (O$_1$ and O$_3$) are 2.490 Å and 2.968 Å (Figure 3-2c), respectively, confirming that an attractive interaction exists, which is supported by electron density overlap (Figure 3-2d-I). The optimized 2.647 Å distance from H15 to the amide carbonyl oxygen (O$^5$) suggests a relatively weaker interaction, supported by electron density overlap (Figure 3-2d-II) and the difference electron density map (Figure 3-A7a). The NPD study on MOF-188$_{13}$ postulated that C$_2$H$_2$ interacts with hydrogen atoms of the N-H portion of the amide via the C≡C electrons. The long distances between C$_2$H$_2$ carbon atoms and the N-H hydrogen atoms (C$_{15}$/C$_{16}$⋯H$_1$ (HN) = 3.995, 4.087 Å, Figure 3-A7b), along with a lack of electron density overlap, indicates that the N-H portion does not assist in C$_2$H$_2$ adsorption. There is a weak Cu⋯H bonding interaction involving acetylene, as seen in Figure 3-A7c, but the DFT-optimized Cu⋯H distance of 3.323 Å indicates this is significantly weaker than the interactions involving carboxylate or amide oxygen.

To directly investigate C$_2$H$_2$ adsorbed in Cu(INAIP), VT $^2$H NMR was performed from 393 to 153 K using 99% D labeled C$_2$H$_2$ (Figure 3-2e). At 393 K, the $^2$H spectrum features a sharp signal at ca. 0 ppm and two broad resonances. The narrow resonance corresponds to a very small amount of highly mobile C$_2$H$_2$ gas and vanishes below 353 K as all C$_2$H$_2$ guests are adsorbed. The two broad resonances arise from the two nonequivalent deuterium
sites in Cu(INAIP). At 153 K, the $^2$H quadrupolar coupling constant ($C_Q$) and $\delta_{iso}(^2H)$ extracted from the broadest resonance are 179 (5) kHz and -20(5) ppm, while the other signal yields a $C_Q$ of 137(4) kHz and $\delta_{iso}(^2H)$ of 40(4) ppm (Table 3-A4). The non-zero $\delta_{iso}$ values are due to the Cu$^{2+}$ paramagnetic influence in Cu(INAIP), however, the paramagnetic interaction seems relatively weak, since the $^2$H spectra of C$_2$H$_2$ in Figure 3-2e resemble a typical Pake doublet in diamagnetic systems. In contrast, strong paramagnetic interactions in MOFs give rise to lopsided, asymmetrical, and chemically shifted $^2$H NMR spectra, such as those of benzene guests in MIL-53(Cr)$^{25}$ and linkers in [M$_2$(bdc)$_2$(dabco)].$^{26}$

C$_2$H$_2$ adsorbed in Cu(INAIP) gives rise to two $^2$H resonances but only a single C$_2$H$_2$ adsorption site exists, in agreement with SCXRD at 110, 153, and 193 K (Figure 3-A8); the C$_2$H$_2$ carbon atoms are not equivalent, thus the deuterium atoms are also not equivalent and reside in distinct local environments. Based on the DFT-optimized local structure (Figure 3-2c), the distance from one H atom in C$_2$H$_2$ (H16) to the closest Cu is 3.323 Å, while the closest H-Cu distance for the other H atom (H15) is 5.200 Å (Figure 3-A9). Atom H16 is closer to Cu$^{2+}$ and experiences a stronger paramagnetic interaction, which leads to a relatively larger $C_Q$ value, thus H16 is assigned to the ‘Site 1’ resonance in Figure 3-2e while H15 corresponds to ‘Site 2.’ In summary, C$_2$H$_2$ adsorption proceeds in a similar, but not identical, manner as CO$_2$. Only one adsorption site is present from 110 to 393 K, and a cooperative binding model exists in which the relatively stronger C$_2$H$_2$-carboxylate oxygen interaction is paired with the secondary C$_2$H$_2$-amide carbonyl interaction.

**CH$_4$ adsorption in Cu(INAIP)**

As methane storage within MOFs is of great interest for applications in the energy industry, CH$_4$ adsorption in Cu(INAIP) was also investigated. The SCXRD structure of CH$_4$-loaded Cu(INAIP) at 85 K (Figure 3-3a) features a distribution of disordered CH$_4$ guests within the MOF channels along the $b$-axis, unlike the cases of ordered CO$_2$ and C$_2$H$_2$ guests. Six unique methane carbon positions were identified and are shown in Figure 3-3b-I (from left to right followed by (occupancy): C16$_B$ (0.120), C16$_A$ (0.131), C15$_B$ (0.100), C15$_D$ (0.049), C15$_A$ (0.203) and C15$_C$ (0.148)). The total occupancy of all six methane carbon atoms is
only 0.751, indicating the adsorptive interaction between CH₄ and Cu(INAIP) is rather weak, in agreement with a prior report.¹⁹ The six methane carbon sites are classified based on local environment: C16ₐ and C16ₖ are close to the amide oxygen and termed amide-proximate (Figure 3-3b-II), while C15ₐ, C15ₖ, C15ₜ and C15ₜₔ are close to the carboxylate oxygen atoms and classified as carboxylate-proximate (Figure 3-3b-III and IV). Based on this data and prior work,²⁷ it appears methane adsorption proceeds via weak hydrogen bonding between methane hydrogen atoms and the neighboring amide and carboxylate oxygen atoms, but this is difficult to confirm without accurate hydrogen positions.

Figure 3-3 The long-range SCXRD structure of CH₄-loaded Cu(INAIP) with hydrogen omitted is shown in (a), along with the adsorbed CH₄ local structure in (b). The DFT-optimized CH₄ local environment are illustrated in (c). An electron density plot including CH₄ and O₅(amide)/H₇ is shown in (d), accompanied by an electron density plot about
CH₄ and O₂ of the carboxylate groups in (e). The static ²H VT SSNMR spectra of CH₄-loaded Cu(INAIP) are shown in (f).

The guest methane hydrogen positions in Cu(INAIP) can be obtained via DFT calculations, which then permits a more detailed examination of methane adsorption and potential hydrogen bonding interactions. In these calculations, all low-occupancy methane carbon atoms were removed, leaving only the two high-occupancy methane carbon atoms (C15A, C15C), which were then coordinated to hydrogen atoms to form two separate methane molecules. The location of both CH₄ molecules and all hydrogen atoms of Cu(INAIP) were computationally optimized, yielding one independent CH₄ site (Figure 3-3c). The H10(CH₄)···O5(amide) distance of 2.509 Å is shorter than the H12(CH₄)···O2(carboxylate group) distance of 2.732 Å, suggesting that the amide group of Cu(INAIP) engages in relatively stronger interactions with CH₄; this is confirmed from the degree of overlap in electron density plots of CH₄ and the oxygen atoms of the amide and carboxylate groups (Figure 3-3d/e) and the corresponding difference electron density map (Figure 3-A10). The short H₇…H₁₀(CH₄) distance of 2.347 Å indicates that a confinement effect is present (Figure 3-3c/d), which increases the H₁₀(CH₄)···O₅(amide) interaction energy.

Static ²H VT SSNMR experiments were performed on CH₄-loaded Cu(INAIP) (CH₃D, 98% D) to investigate the apparent guest disorder in this system (Figure 3-3f). A broad ²H powder pattern lacking typical quadrupolar features was obtained at all experimental temperatures (Figure 3-3f, Figure 3-A11). The presence of a distribution of six unique disordered methane sites is confirmed from the broad, featureless ²H spectrum that is nearly 20 kHz wide; the various distance-dependent weak paramagnetic influences on methane carbon atoms from nearby Cu²⁺ centers (all methane carbon - Cu²⁺ distances are larger than 4 Å) also make sizable contributions to spectral broadening. Based on SCXRD, SSNMR, and computational data, CH₄ adsorption in Cu(INAIP) relies on multiple interactions, including those between methane hydrogen atoms and oxygen atoms of both the amide and carboxylate groups. The MOF topology and atoms surrounding the methane guests, namely framework aromatic rings and hydrogen atoms, result in a confinement effect on adsorbed CH₄. The multiple competing and comparable binding interactions may be responsible for
the observed distribution of CH\textsubscript{4} guests in Cu(INAIP), which contrasts with the single adsorption site for CO\textsubscript{2} and C\textsubscript{2}H\textsubscript{2}.

3.3 Conclusion

To conclude, gas adsorption within the prototypical amide-functionalized MOF Cu(INAIP) has been thoroughly investigated using a combination of SCXRD, SSNMR and computational methods. SCXRD was used to locate the exact gas adsorption sites, while VT SSNMR spectra were able to probe the local environment about adsorbed gases across a large temperature range, yielding information on the presence and position of nearby paramagnetic metal centers. Computational methods have identified the various interactions responsible for the adsorption of gas molecules, yielding key insights into the host-gas interactions that are unavailable by direct experimental measurement. This work demonstrates that the carbonyl group of the amide functionality can act as the primary gas binding site; this contrasts with a previous report\textsuperscript{13} that indicated gas adsorption occurs via the N-H site of the amide. A cooperative binding model was found to exist in Cu(INAIP) in which the carbonyl group of the amide plays different roles in the adsorption of specific gas molecules, strengthening our understanding of host-gas interactions and gas adsorption in amide-functionalized MOFs. This work lays a solid foundation for future studies of the effect of amide functional groups on gas adsorption in MOFs, and also provides a comprehensive strategy to investigate gas adsorption in other MOFs and other porous materials.

3.4 References

3.5 Appendix

Section A1: Experimental details
Sample preparation

All reagents and chemicals were obtained from Alfa Aesar and used as received unless otherwise noted. 5-(isonicotamido)isophthalic acid (H$_2$INAIP) was prepared according to the literature method.$^1$ Yield: 60%. $^1$H-NMR (600 MHz, D$_6$-DMSO, 22 °C): δ =10.80 ppm (s, 1H), 8.79-8.77 ppm (d, 2H, J=6.0 Hz), 8.64 ppm (s, 2H), 8.22 ppm (s, 1H), 7.89-7.87 ppm (d, 2H, J=6.0 Hz).

Cu(INAIP) was prepared following the previously reported procedure with minor modifications.$^2$ A mixture of 0.0465 g Cu(NO$_3$)$_2$·2.5 H$_2$O, 0.0576 g H$_2$INAIP, and 0.0160 g NaOH was dissolved in 8 mL of deionized H$_2$O. The reagent mixture was then placed in a Teflon chamber within a Teflon-lined stainless steel autoclave, which was sealed and heated in an oven at 160 °C for 3 days. After cooling the autoclave to room temperature and letting it rest without agitation for 12 h, the product was obtained as green rectangular crystals, which were isolated by vacuum filtration and washed with H$_2$O three times. The crystals were then dried in an oven at 90 °C for 4 hours before MOF activation was performed (vide infra).

Sample preparation for SCXRD. A small amount of single crystals was packed into an L-shaped glass tube attached to a Schlenk line. The glass tube was then heated at 150 °C under dynamic vacuum (≤ 1 mbar) for ca. 12 hours to activate the MOF (i.e., to remove all solvent from the MOF channels). For samples loaded with a guest gas, a known amount of $^{13}$CO$_2$, C$_2$D$_2$ or CH$_3$D ($^{13}$CO$_2$: Sigma-Aldrich, 99% $^{13}$C isotope enriched, C$_2$D$_2$: CDN Isotopes, 99% deuterium enriched, and CH$_3$D: Sigma-Aldrich, 98% deuterium enriched), which are herein referred to as simply CO$_2$/C$_2$H$_2$/CH$_4$, was introduced into the same empty Schlenk line. The labeled gas in the Schlenk line was then condensed and trapped within the MOF sample by immersing the bottom of the L-shaped glass tube containing the MOF sample in liquid nitrogen (77 K) for ca. 5 min to achieve a “saturated” loading level. The L-shaped tube was then flame-sealed off from the vacuum line and kept at room temperature. After 3 days, the glass tube was broken, and the gas-saturated single crystal sample was immediately coated with paratone oil to trap the gas within the MOF. An optical microscope was used to select high-quality single crystals for structural analysis.
**Sample preparation for static in situ VT SSNMR.** Single crystals of Cu(INAIP) were ground into a fine powder, packed into an L-shaped glass tube, and then activated using the same vacuum line and procedure as described for sample preparation for SCXRD experiments (*vide supra*). It should be noted that PXRD was performed on ground-up as-made and activated samples to confirm that the structure remained intact after both grinding and activation (Figure 3-A18). The samples were saturated with the guest gas, flame-sealed off from the vacuum line, and brought back to room temperature before SSNMR experiments were performed. In terms of guest gases, while $^{13}$CO$_2$ was used, $^{13}$C-labeled C$_2$H$_2$ and CH$_4$ were not employed for $^{13}$C SSNMR investigations. For C$_2$H$_2$, only doubly labeled $^{13}$C compound is available. The strong $^{13}$C-$^{13}$C homonuclear dipolar coupling and the $^{13}$C CSA both contribute to and therefore complicate the observed $^{13}$C lineshape, making spectra interpretation very difficult. For $^{13}$C-labeled CH$_4$, the very symmetrical environment of $^{13}$C in a highly mobile CH$_4$ and the weak interaction with MOF framework will likely produce a sharp peak, providing little additional information.

**Sample preparation for $^{13}$C MAS SSNMR.** The L-shaped glass tube containing the powdered Cu(INAIP) sample saturated with $^{13}$CO$_2$ was broken after in situ VT SSNMR experiments were completed, and the CO$_2$-saturated sample was then immediately packed into a 4.0 mm SSNMR rotor. The rotor was spun at a frequency of 14 kHz.

**SCXRD.** All SCXRD measurements were made on a Bruker Kappa Axis Apex2 diffractometer at a temperature of 110 K for CO$_2$, 85 K for CH$_4$, and temperatures of 110 K, 153 K, and 193 K for C$_2$H$_2$. The frame integration was performed using SAINT. The resulting raw data was scaled and absorption corrected using a multi-scan averaging of symmetry equivalent data using SADABS. Structures were solved by using a direct methodology incorporated in the SHELXT program. All non-hydrogen framework atoms were obtained from the initial structural solution. The hydrogen atoms were introduced at idealized positions. The structural model was fit to the data using a full matrix least-squares method based on F$^2$. The calculated structure factors included corrections for anomalous dispersion from the usual tabulation. The structure was refined using the SHELXL-2014 program from the SHELX suite of crystallographic software.
SSNMR. All SSNMR experiments were performed using a Varian Infinity Plus NMR spectrometer, equipped with an Oxford 9.4 T wide-bore magnet and a 5 mm HX static Varian/Chemagnetics probe unless otherwise noted.

Static $^{13}$C NMR spectra [$\nu_0(^{13}\text{C}) = 100.5$ MHz] were referenced to TMS using the high-frequency resonance of ethanol at 58.05 ppm as a secondary reference. Experiments were performed using the DEPTH-echo pulse sequence, with a 90° pulse width of 2.0 $\mu$s and a 180° pulse width of 4.0 $\mu$s. The spectral width was 200 kHz and the calibrated recycle delays were a very short 1 s. The number of scans required for static VT $^{13}$C SSNMR acquisition are included in Table 3-A2.

Static $^{2}$H NMR spectra were referenced to the $^{2}$H resonance of D$_2$O(l) at 4.8 ppm as a secondary reference. A quadrupolar echo pulse sequence of the form ($\pi/2$ – $\tau_1$ – $\pi/2$ – $\tau_2$) was used with a $\pi/2$ pulse width of 4.5 $\mu$s, a $\tau_1$ of 30.0 $\mu$s and a $\tau_2$ of 30.0 $\mu$s. The spectral width was 1000 kHz and the calibrated $^{2}$H recycle delay was 0.5 s. The number of scans required for static $^{2}$H VT SSNMR experiments are included in Table 3-A2.

The direct-excitation $^{13}$C MAS NMR spectrum was acquired with a 4 mm HXY Varian/Chemagnetics MAS NMR probe, and referenced to TMS using the high-frequency $^{13}$C resonance of adamantane at 38.52 ppm as a secondary reference. The MAS experiments were performed at a spinning frequency of 14 kHz and employed a spectral width of 100 kHz, a 90° pulse length of 2.5 $\mu$s, and a recycle delay of 2 s. In total, 360 scans were collected.
Section 2: A summary of reported theoretical calculations for various amide-functionalized MOFs.

Table 3-A1  A summary of reported theoretical calculations for various amide-functionalized MOFs.

<table>
<thead>
<tr>
<th>MOF</th>
<th>Calc. method</th>
<th>Potential binding sites</th>
<th>Calculated gas binding sites</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuBTB/CuTATB</td>
<td>GCMC</td>
<td>OMS(^b) &amp; amide</td>
<td>OMS(\cdots)CO(_2)</td>
<td>Three different types of binding sites are present: the Cu(^{2+}) open metal sites, the carbonyl sites (C=O) and the N-H sites. The order of binding energy is C=O (-9.24 kJ/mol) &gt; OMS (-9.03 kJ/mol) &gt; NH (-0.168 kJ/mol), indicating that the carbonyl group and the OMS are the two primary adsorption sites.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>C=O(\cdots)CO(_2), NH(\cdots)CO(_2)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NJU-Bai3</td>
<td>GCMC</td>
<td>OMS &amp; amide</td>
<td>OMS(\cdots)CO(_2)</td>
<td>The order of binding energies is OMS (-2.67 kcal/mol) &gt; C=O (-2.01 kcal/mol) &gt; NH (-0.83 kcal/mol)</td>
</tr>
<tr>
<td>(ref:11)</td>
<td></td>
<td></td>
<td>C=O(\cdots)CO(_2), NH(\cdots)CO(_2)</td>
<td></td>
</tr>
<tr>
<td>Zn(BDC)BPDA</td>
<td>DFT(^c)</td>
<td>Amide</td>
<td>C=O(\cdots)CO(_2)</td>
<td>The calculation results reveal that the carbonyl group of the amide is the CO(_2) adsorption site, with a binding energy of -11.1 kJ/mol. CO(_2) adsorption follows a cooperative binding model: the primary source of binding energy comes from the interaction between the carbon atom of CO(_2) and the carbonyl oxygen atom of the amide. In addition, the oxygen atom of CO(_2) also engages in weak interactions with adjacent protons.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co(HL)</td>
<td>DFT</td>
<td>OMS &amp; amide</td>
<td>OMS(\cdots)CO(_2), C=O(\cdots)CO(_2)</td>
<td>The OMS and the carbonyl group of the amide are both strong adsorption sites for CO(_2). The interaction energies of OMS(\cdots)CO(_2) and C=O(\cdots)CO(_2) are 29.5 kJ/mol and 34.2 kJ/mol, respectively.</td>
</tr>
<tr>
<td>(ref:13)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NKU-108</td>
<td>DFT</td>
<td>OMS &amp; amide</td>
<td>OMS(\cdots)CO(_2), C=O(\cdots)CO(_2)</td>
<td>The interaction energies of OMS(\cdots)CO(_2) and C=O(\cdots)CO(_2) are 32.07 kJ/mol and 24.19 kJ/mol, respectively, suggesting that the OMS and the carbonyl of the amide are both strong adsorption sites.</td>
</tr>
<tr>
<td>(ref:14)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NJU-Bai17</td>
<td>GCMC</td>
<td>OMS &amp; amide</td>
<td>OMS(\cdots)C(_2)H(_2), C=O(\cdots)C(_2)H(_2)</td>
<td>The OMS and the amide carbonyl group are both adsorption sites for C(_2)H(_2). The binding energies of OMS(\cdots)C(_2)H(_2) and C=O(\cdots)C(_2)H(_2) are -25.81 kJ/mol and -18.06 kJ/mol, respectively. The interaction between C(_2)H(_2) and the carbonyl involves the formation of an O--H--C hydrogen bond.</td>
</tr>
<tr>
<td>(ref:15)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu-TPBTM</td>
<td>GCMC</td>
<td>OMS &amp; amide</td>
<td>OMS(\cdots)CO(_2)</td>
<td>The calculation results indicate that the negatively charged carbonyl oxygen atom of the amide concentrates additional positive charge on the OMS, resulting in a stronger binding interaction between the OMS and CO(_2). In addition, no adsorption of CO(_2) proximate to the amide functional group was found.</td>
</tr>
</tbody>
</table>

\(^a\) Grand canonical Monte Carlo simulation. \(^b\) Open metal site. \(^c\) Density functional theory.
Table 3-A2. The number of scans collected for static SSNMR experiments.

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>(^{13}\text{C} \text{SSNMR (CO}_2\text{)})</th>
<th>(^{1}\text{H} \text{SSNMR (C}_2\text{D}_2\text{)})</th>
<th>(^{2}\text{H} \text{SSNMR (CH}_3\text{D)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>393</td>
<td>1889</td>
<td>15840</td>
<td></td>
</tr>
<tr>
<td>373</td>
<td>1431</td>
<td></td>
<td></td>
</tr>
<tr>
<td>353</td>
<td>1216</td>
<td>5628</td>
<td></td>
</tr>
<tr>
<td>333</td>
<td>2192</td>
<td></td>
<td></td>
</tr>
<tr>
<td>313</td>
<td>1082</td>
<td>2428</td>
<td></td>
</tr>
<tr>
<td>293</td>
<td>1056</td>
<td></td>
<td>1352</td>
</tr>
<tr>
<td>273</td>
<td>736</td>
<td>3156</td>
<td>1452</td>
</tr>
<tr>
<td>253</td>
<td>810</td>
<td></td>
<td>1512</td>
</tr>
<tr>
<td>233</td>
<td>3593</td>
<td>4164</td>
<td>804</td>
</tr>
<tr>
<td>213</td>
<td>736</td>
<td></td>
<td>1260</td>
</tr>
<tr>
<td>193</td>
<td>1538</td>
<td>3296</td>
<td>1632</td>
</tr>
<tr>
<td>173</td>
<td>1518</td>
<td></td>
<td>4000</td>
</tr>
<tr>
<td>153</td>
<td>890</td>
<td>3340</td>
<td>2472</td>
</tr>
<tr>
<td>133</td>
<td>1712</td>
<td></td>
<td>2688</td>
</tr>
<tr>
<td>123</td>
<td></td>
<td></td>
<td>1080</td>
</tr>
</tbody>
</table>

Section 3: Theoretical calculations

Geometry optimizations were performed using the SCXRD results as a starting point, and only the H atoms of the framework and guests were optimized for CO\(_2\)- and C\(_2\)H\(_2\)-loaded Cu(INAIP). For CH\(_4\)-loaded Cu(INAIP), all of the low-occupancy CH\(_4\) carbon atoms were deleted, leaving only the two highest-occupancy CH\(_4\) carbon atoms. Hydrogen atoms were generated and attached to these two carbon atoms, and then both the CH\(_4\) molecules and all hydrogen atoms of the Cu(INAIP) framework were allowed to relax during the optimization, resulting in one independent CH\(_4\) site. All structural optimizations and the difference electron density plots (Δρ) were calculated using the generalized gradient approximation (GGA), with the Perdew, Burke, and Ernzerhof (PBE) functional,\(^{17}\) double numerical plus polarization (DNP) basis set,\(^{18}\) and DMol\(^3\) code.\(^{18-19}\) Grimme’s DFT-D\(^{20}\) approach was used to consider dispersion interactions. Δρ indicates the interaction between CuINAIP and gas based on electron transform, which was defined as,

\[ \Delta \rho = \rho(\text{CuINAIP-gas}) - \rho(\text{CuINAIP}) - \rho(\text{gas}) \]
Where $\rho(\text{CuINAIP-gas})$, $\rho(\text{CuINAIP})$ and $\rho(\text{gas})$ are the electronic density of CuINAIP-gas, CuINAIP and gas.

**Section 4:**

Figure 3-A1 (a) The extended lattice of the as made Cu(INAIP) crystal structure, as pictured along the b-axis. The solvent water molecules are removed for clarity. (b) Schematic representation of the 4-fold interpenetrated (10,3)-b topology of Cu(INAIP). (c) The local coordination environment of Cu within Cu(INAIP). (d) The local environment of linker INAIP in Cu(INAIP). (e) A picture of activated Cu(INAIP) in single crystal form, as taken through an optical microscope. (f) The extended lattice of the empty activated Cu(INAIP) crystal structure, as pictured along the b-axis. Note the absence of solvent in the pores.
Figure 3-A2 The short-range SCXRD structure about adsorbed CO$_2$ and the nearby N-H group in Cu(INAIP), including the relevant CO$_2$-NH distances. The relatively long distances (> 3.9 Å) between CO$_2$ oxygen atoms and N-H hydrogen atoms indicate that no substantial adsorptive interaction exists between these species.
Figure 3-A3 (a): $^{13}$C VT SSNMR spectra (blue traces) and simulations (red traces) of $^{13}$CO$_2$-loaded Cu(INAIP) at temperatures ranging from 373 to 153 K. The simulated contribution of the signal originating from free CO$_2$ at high temperatures is shown in green. The experimental $^{13}$C SSNMR spectrum of $^{13}$CO$_2$ in Cu(INAIP) at 373 K was simulated to extract CO$_2$ dynamics using the EXPRESS software package, although the minor influence of the paramagnetic interaction injects a small amount of uncertainty into simulations. The single $^{13}$C powder pattern was successfully simulated, revealing that there is a localized rotation of CO$_2$ molecules modeled by a threefold ($C_3$) rotation or “wobbling,” along with a non-localized twofold ($C_2$) hopping of CO$_2$ guests between symmetry-equivalent adsorption sites. The rate of both motions is in the fast regime on the NMR timescale (i.e., $10^7$ Hz). A depiction of this two-motion model is shown in (b), in which $\alpha$ denotes the local wobbling angle, and $\beta$ represents the angle for two-fold hopping between two symmetry-equivalent adsorption sites. For the $^{13}$C NMR spectrum obtained at 373 K (Figure 3-A3a), dynamic simulations indicated that the CO$_2$ moved through a wobbling angle of $23^\circ$ and a hopping angle of $27^\circ$. 
Table 3-A3 The $^{13}$C SSNMR parameters of $^{13}$CO$_2$ in Cu(INAIP) at different temperatures, as obtained from simulations of the NMR spectra shown in Figure 3-1c and Figure 3-A3.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$\delta_{iso}$ (ppm)$^a$</th>
<th>$\Omega$ (ppm)</th>
<th>$\kappa$</th>
</tr>
</thead>
<tbody>
<tr>
<td>393</td>
<td>121(2)</td>
<td>188(3)</td>
<td>0.48(2)</td>
</tr>
<tr>
<td>373</td>
<td>120(2)</td>
<td>201(3)</td>
<td>0.52(3)</td>
</tr>
<tr>
<td>353</td>
<td>121(2)</td>
<td>201(3)</td>
<td>0.52(2)</td>
</tr>
<tr>
<td>333</td>
<td>120(2)</td>
<td>201(2)</td>
<td>0.52(2)</td>
</tr>
<tr>
<td>313</td>
<td>120(2)</td>
<td>205(3)</td>
<td>0.52(2)</td>
</tr>
<tr>
<td>293</td>
<td>119(2)</td>
<td>204(2)</td>
<td>0.54(2)</td>
</tr>
<tr>
<td>273</td>
<td>118(2)</td>
<td>212(4)</td>
<td>0.54(2)</td>
</tr>
<tr>
<td>253</td>
<td>118(2)</td>
<td>224(3)</td>
<td>0.56(3)</td>
</tr>
<tr>
<td>233</td>
<td>120(2)</td>
<td>236(4)</td>
<td>0.55(2)</td>
</tr>
<tr>
<td>213</td>
<td>118(2)</td>
<td>244(4)</td>
<td>0.57(2)</td>
</tr>
<tr>
<td>193</td>
<td>117(2)</td>
<td>255(5)</td>
<td>0.57(2)</td>
</tr>
<tr>
<td>173</td>
<td>118(2)</td>
<td>264(4)</td>
<td>0.57(2)</td>
</tr>
<tr>
<td>153</td>
<td>115(2)</td>
<td>274(5)</td>
<td>0.58(2)</td>
</tr>
<tr>
<td>133</td>
<td>114(2)</td>
<td>280(5)</td>
<td>0.60(3)</td>
</tr>
</tbody>
</table>

$^a$ These CO$_2$ isotropic chemical shifts slightly stray from the usual value of ca. 124-132 ppm due to the relatively weak influence of the nearby paramagnetic Cu(II) metal center.

Figure 3-A4 The $^{13}$C MAS NMR spectrum of $^{13}$CO$_2$-loaded Cu(INAIP) spinning at 14 kHz ($\delta_{iso} = 124$ ppm, full width at half height = 350 Hz). The resonance is slightly broadened due to a weak paramagnetic interaction with Cu$^{2+}$, however, $\delta_{iso}$ is similar to CO$_2$ in diamagnetic systems. See main text for discussion.
**Figure 3-A5** The electron density overlap (a) and difference electron density (b) plots of adsorbed CO$_2$ and the N-H portion of the amide group in Cu(INAIP) are shown. The absence of electron density overlap (Figure 3-A5a) and electron transform (Figure 3-A5b) between (N-H1···O7(CO2)) indicates a lack of attractive/adsorptive interactions; the N-H group of the amide is not responsible for CO$_2$ adsorption in Cu(INAIP). In (a), the relative density bar is given at the bottom right; in (b), yellow is positive and light blue is negative.

**Figure 3-A6** The SCXRD structure in Cu(INAIP) about adsorbed C$_2$H$_2$. The relatively long H1···C15 and H1···C16 distances indicate that the N-H portion of the amide is not responsible for C$_2$H$_2$ adsorption, while the much shorter distance between O5(amide)···H15(C$_2$H$_2$) suggest that the carbonyl portion of the amide acts as the adsorption site.
Figure 3-A7 The difference electron density (a) and electron density overlap (b) plots of adsorbed C$_2$H$_2$ in Cu(INAIP) are shown, indicating that interactions exist between C$_2$H$_2$ hydrogen atoms (H15/16) and both carbonyl (O5) and carboxylate (O1/O3) oxygen atoms. The lack of electronic overlap between (N-H1···C$_2$H$_2$) indicates the N-H group is not responsible for C$_2$H$_2$ adsorption. (c) A difference electron density map illustrating the weak C$_2$H$_2$···Cu interaction in acetylene-loaded Cu(INAIP), as indicated by the black circle, using an isovalue of 0.0004 a.u.. In (a) and (c) yellow is positive, light blue is negative, and the isovalues are 0.0005 a.u. in (a) and 0.0004 a.u. in (c), and in (b), the relative electron density bar is at right.
Figure 3-A8 The local positions of adsorbed C$_2$H$_2$ molecules in Cu(INAIP) are shown, along with select distances, as determined from SCXRD at (a) 153 K and (b) 193 K. The distance between H15(C$_2$H$_2$) and O5(amide) increases from 2.647(2) Å (110 K) to 2.650(2) Å (153 K) and 2.695(2) Å (193 K) due to the increased thermal energy and mobility of C$_2$H$_2$ at higher temperatures.

Table 3-A4 The $^2$H SSNMR parameters of C$_2$D$_2$ adsorbed within Cu(INAIP), as obtained from simulations of the NMR spectra shown in Figure 3-2e of the main text.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$^2$H Site</th>
<th>$\delta_{iso}$ (ppm)$^a$</th>
<th>$\eta_\alpha$</th>
<th>$\Omega$ (ppm)$^a$</th>
<th>$\kappa$</th>
</tr>
</thead>
<tbody>
<tr>
<td>153</td>
<td>Site 1</td>
<td>-20 (6)</td>
<td>0.01 (3)</td>
<td>95 (30)</td>
<td>-0.16 (20)</td>
</tr>
<tr>
<td></td>
<td>Site 2</td>
<td>40 (5)</td>
<td>0.05 (2)</td>
<td>75 (30)</td>
<td>-1.00 (20)</td>
</tr>
<tr>
<td>193</td>
<td>Site 1</td>
<td>15 (5)</td>
<td>0.01 (3)</td>
<td>95 (30)</td>
<td>-0.16 (20)</td>
</tr>
<tr>
<td></td>
<td>Site 2</td>
<td>20 (6)</td>
<td>0.05 (2)</td>
<td>75 (30)</td>
<td>-1.00 (20)</td>
</tr>
<tr>
<td>233</td>
<td>Site 1</td>
<td>-50 (7)</td>
<td>0.15 (2)</td>
<td>95 (30)</td>
<td>-0.16 (20)</td>
</tr>
<tr>
<td></td>
<td>Site 2</td>
<td>-55 (5)</td>
<td>0.05 (2)</td>
<td>75 (30)</td>
<td>-1.00 (20)</td>
</tr>
<tr>
<td>273</td>
<td>Site 1</td>
<td>-50 (7)</td>
<td>0.15 (3)</td>
<td>95 (30)</td>
<td>-0.16 (20)</td>
</tr>
<tr>
<td></td>
<td>Site 2</td>
<td>-55 (5)</td>
<td>0.20 (3)</td>
<td>75 (30)</td>
<td>-1.00 (20)</td>
</tr>
<tr>
<td>313</td>
<td>Site 1</td>
<td>-40 (4)</td>
<td>0.10 (3)</td>
<td>95 (30)</td>
<td>-0.16 (20)</td>
</tr>
<tr>
<td></td>
<td>Site 2</td>
<td>0 (4)</td>
<td>0.33 (4)</td>
<td>75 (30)</td>
<td>-1.00 (20)</td>
</tr>
<tr>
<td>353</td>
<td>Site 1</td>
<td>-40 (5)</td>
<td>0.15 (2)</td>
<td>76 (25)</td>
<td>-0.16 (20)</td>
</tr>
<tr>
<td></td>
<td>Site 2</td>
<td>0 (4)</td>
<td>0.48 (4)</td>
<td>60 (25)</td>
<td>-1.00 (20)</td>
</tr>
<tr>
<td>393</td>
<td>Site 1</td>
<td>-40 (5)</td>
<td>0.12 (2)</td>
<td>76 (25)</td>
<td>-0.16 (20)</td>
</tr>
<tr>
<td></td>
<td>Site 2</td>
<td>0 (3)</td>
<td>0.48 (4)</td>
<td>60 (25)</td>
<td>-1.00 (20)</td>
</tr>
</tbody>
</table>

$^a$ Note that the presence of $\delta_{iso}$ and $\Omega$ values, along with their minor temperature dependence, is due to the weak paramagnetic influence of nearby Cu(II) metal centers. There is no coherent direction of change in the $\delta_{iso}$ value with temperature, for reasons that remain unclear, and will be investigated in a future study.
Figure 3-A9 The various distances between H15(C2H2) and the six nearest adjacent Cu(II) atoms are shown, based on the DFT-optimized SCXRD structure. The shortest H15-Cu distance is 5.200 Å, which is much greater than the shortest H16-Cu distance of 3.323 Å (Figure 3-2c in main text), thus their ²H NMR spectra are influenced by paramagnetic Cu²⁺ to different degrees.

Figure 3-A10. The calculated difference electron density map of adsorbed CH₄ and the surrounding atoms, where yellow is positive, light blue is negative, and the isovalue was chosen to be 0.0003 a.u.
Figure 3-A11 Experimental static $^2$H VT SSNMR spectra of CH$_3$D-loaded Cu(INAIP) at temperatures ranging from 273 to 133 K.

Figure 3-A18. The calculated (red) and experimental (black) PXRD patterns of as made and activated Cu(INAIP), after grinding the single crystal to a powder.
### Table 3-A5 A summary of the obtained Cu(INAIP) SCXRD data.

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Cu(INAIP) (110K)</th>
<th>Cu(INAIP)-CO₂ (110K)</th>
<th>Cu(INAIP)-C₂H₂ (110K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C₁₄H₈CuN₂O₅</td>
<td>C₃₀H₁₆Cu₂NaO₁₄</td>
<td>C₁₆H₁₂CuN₂O₅</td>
</tr>
<tr>
<td>Formula weight</td>
<td>347.76</td>
<td>783.55</td>
<td>373.80</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P₂₁/n</td>
<td>P₂₁/n</td>
<td>P₂₁/n</td>
</tr>
<tr>
<td>a / Å</td>
<td>8.1456(13)</td>
<td>7.9968(16)</td>
<td>8.4025(11)</td>
</tr>
<tr>
<td>b / Å</td>
<td>10.5280(16)</td>
<td>10.6693(19)</td>
<td>10.2909(12)</td>
</tr>
<tr>
<td>c / Å</td>
<td>17.657(3)</td>
<td>17.581(3)</td>
<td>17.774(3)</td>
</tr>
<tr>
<td>α / °</td>
<td>90.00</td>
<td>90.00</td>
<td>90.00</td>
</tr>
<tr>
<td>β / °</td>
<td>103.218(5)</td>
<td>102.298(8)</td>
<td>103.533(6)</td>
</tr>
<tr>
<td>γ / °</td>
<td>90.00</td>
<td>90.00</td>
<td>90.00</td>
</tr>
<tr>
<td>V / Å³</td>
<td>1474.1(4)</td>
<td>1465.6(5)</td>
<td>1494.2(3)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>F(000)</td>
<td>700</td>
<td>990</td>
<td>756</td>
</tr>
<tr>
<td>T/ K</td>
<td>110</td>
<td>110</td>
<td>110</td>
</tr>
<tr>
<td>ρ calcld. / gcm⁻³</td>
<td>1.567</td>
<td>1.776</td>
<td>1.662</td>
</tr>
<tr>
<td>GOF (F²)</td>
<td>1.092</td>
<td>1.070</td>
<td>1.088</td>
</tr>
<tr>
<td>R₁, wR₂ (I&gt;2σ(I))</td>
<td>0.0363, 0.1003</td>
<td>0.0312, 0.0892</td>
<td>0.0370, 0.0956</td>
</tr>
<tr>
<td>R₁, wR₂ (all data)</td>
<td>0.0366, 0.1006</td>
<td>0.0327, 0.0904</td>
<td>0.0409, 0.0977</td>
</tr>
</tbody>
</table>

### Table 3-A6 A summary of the obtained Cu(INAIP) SCXRD data (continued).

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Cu(INAIP)-C₂H₂ (153K)</th>
<th>Cu(INAIP)-C₂H₂ (193K)</th>
<th>Cu(INAIP)-0.75CH₄ (85K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C₁₆H₁₀CuN₂O₅</td>
<td>C₁₆H₁₀CuN₂O₅</td>
<td>C₁₄H₈CuN₂O₅</td>
</tr>
<tr>
<td>Formula weight</td>
<td>373.80</td>
<td>373.80</td>
<td>356.17</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P₂₁/n</td>
<td>P₂₁/n</td>
<td>P₂₁/n</td>
</tr>
<tr>
<td>a / Å</td>
<td>8.4584(12)</td>
<td>8.5188(12)</td>
<td>8.1474(15)</td>
</tr>
<tr>
<td>b / Å</td>
<td>10.2551(14)</td>
<td>10.2071(14)</td>
<td>10.5098(17)</td>
</tr>
<tr>
<td>c / Å</td>
<td>17.773(3)</td>
<td>17.775(3)</td>
<td>17.662(3)</td>
</tr>
<tr>
<td>α / °</td>
<td>90.00</td>
<td>90.00</td>
<td>90.00</td>
</tr>
<tr>
<td>β / °</td>
<td>103.479(3)</td>
<td>103.329(3)</td>
<td>103.064(7)</td>
</tr>
<tr>
<td>γ / °</td>
<td>90.00</td>
<td>90.00</td>
<td>90.00</td>
</tr>
<tr>
<td>V / Å³</td>
<td>1499.2(4)</td>
<td>1504.0(4)</td>
<td>1473.2(4)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>F(000)</td>
<td>756</td>
<td>756</td>
<td>717</td>
</tr>
<tr>
<td>T/ K</td>
<td>153</td>
<td>193</td>
<td>85</td>
</tr>
<tr>
<td>ρ calcld. / gcm⁻³</td>
<td>1.656</td>
<td>1.651</td>
<td>1.606</td>
</tr>
<tr>
<td>GOF (F²)</td>
<td>1.087</td>
<td>1.091</td>
<td>1.072</td>
</tr>
<tr>
<td>R₁, wR₂ (I&gt;2σ(I))</td>
<td>0.0348, 0.0909</td>
<td>0.0342, 0.0910</td>
<td>0.0336, 0.0865</td>
</tr>
<tr>
<td>R₁, wR₂ (all data)</td>
<td>0.0357, 0.0916</td>
<td>0.0353, 0.0918</td>
<td>0.0366, 0.0879</td>
</tr>
</tbody>
</table>
References

(3). *Journal*, Bruker-AXS, SAINT version 2013.8, 2013, Bruker-AXS, Madison, WI 53711, USA.
Chapter 4

4 Loading Across the Periodic Table: Introducing Fourteen Different Metal Ions to Enhance MOF Performance

4.1 Introduction

MOFs are porous materials that incorporate a diverse range of metal centers and organic linkers; this variation naturally gives rise to a plethora of unique materials that exhibit a wide array of topologies, pore geometries, and interesting properties. MOFs have realized many applications in the fields of chemistry and materials science due to their structural versatility, high surface areas, and tunable pore sizes.\(^1\)-\(^2\) Although the MOF composition and synthesis conditions are responsible for its resulting properties,\(^3\) post-synthetic strategies such as loading additional metal centers within the framework have been used to enhance MOF performance for applications in catalysis,\(^4\)-\(^5\) gas storage,\(^6\) drug delivery,\(^7\) and light emission.\(^8\)

Among the reported metal loading strategies, a promising route is binding guest metal ions to the organic linkers of the MOF via secondary functional groups, which improves the chemical stability of the MOF due to the chelate effect.\(^9\)-\(^10\) Secondary functional groups also serve as single-site anchor positions for loaded metals, preventing the guest metal atoms from aggregating on the anchor site or from detaching and migrating elsewhere.\(^5\),\(^11\)

Using secondary functional groups as guest metal binding sites yield a controlled number of binding sites with many applications, such as single-site catalysts.\(^5\),\(^11\)-\(^12\) Catechol- and bipyridyl-based moieties are typical choices for linker-based secondary functional groups and have been used to bind many different types of metal guests within MOFs.\(^4\),\(^10\),\(^13\)-\(^16\)

Unfortunately, ligands featuring such catechol or bipyridyl moieties are usually expensive or unavailable commercially, and the usage of toxic solvents (e.g., tetrahydrofuran (THF) and dimethylformamide (DMF)) is often necessary.\(^10\),\(^14\)-\(^15\) The considerable drawbacks have spurred interest in the use of alternate functional groups for metal loading in MOFs, such as the organic carboxyl group, which is one of the most popular chelators in coordination chemistry.

Linkers incorporating the carboxyl group are very popular choices for MOF syntheses due
to the tendency of carboxyl groups and metal ions (M) to form M-O-C linkages and assemble robust three-dimensional porous frameworks.\textsuperscript{17-18} MOFs with free COOH groups have shown promise for gas adsorption,\textsuperscript{19} proton conductivity,\textsuperscript{20} and ammonia removal.\textsuperscript{21} Although COOH-based loading of select alkali metals,\textsuperscript{22-23} transition metals,\textsuperscript{24-25} and lanthanides\textsuperscript{26-28} in MOFs has been reported, the introduction of many other elements as guests within MOFs has not. In many of the reported experimental routes, organic solvents are necessary to introduce guest metals from outside the s block of the periodic table.\textsuperscript{24-25, 27, 29} For example, loading Cu\textsuperscript{2+} and Ln\textsuperscript{3+} (Ln = Sm, Eu, Dy and Tb) into the [Zn\textsubscript{3}(hbptc)\textsubscript{2}(DMF)\textsubscript{2}]·2DMF MOF requires the use of an acetone solution of the corresponding metal nitrate for at least one week,\textsuperscript{29} and DMF is required to introduce Cu\textsuperscript{2+} to the UIO-66-(COOH)\textsubscript{2} MOF.\textsuperscript{25} The use of toxic organic solvents such as acetone and DMF poses environmental risks and also increases the costs associated with the loading process, limiting practical industrial applications.\textsuperscript{30} In addition, accounts of metal ion loading in MOFs are often ambiguous about metal-COOH coordination, and direct information regarding the loaded metals local chemical environment is sometimes incomplete or absent.\textsuperscript{24, 26-28}

Herein, we reveal that the MIL-121(Al) MOF (Scheme 4-1a)\textsuperscript{31} can bind 14 different types of metal ions located across the periodic table (Li\textsuperscript{+}, Na\textsuperscript{+}, K\textsuperscript{+}, Mg\textsuperscript{2+}, Ca\textsuperscript{2+}, Ba\textsuperscript{2+}, Zn\textsuperscript{2+}, Co\textsuperscript{2+}, Mn\textsuperscript{2+}, Ag\textsuperscript{+}, Cd\textsuperscript{2+}, La\textsuperscript{3+}, In\textsuperscript{3+}, Pb\textsuperscript{2+}) using a simple one-step procedure that is not air-sensitive (Scheme 4-1b). MIL-121 contains infinite chains of AlO\textsubscript{4}(OH)\textsubscript{2} octahedra and an inexpensive multi-carboxylate linker (1,2,4,5-benzenetetracarboxylic acid, BTEC) with free, uncoordinated COOH groups (Scheme 4-1a). This MOF has a free aperture of 8.7 × 5.7 Å and a topology similar to that of the well known MIL-53 MOF in its high temperature form (Scheme 4-1a).\textsuperscript{31-32} The metal ion sources are simple salts and the solvent is water, rendering this an attractive cost-efficient synthetic avenue. In addition to the loaded MIL-121 variants, MIL-121 loaded with Ag nanoparticles (NPs, where the loaded variant is referred to as Ag NPs@MIL-121) can be readily obtained by the reduction of Ag-MIL-121 with methanol through a solvent-exchange process (Scheme 4-1c, see details in the Appendix). The Ag NPs@MIL-121 version, along with Li/Mg/Ca-loaded MIL-121, show enhanced uptake of H\textsubscript{2} and CO\textsubscript{2}. In a very interesting finding, Ag NPs@MIL-121 exhibits
excellent catalytic activity in the reduction of 4-nitrophenol (4-NP).

Scheme 4-1. A depiction of one individual pore in MIL-121 is shown in (a), with the same pore after the metal loading process via the acid-base reaction or cation exchange route shown in (b). It should be noted that the hydration status of the metal in (b) is not certain. In (c), the MIL-121 pore is illustrated after the reduction process forms metal NPs (Ag) in the MOF. The guest metal is shown in green, with carbon in grey, oxygen in red, and aluminium in blue.

Information regarding the location and amount of the loaded metal, along with its local environment, is critical for understanding the origins and enhancement of specific properties in metal-loaded MOFs. X-ray and neutron diffraction are typical characterization routes, but only probe long-range structure and cannot examine guest metal ions unless their environment is remarkably ordered, which is rare. Spectroscopic techniques like IR, Raman and XAS (X-ray adsorption spectroscopy) have been used to probe the local environment of metals loaded within MOFs, but they only provide averaged structural information when multiple guest metal sites are involved. In contrast, solid state NMR (SSNMR) spectroscopy is very sensitive to the local environment of each unique guest metal site, and can yield detailed information on the binding between loaded metals and the framework in porous materials. In this work, multinuclear SSNMR has been employed to probe the local structure of metal-loaded MIL-121 variants. The interaction between guest metal and the metal centers/ligands of the MOF have been examined, along with the relationship between guest metals and the COOH “anchor site,” and direct structural information regarding the guest metal local environment has been obtained.
4.2 Results and discussion

Loading method

Metal loading of MIL-121 was performed in two ways: (1) for Li/Na/K/Ca/Ba-MIL-121, metal hydroxide or carbonate salts (LiOH, Na$_2$CO$_3$, K$_2$CO$_3$, Ca(OH)$_2$ and Ba(OH)$_2$) were used as metal sources, and the metals could be rapidly introduced into the MOF through a simple acid-base reaction which only takes several minutes; (2) for Mg/Zn/Co/Mn/Ag/Cd/La/In/Pb-MIL-121, the corresponding metal hydroxide or carbonate salts are barely soluble in water, but the corresponding metal acetate salts are soluble and can be used to introduce metals through a cation-exchange process that can take from a few minutes to several days. Detailed information regarding the metal loading process is listed in Tables 4-A1 and A2 (Appendix).

Characterization of metal-loaded MIL-121

MIL-121 loaded with guest alkali metals (Li/Na/K) retains framework integrity through the loading process, as evidenced by the nearly identical metal-loaded and parent MIL-121 powder X-ray diffraction (PXRD) patterns (Figure 4-A1). However, the PXRD patterns of other loaded MIL-121 variants feature extra reflections in addition to those of parent MIL-121 (Figure 4-A2), indicating that the overall topology of MIL-121 remains but the loaded metal ions introduce some long-range structural changes as results of the guest-metal binding to the linker COOH group. The $^{27}$Al MAS SSNMR spectra of metal-loaded and parent MIL-121 samples indicate the Al metal centers of the MIL-121 MOF are not directly involved in the loading process (Figure 4-A3, Table 4-A4), implying that guest metal centers have direct interaction with the free COOH groups of the BTEC ligands and no ion-exchange processes with Al metal centers are involved. Interestingly, treating metal-loaded MIL-121 with aqueous Na$_2$S solution causes the PXRD pattern to largely revert to the original PXRD pattern of parent MIL-121, indicating that the long-range structural changes in MIL-121 introduced by these guest metals are reversible; Ag-MIL-121 and Cd-MIL-121 are shown as two examples in Figures 4-A4 and 4-A5. The Na$_2$S treatment causes metal sulfide compounds to precipitate inside the MOF channels, forming the corresponding metal sulfide nanoparticles. Metal loading and subsequent Na$_2$S treatment
is a facile route for creating metal sulfide NPs within MIL-121, will be discussed in more
detail within a future manuscript.

To investigate the locations and local environments of guest metals loaded within MIL-
121, multinuclear SSNMR was performed. The metal-loaded MIL-121 samples of MIL-
121 used for characterization purposes required relatively high loading levels to yield
SSNMR spectra of acceptable signal-to-noise ratio (S/N). Selected $^1$H-$^{13}$C CP/MAS and
$^1$H MAS SSNMR spectra are shown in Figure 4-1, and the remainder can be found in the
Appendix (Figures 4-A6-9). The $^1$H-$^{13}$C CP/MAS SSNMR spectrum of MIL-121 features
three resonances (Figure 4-1a). The C1 and C2 resonances at ca. 172 ppm overlap and
originate from free and Al-coordinated carboxylate groups that exhibit very similar
chemical shifts,\textsuperscript{31} while the C3 resonance at 134.9 ppm and the C4/C5 resonance at 130.0
ppm are assigned to carbon atoms of the phenyl group.\textsuperscript{31} $^1$H-$^{13}$C CP/MAS SSNMR spectra of metal-loaded MIL-121 samples exhibit three significant changes versus parent MIL-121,
denoted I, II, and III. Na-MIL-121 and Ag-MIL-121 (Figure 4-1a) exemplify the type I
change: for Na-MIL-121, a new $^{13}$C resonance appears at ca. 176.4 ppm due to the direct
interaction between guest sodium ion and free COOH, and an additional resonance at 176.8
ppm appears in Ag-MIL-121, suggesting a similar interaction between COOH and loaded
Ag is present. The $^1$H-$^{13}$C CP/MAS spectra of Li/K-loaded MIL-121 variants also exhibit
the same type I change (Figure 4-A6). A Type II change involves multiple new $^{13}$C
resonances appearing near the three original resonances of parent MIL-121, with Ca-MIL-
121 and Zn-MIL-121 shown as examples in Figure 4-1a. In a type II change, the BTEC
linker symmetry is reduced after binding the metal ion, increasing the number of non-
equivalent carbon atoms and the amount of corresponding $^{13}$C resonances. Mg/Ba/Cd/La/In/Pb-MIL-121 all feature type II changes in their $^1$H-$^{13}$C CP/MAS spectra (Figure 4-A7). The $^1$H-$^{13}$C CP/MAS spectra of Co-MIL-121 and Mn-MIL-121 (Figure 4-
1a) exhibit a type III change, where the lineshape is significantly broadened compared to
that of parent MIL-121. In these type III instances, the spectral broadening arises from the
proximity-dependent interaction between $^{13}$C nuclei and the unpaired electrons localized
on the paramagnetic Co$^{2+}$ and Mn $^{2+}$. The paramagnetic influence alters the observed
chemical shifts and increases the relative breadths and areas of $^{13}$C SSNMR resonances.\textsuperscript{38}
These broaden NMR spectra hint that loaded Co and Mn are probably situated close to the
organic linker of MIL-121 and a direct interaction between the guest metals and COO- is possible but not obvious as other metals due to the paramagnetic influence.

**Figure 4-1** $^1$H−$^{13}$C CP/MAS SSNMR spectra of MIL-121 and Na/Ag/Ca/Zn/Mn/Co-MIL-121 are illustrated in Figure 4-1a; the corresponding $^1$H MAS SSNMR spectra of these samples are provided in Figure 4-1b. A depiction of the BTEC linker with corresponding labels for each unique carbon and hydrogen site is shown at the top of each spectral stack. In (b), the different colored lineshapes beneath the black experimental spectra are deconvolutions of individual resonance contributions to the overall $^1$H SSNMR spectra. The * label denotes spinning sidebands. The weak signal denoted by # in $^1$H−$^{13}$C CP/MAS and $^1$H MAS SSNMR spectra of Na-MIL-121 likely originates from a very small amount of an impurity.

$^1$H SSNMR is highly sensitive to both subtle and major differences in the local chemical environment about hydrogen. The experimental and simulated $^1$H MAS SSNMR spectra
of MIL-121 and the metal-loaded Na/Ag/Ca/Zn/Mn/Co-MIL-121 variants are illustrated in Figure 4-1b. The resonance denoted H1 at ca. 12 ppm originates from the free COOH group on the BTEC linker, while the H2 resonance at ca. 8 ppm arises from BTEC phenyl hydrogens. There are two H1 and two H2 atoms on the BTEC linker (Figure 4-1b), but replacement of the COOH hydrogen atom with the guest metal will naturally reduce the amount of H1, altering the relative areas of the H1 and H2 resonances in $^1$H MAS spectra and yielding an approximate level of loading. A comparison of the intensities of H1 in Na/Ag/Ca/Zn-MIL-121 with that of H1 in parent MIL-121 (Figure 4-1b) reveals that a large amount of H1 hydrogens located on the –COOH group have been replaced by the corresponding metal ions. By comparing the H1/H2 ratio in parent MIL-121 to metal-loaded MIL-121, the approximate guest metal loading level in each variant can be calculated (Figure 4-A8). The calculated percentages of H1 replaced by guest metals in Na/Ag/Ca/Zn-MIL-121 are 61%, 29%, 43% and 50%, respectively. The $^1$H MAS spectra and corresponding metal loading levels of all MIL-121 variants can be found in Figure 4-A9 and Table 4-A5. The $^1$H MAS spectra of Co-MIL-121 and Mn-MIL-121 are significantly influenced by the paramagnetic guest metals, much like the corresponding $^1$H-$^{13}$C CP/MAS spectra, and feature two broad $^1$H resonances. The strong paramagnetic influence on these broad $^1$H MAS spectra is another compelling piece of evidence that guest metals have direct interaction with the COO$^-$ linker group. Because of this significant paramagnetic influence, $^1$H MAS spectra of Co/Mn-MIL-121 cannot be used to estimate the guest metal loading level.

In order to directly investigate the local environment of the guest metal, SSNMR experiments were performed on the metal centers of ten loaded MIL-121 samples (Li/Na/K/Mg/Ca/Zn/Cd/La/In/Pb). The metal NMR experiments on Li/Na/Cd/La/Pb were carried on a 9.4 T magnet, owing to the favorable NMR properties of their NMR-active nuclei such as high natural abundance, a zero or moderate nuclear quadrupole moment, and a medium-to-high gyromagnetic ratio (i.e., Larmor frequency). For K/Mg/Ca/Zn/In-MIL-121, a high magnetic field of 21.1 T was used since these are all challenging, unreceptive nuclei with unfavorable NMR properties. The metal SSNMR spectra reveal that some guest metal coordination environments are remarkably ordered, while other guest metals reside in a distribution of similar local environments. An ordered guest metal environment
is apparent from the metal SSNMR spectra of Ca-MIL-121 (Figure 4-2a) and Pb-MIL-121 (Figure 4-2b). There are two individual resonances in the $^{43}$Ca MAS NMR spectrum of Ca-MIL-121, and two powder patterns in the static $^{207}$Pb SSNMR spectrum of Pb-MIL-121, suggesting that two distinct guest metal local environments are present in these MOFs. The Ca site 1 is probable an ionic calcium metal while the Ca site 2 (chemical shift: ca. -17 ppm) is very close to one site of calcium acetate monohydrate, indicating a similar local environment.$^{42}$ In contrast, the metal SSNMR spectra of Li/Na/K/Mg/Zn/Cd/La/In-MIL-121 yield relatively broad and featureless powder patterns that signify a distribution of similar guest metal environments are present. The $^{111}$Cd nucleus has a spin number of 1/2 with a natural abundance of 12.8 % and a moderate gyromagnetic ratio. $^{111}$Cd MAS NMR is a good opportunity to compare the local environment of loaded Cd inside the MIL-121 with that of cadmium in the metal source, cadmium acetate. The $^{111}$Cd resonance of Cd-MIL-121 (Figure 4-2c) is much broader than that of cadmium acetate; the full width at half height of the $^{111}$Cd resonance is 1358 Hz in Cd-MIL-121 versus 142 Hz in cadmium acetate, revealing that a distribution of similar guest Cd sites are present. The Cd chemical shift ranges between ca. -100 ppm to 150 ppm for oxygen coordinated Cd$^{2+}$, and is sensitive to factors such as the coordination number and geometry.$^{43-44}$ The $^{111}$Cd chemical shift of Cd-MIL-121 is ca. -75 ppm, while that of cadmium acetate is ca. +40 ppm, indicating that the Cd local environment is significantly modified after binding to linker COOH groups.
Figure 4-2  a): The $^{43}$Ca MAS NMR spectrum of Ca-MIL-121 (spinning speed: 8 kHz) and simulated MAS spectrum of the guest metal source Ca(OH)$_2$ at 21.1 T are shown. b): The static $^{207}$Pb WURST-CPMG NMR spectra of Pb-MIL-121 and the guest metal source Pb(OAc)$_2$·3H$_2$O at 9.4 T are illustrated, along with simulations of both powder patterns.
In c), $^1$H-$^{111}$Cd CP/MAS NMR spectra of Cd-MIL-121 and the guest metal source Cd(OAc)$_2$·2H$_2$O (spinning speed: 12 kHz) at 9.4 T are depicted. The 21.1 T $^{39}$K MAS NMR spectrum of K-MIL-121 (spinning speed: 8 kHz) and the simulated MAS spectrum of the guest metal source K$_2$CO$_3$ are provided in d). In e), the 21.1 T $^{25}$Mg MAS SSNMR spectrum of Mg-MIL-121 (spinning speed: 8 kHz) is shown, along with a MAS spectral simulation of the metal source Mg(OAc)$_2$. The $^{67}$Zn static NMR spectrum of Zn-MIL-121 and simulated spectra of the guest metal source Zn(OAc)$_2$·2H$_2$O and non-hydrated Zn(OAc)$_2$ at 21.1 T are given in f). The static $^{139}$La WURST-CPMG NMR spectrum of La-MIL-121 and the guest metal source La(OAc)$_3$·1.5H$_2$O long with simulated spectrum of non-hydrated La(OAc)$_2$ at 9.4 T are illustrated in g). In h), the static $^{115}$In SSNMR spectra of In-MIL-121 and guest metal source In(OAc)$_3$ at 21.1 T are shown. The silver K-edge EXAFS of Ag-MIL-121 and metal source AgOAc are depicted in i), along with an XPS analysis of Ag NPs@MIL-12 in j). The * label denotes spinning sidebands.

The metal SSNMR spectra of the guest metal sources K$_2$CO$_3$ and Mg(OAc)$_2$ are relatively narrow and contain features typical of quadrupolar nuclei (i.e., distinct spectral “horns”), but the MAS spectra of K-MIL-121 (Figure 4-2d) and Mg-MIL-121 (Figure 4-2e) present significantly broadened and featureless resonances, suggesting that a distribution of guest K$^+$ and Mg$^{2+}$ sites with similar local environments are present after loading metal into the MOF. A similarly broad resonance can also be observed in the $^7$Li and $^{23}$Na SSNMR spectra of Li/Na-MIL-121 (Figure 4-A10). The simulated static $^{67}$Zn ($I = 5/2$) SSNMR spectra of both hydrated and non-hydrated zinc acetate metal source are relatively narrow and well-defined, while the static $^{67}$Zn SSNMR spectrum of Zn-MIL-121 (Figure 4-2f) is notably broadened, lacks distinct quadrupolar powder pattern features, and tails off in the low frequency direction, implying that a distribution of guest Zn metal sites are present. The static $^{139}$La SSNMR spectra of La-MIL-121 (Figure 4-2g) also indicates that a similar situation is present, where the loaded La metal resides in a distribution of chemically similar local environments. In contrast, the metal source In(OAc)$_3$ gives rise to a broad $^{115}$In spectrum at 21.1 T ($I = 9/2$, Figure 4-2h), however, guest indium loaded within In-MIL-121 gives rise to a much narrower and featureless $^{115}$In resonance, indicating that guest indium metal is largely ionic in nature and resides in a relatively tight distribution of local environments. Using the Quadfit simulation software, the distributions of $^{23}$Na, $^{39}$K,
$^{25}$Mg, $^{67}$Zn, $^{139}$La and $^{115}$In NMR parameters from their corresponding metal SSNMR spectra could be determined (Figures 4-A10-11, Table 4-A6), yielding direct information on the range of local environments present about each loaded metal. For example, the $C_Q$ distributions are centered at 11.0 MHz ($^{67}$Zn) and 50.0 MHz ($^{115}$In), ranging from 8.5 to 13.5 MHz for $^{67}$Zn and from 32.5 to 67.5 MHz for $^{115}$In. The $\eta_Q$ distributions are centered at 1.00 for both $^{67}$Zn and $^{115}$In, ranging from 0.65 to 1.00 for $^{67}$Zn and from 0.80 to 1.00 for $^{115}$In.

Given the very challenging nature of $^{109}$Ag SSNMR experiments and the paramagnetic character of Co and Mn, X-ray adsorption spectroscopy (XAS) was performed to characterize the metal environments in Ag/Co/Mn-MIL-121. The extended X-ray absorption fine structure (EXAFS) spectra of Ag-MIL-121 and the AgOAc metal source (Figure 4-2i) both feature a white line at 25514 eV, revealing that the Ag oxidation state in Ag-MIL-121 is +1. Multinuclear SSNMR ($^{13}$C, $^1$H, $^{27}$Al) and XAS studies on Ag-MIL-121 indicate a possible Ag$^+$ local structural model (see Figures 4-A13 and A14), in which the Ag$^+$ is coordinated to two oxygen atoms from two adjacent free carboxylate groups. The XAS experimental data and corresponding analysis on Co/Mn-MIL-121 can be found in Figures 4-A15-A18 and suggest that the local environment of Co/Mn guests in MIL-121 is similar to the local environments in their respective metal sources.

In the course of this study, we found that the Ag$^+$ guests in Ag-MIL-121 can be reduced using a methanol exchange process (see details in the Appendix) to generate Ag NPs, which have a wide range of applications.$^{50-51}$ After the methanol exchange process, the color of Ag-MIL-121 turned from light yellow to black, suggesting the loaded Ag$^+$ species was reduced and converted to Ag$^0$ NPs. The existence of Ag$^0$ in Ag NPs@MIL-121 was confirmed by X-ray photoelectron spectroscopic (XPS, Figure 4-2j), where two specific peaks at binding energies of 368 and 375 eV could be observed and are assigned to the Ag 3d$_{5/2}$ and Ag 3d$_{3/2}$ electrons of metal Ag$^0$. PXRD supports these findings, with significant changes in the PXRD pattern reflecting the formation of Ag$^0$ NPs (Figure 4-A19).

Gas adsorption tests
Figure 4.3 In (a), the adsorption-desorption isotherms for H$_2$ in MIL-121 and metal-loaded MIL-121 variants are shown, as obtained at 77 K for pressures under 10 bar. The adsorption isotherms for CO$_2$ in MIL-121 and metal-loaded MIL-121 variants at 273 K under 1 atm are illustrated in (b). Finally, in (c), the adsorption-desorption isotherms for N$_2$ in MIL-121 and metal-loaded MIL-121 variants at 77 K under 1 bar are depicted. In these diagrams, solid circles represent adsorption measurement points while open circles are desorption measurement points.

Loading guest metals within MOFs can introduce or influence host-guest interactions underpinning guest gas adsorption, leading to enhanced uptake of industrially relevant gases such as CO$_2$ and H$_2$.$^{52-53}$ The introduction of guest cations with high charge densities, including Li$^+$ and Mg$^{2+}$, has been found to enhance selective gas adsorption and storage capacities in MOFs.$^{6, 54}$ With such applications in mind, the free COOH groups on the BTEC linker of MIL-121 can serve as ideal anchor sites for guest metal ions, exposing the
loaded metal directly to the guest gases within the MOF interior and preventing steric blockage of the guest metal sites by surrounding atoms. The adsorption of H\textsubscript{2} and CO\textsubscript{2} in Li/Mg/Ca-MIL-121 and Ag NPs@MIL-121 (Figure 4-3a, b) was found to be highly enhanced versus unmodified parent MIL-121, and is strongly dependent on the guest metal loading level. The optimized mass percentage of loaded metals was determined to be 0.74 wt % Li, 0.52 wt % Mg, 4.01 wt % Ca, and 1.80 wt % Ag, as determined by inductively coupled plasma mass spectrometry (ICP-MS).

The gas adsorption data for Li/Mg/Ca-MIL-121 and Ag NPs@MIL-121 using various metal loading levels can be found in Figures 4-A20-A23. At 77 K and 10 bar, the uptake of H\textsubscript{2} in parent MIL-121 is 8.4 cm\textsuperscript{3}/g (Figure 4-3a). After the introduction of specific guest metals, H\textsubscript{2} uptake increases by 34.3% (Ag NPs), 56.1% (Ca), 78.1% (Mg) and 102.0% (Li) (Figure 4-3a, Table 4-A8). Enhanced CO\textsubscript{2} uptake at 273 K and 1 atm was observed in metal-loaded MIL-121 with Li (52.0 %), Mg (27.7 %), and Ca (25.5 %) guests (Figure 4-3b, Table 4-A8). The Ag NPs@MIL-121 sample exhibits the largest CO\textsubscript{2} adsorption capacity, 93.5 cm\textsuperscript{3}/g, which is 69.4% greater than that of parent MIL-121 (55.2 cm\textsuperscript{3}/g). Interestingly, N\textsubscript{2} gas adsorption at 77K and 1 atm is drastically reduced within the loaded MOFs (Figure 4-3c, Table 4-A8); the BET surface areas are 135.9 m\textsuperscript{2}/g, 25.0 m\textsuperscript{2}/g, 16.2 m\textsuperscript{2}/g, 17.3 m\textsuperscript{2}/g and 43.6 m\textsuperscript{2}/g for parent MIL-121, Li/Mg/Ca-MIL-121 and Ag NPs@MIL-121 (1.80 wt%), respectively. It appears that the introduction of guest metals causes a large reduction in available pore space and the calculated BET surface area within the MOF. In this instance, however, the BET surface area of the metal-loaded MOF does not seem to be directly connected to its CO\textsubscript{2} adsorption capacity. For example, the quantity of CO\textsubscript{2} adsorbed in Ag NPs@MIL-121 (93.5 cm\textsuperscript{3}/g or 18.3 wt%) is comparable to that of MOF-5 (6.2 wt%, 273 K, 1 bar),\textsuperscript{57} UiO-66 (97.7 cm\textsuperscript{3}/g, 273 K, 1 bar)\textsuperscript{58} and SIFSIX-2-Cu (41.4 cm\textsuperscript{3}/g, 293 K, 1 bar),\textsuperscript{59} despite the much higher BET surface areas of 2833 m\textsuperscript{2}/g for MOF-5, 1250 m\textsuperscript{2}/g for UiO-66, and 3134 m\textsuperscript{2}/g for SIFSIX-2-Cu. This data reveals that loading guest metals within MIL-121 not only strengthens interactions between the adsorbed gas molecules and the MOF, but can also promote selective adsorption of H\textsubscript{2} and CO\textsubscript{2} over N\textsubscript{2}.

Enhancements in MOF H\textsubscript{2} and CO\textsubscript{2} adsorption capacities with the introduction of s-block
metals with high charge densities such as Li\(^+\) and Mg\(^{2+}\) have been observed from both experimental results and theoretical calculations;\(^{54, 56, 60-61}\) Li\(^+\) is regarded as one of the most effective metals for enhancing the gas capacity of porous materials.\(^{62-63}\) The current work shows that metallic Ag\(^0\) NPs in MIL-121 also exhibit a high affinity for gas molecules, and in fact, perform better than Li\(^+\) for the adsorption of CO\(_2\) in this system. Although Ag-loaded porous materials have shown enhanced gas capacity and selectivity in other systems, such as the adsorption of Xe over Kr,\(^{64-65}\) to the best of our knowledge the current work is a rare example of how Ag\(^0\) has tremendous potential for the selective adsorption of CO\(_2\).

**Catalytic performance**

![Figure 4-4](image)

**Figure 4-4** a) and b): The TEM images of Ag NPs@MIL-121 (1.80 wt\%) are shown at two different scales, as indicated by the scale in the bottom left of each image. c): A series of UV-vis absorption spectra are provided of the reduction of 4-NP by NaBH\(_4\) in the presence of Ag/100@MIL-121 (1.80 wt\%) as catalyst, as obtained over 16 minutes. d): A plot of \(\ln \left(\frac{C_t}{C_0}\right)\) of 4-NP versus time for the catalyst.

Silver nanoparticles have well-documented catalytic activities for organic
transformations, thus Ag NPs@MIL-121 (1.80 wt%) was tested for the model catalytic reduction of 4-nitrophenol (4-NP) by NaBH$_4$ in water. The 4-NP catalytic reduction is one of the most common reactions used to test the catalytic performance of metal nanoparticles in aqueous solution, and this reduction cannot proceed without a catalyst. In addition, the reduction of 4-NP has real-world practical applications, as 4-NP is a toxic organic pollutant that has been extensively used in pesticides and herbicides. The reduction of 4-NP yields 4-aminophenol (4-AP), which is an important non-hazardous chemical with applications including film development, corrosion inhibition, as a drying agent, and as an important intermediate in the synthesis of paracetamol.

The morphology and structure of Ag NPs@MIL-121 (1.80 wt%) was first examined using TEM, with results shown in Figures 4-4a and 4-4b. The Ag NPs@MIL-121 (1.80 wt%) sample was preheated at a temperature of 320 °C for 8 hours under vacuum (see Appendix for details) before TEM examination. The morphology of the Ag NPs@MIL-121 crystallite (Figure 4-4a) is almost the same as the parallelepiped-shaped crystal of as-made MIL-121, revealing that the Ag NPs@MIL-121 MOF is extremely stable to the harsh conditions and treatments involved in the metal loading, reduction, and preheating processes. The TEM images clearly show that the reduced Ag NPs are decorated homogeneously inside MIL-121 (Figure 4-4b) and measure uniformly around 3 nm in diameter. The observed dispersion of Ag NPs inside MIL-121 suggests that there is minimal aggregation or leaching during the reduction of Ag$^+$ in Ag-MIL-121 to Ag$^0$ in Ag NPs@MIL-121.

The reduction of 4-NP to 4-AP can be conveniently monitored using UV-vis absorption spectroscopy. After the addition of 3.46 mg Ag NPs@MIL-121 (1.80 wt%) to 2.33 mL of a 4-NP mixture, the bright yellow of 4-NP rapidly faded to colorless in less than 20 seconds, indicating that Ag NPs@MIL-121 (1.80 wt%) must have remarkable catalytic activity. Unfortunately, this short reaction time makes it very challenging to monitor the catalytic performance of Ag NPs@MIL-121 using UV-vis absorption spectroscopy. To address this issue, the Ag NPs@MIL-121 sample was diluted by a factor of 100 and then denoted as Ag/100@MIL-121. The UV-vis adsorption spectra of the 4-NP reduction obtained using Ag/100@MIL-121 is shown in Figure 4-4c. The absorption at 400 nm
corresponds to 4-NP ions under alkaline conditions, and quickly decreases after the addition of the Ag/100@MIL-121 catalyst, while an absorption at 300 nm from the 4-AP product appears and grows in intensity. The whole reduction process was finished after 16 mins after the addition of only ca. 0.034 mg of Ag/100@MIL-121 catalyst.

Since a large excess of NaBH₄ compared to 4-NP was used (molar ratio 1589:1), pseudo-first-order kinetics with respect to 4-NP can be applied to evaluate the reaction rate. After plotting \( \ln \left( \frac{C_t}{C_n} \right) \) vs time (\( C_t \) and \( C_n \) are the 4-NP concentrations at time \( t \) and 0, respectively), the pseudo-first-order reaction rate constant (\( \kappa \)) was determined to be 0.0053 s⁻¹ (Figure 4-4d). Taking into account the small mass of catalyst used, the \( \kappa_m \) (\( \kappa \)/mass) value reaches 156 s⁻¹ g⁻¹, which is one of the highest values among reported noble metal-based catalysts (Table 4-A9). In addition to the presence of Ag NPs, another contributing factor to the remarkable catalytic activity of Ag NPs@MIL-121 may be the acidic free COOH functional group of the linker; recent reports have shown that the existence of acidic functional groups can enhance the catalytic performance of metal NPs embedded in MOFs.

**4.3 Conclusion**

We have developed a straightforward, cost-efficient approach for loading 14 different metal ions from across the periodic table within the MIL-121 MOF. Multinuclear SSNMR has been applied to characterize the guest metals. \(^1\)H-\(^{13}\)C CP/MAS SSNMR spectra confirm the direct interaction between loaded metals and the free carboxylic acid groups of the BTEC linker, while the loading level can be readily estimated from \(^1\)H MAS SSNMR spectra. Multinuclear metal SSNMR spectra unambiguously indicate if the guest metal local environments are crystalline or disordered. The Li/Mg/Ca-MIL-121 and Ag NPs@MIL-121 MOFs exhibit enhanced uptake of H₂ and CO₂ but decreased uptake of N₂, unlocking possible applications in selective adsorption. Furthermore, Ag NPs@MIL-121 features a high catalytic activity towards the reduction of 4-NP and may be an effective catalyst for many other reactions.

Our work illustrates how free carboxylic acid groups on MOF linkers are an ideal anchor site for binding guest metal ions, and this route also provides a facile route for constructing
single-site catalysts in porous materials. In addition, we have showed that multinuclear SSNMR Spectroscopy is an effective tool to understand the relationship between guest metals and the host matrix and can provide direct local environment information about loaded metals which isn’t straightforward from other techniques. This work opens a door to the future introduction of many guest metals and associated performance enhancements in a wide variety of COOH-functionalized MOFs and related porous materials.

4.4 References

10320.


(45). D. Laurencin and M. E. Smith, Prog. Nucl. Magn. Reson. Spectrosc., 2013, 68, 1-
4.5 Appendix

Section A: Experimental details

Sample preparation

**MIL-121** was prepared using minor modifications of the previously reported procedure.\(^1\) A mixture of 4.80 g of \(\text{Al(NO}_3\text{)}_3 \cdot 9\text{H}_2\text{O}\) (Alfa Aesar, 98%) and 1.20 g of pyromellitic acid (1,2,4,5-benzenetetracarboxylic acid (BTEC), Sigma-Aldrich, 96%) was dissolved in 20.0 mL of deionized \(\text{H}_2\text{O}\) and 3.2 mL of 4.0 M \(\text{HNO}_3\). After stirring for 20 min, the reagent mixture was placed in a Teflon chamber within a Teflon-lined stainless steel autoclave, which was then sealed and heated in an oven at 210 °C for 16 h. After cooling the autoclave to room temperature, the product was obtained as a white powder suspended in solution; the white powdered as-made MIL-121 product was then isolated by centrifugation and dried in an oven at 90 °C.

**Activation process for MIL-121**: To remove unreacted BTEC ligand from the pores of as-made MIL-121, a solvent exchange procedure was used followed by activation. 0.20 g of as-made MIL-121 was mixed with 20.0 mL of methanol (MeOH), and the mixture was then decanted into a Teflon container within a Teflon-lined stainless steel autoclave. The autoclave was heated in an oven at 150 °C for 24 h, and then the MeOH solvent was decanted and replaced with fresh MeOH. This solvent exchange process was performed twice in total, and the final resulting methanol-exchanged MIL-121 product was then heated at 250 °C under a dynamic vacuum (\(\leq 1\) mbar) for ca. 12 h to purge all MeOH from the pores and yield activated MIL-121. **Unless otherwise noted, all MIL-121 samples used and mentioned in this study were prepared and activated using this procedure.**

**Metal loading process for MIL-121**: The loading process for introducing metal guests to MIL-121 was carried out in a very specific manner that is highly dependent on the nature of the metal. Specific details for introducing each type of metal to MIL-121 are outlined below in Table 4-A1 and Table 4-A2. The loaded samples described in Table S1 were used for solid state NMR (SSNMR) and X-ray absorption spectroscopy (XAS) tests, which required relatively higher loading levels to yield spectra of an acceptable signal-to-noise
ratio (S/N). The metal-loaded MIL-121 samples listed in Table 4-A2 were tested for their performance in gas adsorption, and were treated with relatively lower concentrations of metal precursors for a shorter time versus the samples in Table 4-A1, since high loading levels of metal guests usually leads to poor porosities.

**Ag NP@MIL-121** was obtained using Ag-loaded MIL-121 described in Table 4-A1 as a starting point: 0.40 g of Ag-MIL-121 was mixed with 20.0 mL of methanol (MeOH), and the mixture was then decanted into a Teflon container within a Teflon-lined stainless steel autoclave. The autoclave was heated in an oven at 150 °C for 24 h, then the Ag\(^+\) ions in Ag-MIL-121 were reduced into Ag nanoparticles by methanol. After the reduction, the color of the sample was observed to have changed from light yellow (Ag-MIL-121) to black (Ag NP@MIL-121).

**Table 4-A1**: Details of the loading procedure for each metal introduced into MIL-121 for the purposes of SSNMR and XAS experiments.

<table>
<thead>
<tr>
<th>Version of MIL-121</th>
<th>Guest metal source</th>
<th>Experimental process</th>
<th>Additional comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li-MIL-121</td>
<td>LiOH·H(_2)O</td>
<td>0.20 g MIL-121 was mixed with 25 mL of 0.5 M LiOH in a 50 mL centrifugation tube for 2 min at room temperature while stirring, and then the resulting yellow powder was collected from the solution by centrifugation. To remove residual unreacted LiOH, the product was immersed within 25 mL of DI water and stirred for 5 min in a washing process. This washing process was repeated three times before the Li-MIL-121 product was dried at 90 °C.</td>
<td>After the loading process, the color of the powder was observed to be light yellow.</td>
</tr>
<tr>
<td>Na-MIL-121</td>
<td>Na(_2)CO(_3)</td>
<td>0.20 g MIL-121 was mixed with 25 mL of 0.2 M Na(_2)CO(_3) for 15 min in a 50 mL centrifugation tube at room temperature while stirring, and then the resulting yellow powder was collected from solution by centrifugation. To remove residual unreacted Na(_2)CO(_3), the product was immersed into 25 mL DI water and...</td>
<td>After the loading process, the color of the powder changed to yellow.</td>
</tr>
<tr>
<td>MOF</td>
<td>Component Details</td>
<td>Preparation Method</td>
<td>Notes</td>
</tr>
<tr>
<td>--------------</td>
<td>--------------------------------------------------------</td>
<td>--------------------------------------------------------------------------------------------------------</td>
<td>----------------------------------------------------------------------</td>
</tr>
<tr>
<td>K-MIL-121</td>
<td>Anhydrous K$_2$CO$_3$ (Sigma-Aldrich, 99%)</td>
<td>0.80 g MIL-121 was mixed with 25 mL of 0.2 M K$_2$CO$_3$ for 15 min in a 50 mL centrifugation tube at room temperature while stirring, and then the yellow powder product was collected from solution by centrifugation. To remove residual unreacted K$_2$CO$_3$, the product was immersed in 25 mL of DI water and stirred for 5 min. This washing process was repeated three times before the K-MIL-121 product was isolated and dried at 90 °C.</td>
<td>After the loading process, the color of the powder changed to yellow.</td>
</tr>
<tr>
<td>Mg-MIL-121</td>
<td>Mg(OAc)$_2$·4H$_2$O  (Sigma-Aldrich, 99%)</td>
<td>0.60 g MIL-121 was mixed and stirred with 25 mL of 0.2 M Mg(OAc)$_2$ for 2 days in a 50 mL centrifugation tube at 90 °C. During the mixing process, the Mg(OAc)$_2$ solution was replaced with fresh Mg(OAc)$_2$ solution once, and then the powder product was collected by centrifugation at the end of 2 days. To remove any residual unreacted Mg(OAc)$_2$, the product was immersed in 25 mL of DI water and stirred for 5 min. This washing process was repeated four times before the Mg-MIL-121 product was isolated and dried in an oven at 90 °C.</td>
<td>There was no change in the color of the product versus the starting MOF; Mg-MIL-121 and parent MIL-121 were both white in colour.</td>
</tr>
<tr>
<td>Ca-MIL-121</td>
<td>Ca(OH)$_2$  (Sigma-Aldrich, 96%)</td>
<td>0.60 g MIL-121 was first mixed with 25 mL of saturated Ca(OH)$_2$ for 10 min in a 50 mL centrifugation tube at room temperature while stirring. The Ca(OH)$_2$ solution was replaced with fresh Ca(OH)$_2$ solution after 5 min of stirring. The powder product was then collected from solution by centrifugation. To remove residual unreacted Ca(OH)$_2$, the product was immersed in 25 mL of DI water and stirred for 5 min. This washing process was repeated three times in</td>
<td>To prepare a saturated solution of Ca(OH)$_2$, 0.10 g of Ca(OH)$_2$ was dissolved in 25 mL of DI water. After stirring for 20 min at room temperature, the clear saturated Ca(OH)$_2$ solution was obtained by centrifugation. After the loading process, the product was the same white color as parent MIL-121.</td>
</tr>
<tr>
<td>Complex</td>
<td>Synthesis Details</td>
<td></td>
<td></td>
</tr>
<tr>
<td>---------</td>
<td>------------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ba-MIL-121 (Ba(OH)$_2$·8H$_2$O (J.T. Baker Chemicals, Co., 99%))</td>
<td>0.60 g MIL-121 was mixed with 25 mL of an unsaturated Ba(OH)$_2$ solution in a 50 mL centrifugation tube for 5 min at room temperature while stirring, with the resulting powder collected by centrifugation. To remove residual Ba(OH)$_2$, the product was immersed in 25 mL of DI water and stirred for 5 min. This washing process was repeated three times before the Ba-MIL-121 product was isolated and dried in an oven at 90 °C.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn-MIL-121 (Zn(OAc)$_2$·2H$_2$O (Strem Chemicals, 98%))</td>
<td>0.20 g MIL-121 was mixed with 25 mL of 0.04 M Zn(OAc)$_2$ for 2 hours in a 50 mL centrifugation tube at 90 °C. The resulting powder was then collected from solution by centrifugation. To remove residual unreacted Zn(OAc)$_2$, the product was immersed in 25 mL of DI water and stirred for 5 min. This washing process was repeated four times before the final Zn-MIL-121 product was obtained and dried in an oven at 90 °C. After the loading process, the product was the same white color as parent MIL-121.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co-MIL-121 (Co(OAc)$_2$·4H$_2$O (Sigma-Aldrich, 99%))</td>
<td>0.20 g MIL-121 was mixed with 25 mL of 0.02 M Co(OAc)$_2$ for 9 hours in a 50 mL centrifugation tube at 90 °C, and then the resulting powder was collected by centrifugation. To remove residual unreacted Co(OAc)$_2$, the product was immersed in 25 mL of DI water and stirred for 5 min. This washing process was repeated four times before the Co-MIL-121 product was isolated and dried in an oven at 90 °C. After the loading process, the color of the powder changed to purple.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn-MIL-121 (Mn(OAc)$_2$·4H$_2$O (Sigma-Aldrich, ≥99%))</td>
<td>0.20 g MIL-121 was mixed with 25 mL of 0.05 M Mn(OAc)$_2$ for 2 hours in a 50 mL centrifugation tube at 90 °C. The resulting powder was collected from solution by centrifugation. After the loading process, the color of the powder changed to tan.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
centrifugation. To remove any residual unreacted Mn(OAc)$_2$, the product was immersed in 25 mL of DI water and stirred for 5 min. This washing process was repeated four times in total before the Mn-MIL-121 product was isolated and dried in an oven at 90 °C.

<table>
<thead>
<tr>
<th>Material</th>
<th>Molecule</th>
<th>Mass (g)</th>
<th>Solvent</th>
<th>Temperature</th>
<th>Time</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag-MIL-121</td>
<td>AgOAc (Alfa Aesar, 99%)</td>
<td>0.40</td>
<td>25 mL of 0.08 M AgOAc</td>
<td>16 hrs</td>
<td>50 mL centrifugation tube at room temperature</td>
<td>After the loading process, the color of the powder became light yellow.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cd-MIL-121</td>
<td>Cd(OAc)$_2$·2H$_2$O (Alfa Aesar, 98%)</td>
<td>0.60</td>
<td>25 mL of 0.1 M Cd(OAc)$_2$</td>
<td>3 days</td>
<td>50 mL centrifugation tube at 60 °C</td>
<td>After the loading process, the product was the same white color as parent MIL-121.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>La-MIL-121</td>
<td>La(OAc)$_3$·1.5H$_2$O (Alfa Aesar, 99.9%)</td>
<td>0.60</td>
<td>25 mL of 0.1 M La(OAc)$_3$</td>
<td>3 days</td>
<td>50 mL centrifugation tube at room temperature</td>
<td>After the loading process, the color of MIL-121 changed to light red.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
In-MIL-121
(Sigma-Aldrich, 99.99%)

In(OAc)$_3$

0.20 g MIL-121 was mixed with 25 mL of 0.0015 M In(OAc)$_3$ for 36 hours in a 50 mL centrifugation tube at 90 °C. During the mixing process, the In(OAc)$_3$ solution was replaced with a fresh In(OAc)$_3$ solution once. The resulting powder was then collected by centrifugation. To remove residual unreacted In(OAc)$_3$, the product was immersed in 25 mL of DI water and stirred for 5 min. This washing process was repeated five times before the In-MIL-121 product was isolated from solution and dried in an oven at 90 °C.

After the loading process, the product was the same white color as parent MIL-121.

Pb-MIL-121
(Alfa Aesar, 99%)

Pb(OAc)$_2$·3H$_2$O

0.20 g MIL-121 was mixed with 25 mL of 0.025 M Pb(OAc)$_2$ for 1 day in a 50 mL centrifugation tube at 60 °C, after which the resulting powder was collected by centrifugation. To remove residual unreacted Pb(OAc)$_2$, the product was immersed in 25 mL of DI water and stirred for 5 min. This washing process was repeated four times before the Pb-MIL-121 product was isolated and dried in an oven at 90 °C.

After the loading process, the color of the powder was tan.
Table 4-A2: Details of the loading procedure for each metal introduced within MIL-121 for the purpose of gas adsorption tests.\(^a\)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Trial 1 (conc., time)</th>
<th>Trial 2 (conc., time)</th>
<th>Trial 3(^b) (conc., time)</th>
<th>Trial 4 (conc., time)</th>
<th>Trial 5 (conc., time)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li-MIL-121</td>
<td>0.025 M, 5 min</td>
<td>0.035 M, 5 min</td>
<td>0.05 M, 5 min (0.74 wt%)</td>
<td>0.0625 M, 5 min</td>
<td>0.075 M, 5 min</td>
</tr>
<tr>
<td>Mg-MIL-121</td>
<td>0.02 M, 15 min</td>
<td>0.03 M, 15 min</td>
<td>0.04 M, 15 min (0.52 wt%)</td>
<td>0.05 M, 15 min</td>
<td>0.06 M, 15 min</td>
</tr>
<tr>
<td>Ca-MIL-121</td>
<td>0.01 M, 5 min</td>
<td>0.015 M, 5 min</td>
<td>0.02 M, 5 min (4.01 wt%)</td>
<td>0.025 M, 5 min</td>
<td>0.08 M, 15 min</td>
</tr>
<tr>
<td>Ag-MIL-121</td>
<td>0.015 M, 15 min</td>
<td>0.02 M, 15 min</td>
<td>0.025 M, 15 min (1.80 wt%)</td>
<td>0.03 M, 15 min</td>
<td>0.08 M, 1 h</td>
</tr>
</tbody>
</table>

\(^a\) The loading procedure for the samples was analogous to that described in Table 4-A1, with the only differences involving a lower concentration of the metal reagent and a shorter loading time, as described above in Table 4-A2.

\(^b\) The concentration and time outlined in Trial 3 of each loaded MIL-121 variant was found to yield a product that exhibited the highest CO\(_2\) adsorption for that particular metal guest; the weight percentage of metal introduced within the MOF was then determined by ICP-MS.

**SSNMR Measurements:**

We successfully performed metal SSNMR experiments on 10 metal-loaded MIL-121 samples (Li/Na/K/Mg/Ca/Zn/Cd/La/In/Pb), and XAS (including XANES and EXAFS) were carried on Ag/Co/Mn-MIL-121 due to the very challenging nature of running SSNMR experiments on these nuclei (e.g., paramagnetism, low resonant frequency, etc.).

All \(^1\)H, \(^7\)Li, \(^{13}\)C, \(^{23}\)Na, \(^{27}\)Al, and \(^{111}\)Cd SSNMR experiments were acquired at a magnetic field of 9.4 T using a Varian InfinityPlus wide-bore NMR spectrometer equipped with a 4 mm HXY Varian/Chemagnetics probe unless otherwise noted; \(^{139}\)La and \(^{207}\)Pb experiments were performed on the same spectrometer using a 5 mm HX static Varian/Chemagnetics probe. All \(^{25}\)Mg, \(^{39}\)K, \(^{43}\)Ca, \(^{67}\)Zn and \(^{115}\)In SSNMR experiments were acquired at a magnetic field of 21.1 T using a Bruker Avance II NMR spectrometer located at the National Ultrahigh-Field NMR Facility for Solids (Ottawa, ON, Canada).

**NMR experiments at 9.4 T**

\(^{13}\)C and \(^1\)H SSNMR spectra \([\nu_0(\text{\^{13}C}) = 100.5 \text{ MHz}, \nu_0(\text{\textsuperscript{1}H}) = 399.5 \text{ MHz}]\) were referenced to TMS using adamantane as a secondary reference; the high-frequency \(^{13}\)C resonance at 38.57 ppm and the \(^1\)H resonance at 1.85 ppm were used for the secondary referencing
procedure. \(^2\)\(^1\)H–\(^{13}\)C cross-polarization magic angle spinning (CP/MAS) experiments were performed with proton decoupling at a spinning frequency of 12 kHz using a spectral width of 100 kHz, along with a \(^1\)H 90º pulse length of 4.6 \(\mu\)s, contact time of 7 ms and a recycle delay of 2 s. \(^1\)H MAS experiments were performed at a spinning frequency of 12 kHz and a spectral width of 100 kHz, utilizing a 90º pulse of 4.4 \(\mu\)s and a recycle delay of 1 s. The number of scans for each spectrum can be found in Table 4-A3.

\(^{7}\)Li MAS SSNMR spectroscopy: 1.0 M LiCl/H\(_2\)O was used as the chemical shift reference at 0.0 ppm. \(^3\) \(^7\)Li MAS spectra [\(\nu_0(\text{\(^7\)Li}) = 155.6\) MHz] were acquired using a spinning speed of 12 kHz and a spectral width of 200 kHz. The spectra were obtained using a 90º - 90º solid echo pulse sequence with proton decoupling. The \(^7\)Li central transition (CT)-selective 90º pulse length was 2 \(\mu\)s and the recycle delay was 2 s. The number of scans for each spectrum can be found in Table 4-A3.

\(^{23}\)Na MAS SSNMR spectroscopy: 1.0 M NaCl/H\(_2\)O was used as the chemical shift reference at 0.0 ppm. \(^3\) \(^{23}\)Na MAS spectra [\(\nu_0(\text{\(^{23}\)Na}) = 105.7\) MHz] were acquired using a spinning speed of 13.333 kHz and a spectral width of 50 kHz. The spectra were acquired using a 90º - 90º solid echo pulse sequence with proton decoupling, along with a \(^{23}\)Na CT-selective 90º pulse length of 2.13 \(\mu\)s and a recycle delay of 2 s. The number of scans for each spectrum can be found in Table 4-A3.

\(^{27}\)Al MAS SSNMR spectroscopy: \(^{27}\)Al MAS experiments [\(\nu_0(\text{\(^{27}\)Al}) = 104.1\) MHz] were referenced to 1.0 M Al(NO\(_3\))\(_3\) at 0.0 ppm. \(^3\) The experiments were acquired using a 90º - 90º solid echo pulse sequence with proton decoupling, using a \(^{27}\)Al CT-selective 90º pulse length of 1.58 \(\mu\)s and a recycle delay of 1 s at spinning rate of 15 kHz. The spectral window was 150 kHz and the number of scans for each spectrum can be found in Table 4-A3.

\(^1\)H–\(^{111}\)Cd CP/MAS spectroscopy: \(^1\)H–\(^{111}\)Cd CP/MAS experiments [\(\nu_0(\text{\(^{111}\)Cd}) = 84.7\) MHz] were referenced to 0.1 M Cd(ClO\(_4\))\(_2\) at 0.0 ppm. \(^4\) The experiments were carried out at a spinning frequency of 12 kHz using a spectral width of 50 kHz, as well as a \(^1\)H 90º pulse length of 4.4 \(\mu\)s, contact time of 7 ms and a recycle delay of 2 s with proton decoupling. The number of scans for each spectrum can be found in Table 4-A3.
\textsuperscript{139}La \textit{static SSNMR spectroscopy}: A 1.0 M aqueous LaCl\textsubscript{3} solution was used as a chemical shift reference ($\nu_0^{(139)\text{La}} = 56.4$ MHz, $\delta_{\text{iso}}^{(139)\text{La}} = 0.0$ ppm). These static \textsuperscript{139}La SSNMR spectra were acquired using the WURST-CPMG pulse sequence\textsuperscript{6-8} with a WURST-80 pulse and \textsuperscript{1}H decoupling. The calibrated \textsuperscript{139}La recycle delay employed was 0.25 s, while the spikelet separation in the frequency domain was 3333.33 Hz, and the spectral window was 1000 kHz. The number of scans for each spectrum can be found in Table 4-A3.

\textsuperscript{207}Pb \textit{static SSNMR spectroscopy}: A saturated solution of Pb(NO\textsubscript{3})\textsubscript{2} at room temperature was used as a chemical shift reference ($\nu_0^{(207)\text{Pb}} = 83.3$ MHz, $\delta_{\text{iso}}^{(207)\text{Pb}} = -2970$ ppm). The static \textsuperscript{207}Pb spectra were acquired using the WURST-CPMG pulse sequence\textsuperscript{6-8} with a WURST-80 pulse and \textsuperscript{1}H decoupling. The calibrated \textsuperscript{207}Pb recycle delay was an unusually short value of 2 s, while the spikelet separation in the frequency domain was 3333.33 Hz, and the spectral window was 1000 kHz. The number of scans for each spectrum can be found in Table 4-A3.

\textbf{NMR experiments at 21.1 T}

\textsuperscript{25}Mg \textit{MAS SSNMR spectroscopy}: A 7 mm single-channel Bruker MAS probe was used to acquire \textsuperscript{25}Mg spectra [$\nu_0^{(25)\text{Mg}} = 55.1$ MHz] at a spinning rate of 8 kHz. \textsuperscript{25}Mg NMR chemical shifts were referenced to a solution of 1.0 M MgCl\textsubscript{2} ($\delta_{\text{iso}}^{(25)\text{Mg}} = 0.0$ ppm).\textsuperscript{3} The spectra were acquired using a 90º - 90º solid echo pulse sequence using a CT-selective 90º pulse length of 4.0 $\mu$s and a recycle delay of 0.5 s. The spectral window was 500 kHz and the number of scans for each spectrum can be found in Table 4-A3.

\textsuperscript{39}K \textit{MAS SSNMR spectroscopy}: A 7 mm HX Bruker MAS low-gamma probe was used to acquire \textsuperscript{39}K spectra [$\nu_0^{(39)\text{K}} = 42.0$ MHz] at a spinning rate of 8 kHz. \textsuperscript{39}K NMR chemical shifts were referenced to a solution of 1.0 M KCl ($\delta_{\text{iso}}^{(39)\text{K}} = 0.0$ ppm).\textsuperscript{3} The spectra were acquired using a 90º - 180º solid echo pulse sequence using a 90º pulse length of 6 $\mu$s, a 180º pulse length of 12 $\mu$s, and a recycle delay of 2 s. The spectral window was 50 kHz and the number of scans for each spectrum can be found in Table 4-A3.

\textsuperscript{43}Ca \textit{MAS SSNMR spectroscopy}: A 7 mm single-channel Bruker MAS probe was used to acquire \textsuperscript{43}Ca MAS spectra [$\nu_0^{(43)\text{Ca}} = 60.5$ MHz] at a spinning rate of 8 kHz. All \textsuperscript{43}Ca
chemical shifts were referenced to a solution of 2.0 M CaCl$_2$/H$_2$O ($\delta_{iso} = 0.0$ ppm).$^3$ The spectra were acquired using a one-pulse sequence with a ca. 45° pulse length of 1.0 $\mu$s and a recycle delay of 5 s. The spectral window was 20 kHz and the number of scans for each spectrum can be found in Table 4-A3.

$^{67}$Zn static SSNMR spectroscopy: A home-built 7 mm single-channel static probe was used to acquire $^{67}$Zn spectra [$\nu_0(^{67}$Zn) = 56.3 MHz]. $^{67}$Zn NMR chemical shifts were referenced to a solution of 1.0 M Zn(NO$_3$)$_2$ ($\delta_{iso} = 0.0$ ppm).$^3$ The spectra were acquired using a 90° - 90° solid echo pulse sequence using a 90° pulse length of 3.0 $\mu$s and a recycle delay of 0.25 s. The spectral window was 500 kHz and the number of scans for each spectrum can be found in Table 4-A3.

$^{115}$In static SSNMR spectroscopy: A home-built 7 mm HX static probe was used to acquire $^{115}$In spectra [$\nu_0(^{115}$In) = 197.1 MHz]. $^{115}$In NMR chemical shifts were referenced to a solution of 0.1 M In(NO$_3$)$_3$/0.5 M HNO$_3$ ($\delta_{iso} = 0.0$ ppm).$^{10}$ The spectra were acquired using a 90° - 90° solid echo pulse sequence with a 90° pulse length of 1.0 $\mu$s and a recycle delay of 0.5 s. The spectral window was 2000 kHz and the number of scans for each spectrum can be found in Table 4-A3.
Table 4-A3 The number of scans collected during multinuclear SSNMR experiments.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$^1$H-$^13$C CP/MAS NMR</th>
<th>$^1$H NMR</th>
<th>$^{27}$Al NMR (as made/activated)</th>
<th>NMR of loaded metal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mil-121</td>
<td>1161</td>
<td>123</td>
<td>748/122</td>
<td>2048</td>
</tr>
<tr>
<td>Li-MIL-121</td>
<td>9505</td>
<td>42</td>
<td>854</td>
<td>4037</td>
</tr>
<tr>
<td>Na-MIL-121</td>
<td>3905</td>
<td>21</td>
<td>5354</td>
<td>40 000</td>
</tr>
<tr>
<td>K-MIL-121</td>
<td>1198</td>
<td>30</td>
<td>846</td>
<td>640 000</td>
</tr>
<tr>
<td>Mg-MIL-121</td>
<td>1198</td>
<td>18</td>
<td>779</td>
<td>120 000</td>
</tr>
<tr>
<td>Ca-MIL-121</td>
<td>4147</td>
<td>50</td>
<td>776</td>
<td>745</td>
</tr>
<tr>
<td>Ba-MIL-121</td>
<td>1207</td>
<td>37</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn-MIL-121</td>
<td>1944</td>
<td>40</td>
<td>5612</td>
<td>390 000</td>
</tr>
<tr>
<td>Co-MIL-121</td>
<td>44 000</td>
<td>40</td>
<td>57 000</td>
<td></td>
</tr>
<tr>
<td>Mn-MIL-121</td>
<td>30 000</td>
<td>79</td>
<td>58 000</td>
<td></td>
</tr>
<tr>
<td>Ag-MIL-121</td>
<td>1175</td>
<td>12</td>
<td>7379</td>
<td></td>
</tr>
<tr>
<td>Cd-MIL-121</td>
<td>2720</td>
<td>38</td>
<td>4448</td>
<td>4 000</td>
</tr>
<tr>
<td>La-MIL-121</td>
<td>27 900</td>
<td>40</td>
<td>1293</td>
<td>225 000</td>
</tr>
<tr>
<td>In-MIL-121</td>
<td>31 000</td>
<td>22</td>
<td>3704</td>
<td>16 000</td>
</tr>
<tr>
<td>Pb-MIL-121</td>
<td>2136</td>
<td>47</td>
<td>1086</td>
<td>2996</td>
</tr>
</tbody>
</table>

Powder X-ray diffraction (PXRD):

All powder X-ray diffraction patterns were recorded using a high resolution Rigaku powder X-ray diffractometer operating using Co Kα radiation ($\lambda = 1.7403$ Å). Reflections were collected at 20 values between 5 and 45° or 2 and 82° depending on the particular sample, with a step size of 0.02°.

X-ray adsorption spectroscopy (XAS):

X-ray absorption fine structure (XAFS) spectra contain two regions of interest: the X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) regions. XANES provides information about the oxidation state and coordination geometry around the target atom, while EXAFS contains structural information encoded in its oscillatory features as a result of constructive and destructive interference between the emitted wave from the absorbing atom and the scattered wave from its neighbours.

The Ag K-edge (25514 eV) XAFS measurements were conducted at the CLS@APS (Canadian Light Source at the Advanced Photon Source) Sector 20-BM (bending magnet), which is part of the CLS/XSD (X-ray Science Division) located at Argonne National.
Laboratory in Argonne, Illinois, USA. The transmission and fluorescence yield (FLY) spectrum of the sample and transmission spectrum of the silver foil reference were collected simultaneously. The Co K-edge and Mn K-edge XAFS measurements were conducted at the Soft X-ray Microcharacterization Beamline (SXRMB) at the CLS in Saskatoon, Saskatchewan, Canada. The collected data was processed using the Athena software included in the Demeter software package for XAS software processing.\textsuperscript{13}

**X-ray photoelectron spectroscopy (XPS):** XPS is a surface-sensitive quantitative spectroscopic technique that can measure chemical state and electronic state of the elements in a material. XPS spectra were recorded on a Kratos Axis NOVA spectrometer using an Al K\textsubscript{\alpha} monochromatic high energy (hν =1486.6 eV) radiation source. All spectra were analyzed using the CasaXPS software (version 2.3.14) and involved a 50% Gaussian and 50% Lorentzian fitting routine with a Shirley background correction.\textsuperscript{14}

**ICP-MS (inductively coupled plasma mass spectrometry):** The quantity of metal guests introduced within MIL-121 was determined using a Thermo Fisher Scientific iCAP Q ICP-MS.

**TEM (transmission electron microscopy):** The size and morphology of silver nanoparticles in Ag NP@MIL-121 was investigated by TEM using a Tecnai G2 F20 instrument.

**Gas adsorption:**

**N\textsubscript{2} and CO\textsubscript{2} adsorption measurements:** N\textsubscript{2} and CO\textsubscript{2} adsorption isotherms were measured by a Micromeritics ASAP 2020 porosity analyzer at separate temperatures of 77 K and 273 K. All samples were preheated in an oven at 320 °C for 8 h to obtain dehydrated samples. Before the adsorption experiment, the dehydrated samples were degassed under vacuum at 220 °C for 10 h.

**H\textsubscript{2} adsorption measurements:** H\textsubscript{2} adsorption isotherms were measured at 77 K using a Micromeritics ASAP-2050 porosity analyzer. The activation process to obtain dehydrated samples was the same as mentioned above.
Reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP):

The reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) by NaBH₄ was chosen as a model reaction to test the catalytic activity of Ag NP@MIL-121. To a mixture of 162.30 mg of NaBH₄ dispersed in 8.30 mL H₂O was added 15.00 mL of 0.18 mmol/L 4-NP and 8.00 mL of distilled water. 2.33 mL of this mixture was added to a quartz cuvette equipped with a small stir bar. Separately, 3.46 mg of the Ag NP@MIL-121 (1.80 wt %) catalyst was dispersed in 30.0 mL water, and 0.3 mL of this suspension was added to the cuvette and termed as Ag/100 NP@MIL-121. The initial molar ratio of 4-NP:NaBH₄ was 1:1589. After introducing the Ag/100 NP@MIL-121 (1.80 wt%) catalyst suspension, the bright yellow solution gradually faded to colorless as the reaction proceeded under stirring conditions. UV-Vis spectra were recorded every 2 min on a Varian Cary 100 bio spectrophotometer to monitor the decrease in absorption at 405 nm, which corresponded to the absorption wavelength of the 4-nitrophenolate starting material.

UV-Vis spectra: The UV-Vis spectra were recorded on a Varian Cary 100 Bio UV-visible spectrophotometer in the wavelength range of 250–500 nm.
Figure 4-A1 The calculated and experimental PXRD patterns for parent MIL-121, along with experimental PXRD patterns of the Li-, Na-, and K-loaded versions of MIL-121.

Figure 4-A2 The PXRD patterns of MIL-121 and the Mg/Ca/Ba/Mn/Co/Zn/Ag/Cd/In/Pb-loaded versions of MIL-121.
Figure 4-A3 The $^{27}$Al MAS NMR spectra of Al(NO$_3$)$_3$•9H$_2$O, dehydrated Al(NO$_3$)$_3$ (obtained by heating Al(NO$_3$)$_3$•9H$_2$O at 300 °C for 6 h), MIL-121, and Li/Na/Mg/Ca/Ba/Zn/Ag/Cd /La/In/Pb-MIL-121 are shown, as obtained using a spinning speed of 15 kHz. The asterisk (*) label denotes spinning sidebands. The legend at top describes what each individual line color represents. Note that the impurity spectrum does not match that of the hydrated or dehydrated Al(NO$_3$)$_3$ reagent. The impurity species corresponds to a narrow linewidth and thus features a highly spherically symmetric local environment about Al; this impurity likely originates from side-product aluminum species formed during the synthesis and/or activation procedures. The extracted $^{27}$Al NMR parameters are given in Table 4-A4 and detailed discussions of the $^{27}$Al NMR spectra and parameters can be found in the main text.
Table 4-A4: The $^{27}$Al NMR parameters of parent and metal-loaded MIL-121 samples, as obtained from simulations of the $^{27}$Al NMR spectra shown in Figure 4-A3.

<table>
<thead>
<tr>
<th>Sample</th>
<th>MIL-121 $^{27}$Al signal</th>
<th>Impurity $^{27}$Al signal</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\delta_{iso}$ (ppm)</td>
<td>$C_Q$ (MHz)</td>
</tr>
<tr>
<td>As made MIL-121</td>
<td>7 (2)</td>
<td>8.40 (10)</td>
</tr>
<tr>
<td>Activated MIL-121</td>
<td>6 (2)</td>
<td>8.65 (9)</td>
</tr>
<tr>
<td>Li-MIL-121</td>
<td>3 (2)</td>
<td>8.59 (10)</td>
</tr>
<tr>
<td>Na-MIL-121</td>
<td>5 (1)</td>
<td>8.40 (8)</td>
</tr>
<tr>
<td>K-MIL-121</td>
<td>9 (3)</td>
<td>8.53 (11)</td>
</tr>
<tr>
<td>Mg-MIL-121</td>
<td>9 (2)</td>
<td>8.79 (9)</td>
</tr>
<tr>
<td>Ca-MIL-121</td>
<td>8 (1)</td>
<td>8.59 (7)</td>
</tr>
<tr>
<td>Ba-MIL-121</td>
<td>9 (2)</td>
<td>8.65 (6)</td>
</tr>
<tr>
<td>Zn-MIL-121</td>
<td>10 (2)</td>
<td>8.53 (10)</td>
</tr>
<tr>
<td>Co-MIL-121$^a$</td>
<td>23 (4)</td>
<td>9.05 (13)</td>
</tr>
<tr>
<td>Mn-MIL-121</td>
<td>13 (3)</td>
<td>8.79 (8)</td>
</tr>
<tr>
<td>Ag-MIL-121</td>
<td>10 (2)</td>
<td>8.59 (9)</td>
</tr>
<tr>
<td>Cd-MIL-121</td>
<td>9 (2)</td>
<td>8.53 (7)</td>
</tr>
<tr>
<td>La-MIL-121</td>
<td>6 (1)</td>
<td>8.93 (9)</td>
</tr>
<tr>
<td>In-MIL-121</td>
<td>12 (2)</td>
<td>8.78 (10)</td>
</tr>
<tr>
<td>Pb-MIL-121</td>
<td>5 (2)</td>
<td>8.33 (9)</td>
</tr>
</tbody>
</table>

$^a$ The $^{27}$Al NMR parameters in Co-MIL-121, including $\delta_{iso}$, $C_Q$ and $\eta_Q$, all differ significantly from those observed in the as-made and activated parent MIL-121 MOF, owing to the presence of the paramagnetic Co center. A fuller explanation can be found in the main text.
**Figure 4-A4** The PXRD patterns of MIL-121, Ag-MIL-121, and Ag-MIL-121 after Na$_2$S treatment are shown. The red box drawn between ca. 11-14° highlights the additional reflections in Ag-MIL-121 that disappear after treatment with Na$_2$S, which indicates that the structural changes introduced by loading MIL-121 with Ag are indeed reversible. A more detailed discussion is given in the main text.

**Figure 4-A5** The PXRD patterns of MIL-121, Cd-MIL-121 and Cd-MIL-121 after treatment with Na$_2$S are shown. The red box drawn between ca. 11-14° highlights the extra reflections in Cd-MIL-121 that disappear after treatment with Na$_2$S, which indicates that the structural changes introduced by loading Cd within MIL-121 are indeed reversible. A more detailed discussion is given in the main text.
Figure 4-A6 $^1$H–$^{13}$C CP/MAS NMR spectra of MIL-121 and the Li/K-loaded versions of MIL-121 are shown, as obtained at a spinning speed of 12 kHz. The resonances located at 174.2 ppm and 177.1 ppm in Li/K-MIL-121 originate from the carbon atoms in -COOLi and -COOK groups, respectively. The minor resonances denoted by an asterisk (*) label in K-MIL-121 originate from impurities.
Figure 4-A7 The $^1$H–$^{13}$C CP/MAS NMR spectra of MIL-121 and Mg/Ba/Cd/La/In/ Pb-MIL-121 obtained at a spinning speed of 12 kHz are illustrated. The vertical red dashed line denotes the resonance assigned to C1/C2 in the MIL-121 framework, and additional resonances appear on the high-frequency side of the C1/C2 resonance in metal-loaded samples due to the presence of the nearby bound guest metal center and its influence on surroundings. In most metal-loaded MIL-121 spectra, there are also additional resonances that appear between ca. 120-150 ppm, which originate from the presence of the bound guest metal that breaks the symmetry equivalence of the carbon atoms in the MOF linkers. Additional details are given in the main text.
The $^1$H MAS NMR spectra of MIL-121 and K-MIL-121 are depicted, as obtained using a spinning speed of 12 kHz. The individual colored lineshapes beneath the experimental spectra are the simulated contributions of each $^1$H resonance to the overall $^1$H spectral lineshape. The asterisk (*) label denotes spinning sidebands. The metal loading level in K-MIL-121 was calculated by subtracting the ratio of H1/H2 (0.58) determined from the $^1$H NMR spectrum of K-MIL-121 from the H1/H2 ratio measured in the parent MOF (0.89); the calculated loading level of 0.31 means that approximately 31% of H1 atoms have been replaced by K$^+$ guests in K-MIL-121. The $^1$H MAS SSNMR spectra and the calculated loading levels of other metal-loaded MIL-121 samples can be found in Figure 4-A9 and Table 4-A5.
Figure 4-A9 The $^1$H MAS NMR spectra of MIL-121 and Li/Mg/Ba/Cd/La/In/Pb-loaded MIL-121 are shown, as obtained using a spinning speed of 12 kHz. The individual colored lineshapes beneath the experimental spectra are deconvolutions of the $^1$H spectra, with a legend specified at top as well as marked in the MIL-121 and Mg-MIL-121 spectra. The asterisk (*) label denotes spinning sidebands. The values of the calculated H1/H2 ratios and loading levels in each sample can be found in Table 4-A5.
Table 4-A5 The calculated H1/H2 ratios between carboxylic (H1) and benzene-based hydrogen atoms (H2) are summarized, as determined based on line-fitting simulations of $^1$H MAS experimental spectra. Refer to Figures 4-1 (main text), 4-A8 and 4-A9 for illustrations of the experimental and simulated lineshapes.

<table>
<thead>
<tr>
<th>Sample</th>
<th>H1/H2 ratio</th>
<th>Metal loading level (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MIL-121</td>
<td>0.894</td>
<td></td>
</tr>
<tr>
<td>Li-MIL-121</td>
<td>0.631</td>
<td>26</td>
</tr>
<tr>
<td>Na-MIL-121</td>
<td>0.280</td>
<td>61</td>
</tr>
<tr>
<td>K-MIL-121</td>
<td>0.580</td>
<td>31</td>
</tr>
<tr>
<td>Mg-MIL-121</td>
<td>0.626</td>
<td>27</td>
</tr>
<tr>
<td>Ca-MIL-121</td>
<td>0.465</td>
<td>43</td>
</tr>
<tr>
<td>Ba-MIL-121</td>
<td>0.319</td>
<td>58</td>
</tr>
<tr>
<td>Zn-MIL-121</td>
<td>0.396</td>
<td>50</td>
</tr>
<tr>
<td>Co-MIL-121a</td>
<td>0.904a</td>
<td></td>
</tr>
<tr>
<td>Mn-MIL-121a</td>
<td>0.916a</td>
<td></td>
</tr>
<tr>
<td>Ag-MIL-121</td>
<td>0.603</td>
<td>29</td>
</tr>
<tr>
<td>Cd-MIL-121</td>
<td>0.701</td>
<td>19</td>
</tr>
<tr>
<td>La-MIL-121</td>
<td>0.694</td>
<td>20</td>
</tr>
<tr>
<td>In-MIL-121</td>
<td>0.726</td>
<td>17</td>
</tr>
<tr>
<td>Pb-MIL-121</td>
<td>0.761</td>
<td>13</td>
</tr>
</tbody>
</table>

* The loading levels of the Co- and Mn-loaded MIL-121 samples were not calculated due to the very broad $^1$H spectral lineshapes that arise from the paramagnetic interaction between $^1$H and the paramagnetic Co- and Mn-guest nuclei. The paramagnetic influence can alter the observed chemical shifts along with relative breadths, areas, and intensities of $^1$H SSNMR lineshapes, injecting a significant degree of uncertainty into these H1/H2 ratios and calculated loading levels.
Figure 4-A10 Multinuclear MAS SSNMR spectra and simulations of metal-loaded MIL-121 samples and their respective guest metal sources or reagents are shown in this Figure. Note the relatively broad and featureless spectra that are evident in the metal-loaded MIL-121 spectra within b), c), and d), which reflect a distribution of local metal environments. In a), the 9.4 T $^7$Li MAS NMR spectra of Li-MIL-121 and the anhydrous LiOH reagent are shown, obtained at a spinning speed of 12 kHz. The $^7$Li MAS NMR spectrum of Li-MIL-121 contains a slightly broad featureless resonance, which probably result from a high lithium mobility such as fast lithium exchange among different sites.\textsuperscript{15-16} The 9.4 T $^{23}$Na MAS NMR spectra of Na-MIL-121 and the Na$_2$CO$_3$ metal source are shown in b), obtained at a speed of 13.333 kHz, while the 21.1 T $^{39}$K MAS NMR spectrum of K-MIL-121 obtained at a speed of 8 kHz and the simulated MAS spectrum of K$_2$CO$_3$ based on a
previous report\textsuperscript{17} are depicted in c). Finally, in d), the 21.1 T $^{25}\text{Mg}$ MAS SSNMR spectrum of Mg-MIL-121 obtained at a spinning speed of 8 kHz along with a simulation of the Mg(OAc)$_2$ MAS spectrum based on previously reported parameters\textsuperscript{18} are shown. The asterisk (*) label denotes spinning sidebands. The black solid lines in b), c), and d) are simulated MAS spectra based on a distribution of quadrupolar parameters constructed using Quadfit,\textsuperscript{12} and the corresponding NMR parameters can be found in Table 4-A6.

**Figure 4-A11** In a), the static $^{67}\text{Zn}$ NMR solid-echo spectrum of Zn-MIL-121 at 21.1 T (blue) and the simulated spectrum of Zn(OAc)$_2$·2H$_2$O based on previously reported parameters\textsuperscript{19} (red) are shown. The static $^{139}\text{La}$ WURST-CPMG NMR spectra of La-MIL-121 (blue) and La(OAc)$_3$·1.5H$_2$O at 9.4 T (red) are illustrated in b), and in c), the $^{115}\text{In}$ static SSNMR solid-echo spectra of In-MIL-121 (blue) and In(OAc)$_3$ (red) at 21.1 T are shown. The black lines are simulated spectra created using the Quadfit software,\textsuperscript{12} which models a distribution of quadrupolar parameters, with the corresponding NMR parameters listed in Table 4-A6.
Table 4-A6 The NMR parameters of various metal-loaded MIL-121 samples, as obtained from simulations of the corresponding metal NMR spectra shown in Figures 4-A10 and A11.\(^a\)

<table>
<thead>
<tr>
<th>Samples</th>
<th>Min. $C_Q$ (MHz)</th>
<th>Max. $C_Q$ (MHz)</th>
<th>Center of $C_Q$ distribution (MHz)</th>
<th>Width of $C_Q$ distribution (MHz)</th>
<th>Min. $\eta_Q$</th>
<th>Max. $\eta_Q$</th>
<th>Center of $\eta_Q$ distribution</th>
<th>Width of $\eta_Q$ distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na-MIL-121</td>
<td>0.0</td>
<td>5.0</td>
<td>3.0</td>
<td>1.5</td>
<td>0.2</td>
<td>0.9</td>
<td>0.7</td>
<td>0.3</td>
</tr>
<tr>
<td>K-MIL-121</td>
<td>0.2</td>
<td>3.2</td>
<td>2.3</td>
<td>1.4</td>
<td>0.2</td>
<td>1.0</td>
<td>0.8</td>
<td>0.2</td>
</tr>
<tr>
<td>Mg-MIL-121</td>
<td>2.5</td>
<td>10.0</td>
<td>3.7</td>
<td>1.6</td>
<td>0.4</td>
<td>1.0</td>
<td>0.5</td>
<td>0.1</td>
</tr>
<tr>
<td>Zn-MIL-121</td>
<td>2.0</td>
<td>17.0</td>
<td>11.0</td>
<td>5.0</td>
<td>0.2</td>
<td>1.0</td>
<td>1.0</td>
<td>0.7</td>
</tr>
<tr>
<td>La-MIL-121</td>
<td>25.0</td>
<td>48.0</td>
<td>34.0</td>
<td>15.0</td>
<td>0.5</td>
<td>1.0</td>
<td>0.7</td>
<td>0.1</td>
</tr>
<tr>
<td>In-MIL-121</td>
<td>40.0</td>
<td>100.0</td>
<td>50.0</td>
<td>35.0</td>
<td>0.1</td>
<td>1.0</td>
<td>1.0</td>
<td>0.4</td>
</tr>
</tbody>
</table>

\(^a\)These NMR parameters were obtained by simulations using the Quadfit software,\(^{12}\) which models the NMR spectra arising from distributions of similar nuclear environments.
Figure 4-A12. Experimental and simulated SSNMR spectra of the guest metal sources used in this study. In a), the 9.4 T $^{23}$Na MAS solid-echo NMR spectrum of the Na$_2$CO$_3$ reagent acquired at a spinning rate of 13.333 kHz is shown. The 9.4 T $^{139}$La static WURST-CPMG NMR spectrum of La(OAc)$_3$·1.5H$_2$O is illustrated in b) along with a simulation, where the pound symbol (#) denotes satellite transitions. The experimental and simulated 21.1 T $^{115}$In static solid-echo NMR spectrum of In(OAc)$_3$ are depicted in c). In d), the 9.4 T $^{207}$Pb static WURST-CPMG SSNMR spectrum of Pb(OAc)$_2$·3H$_2$O is shown; based on the single powder pattern observed in a previously published work, the relatively narrower additional signal shown by the solid red line is assigned to a lead-containing impurity. The pink dotted lines in a), b), c), and d) are simulated spectra generated using WSolids, and the corresponding NMR parameters can be found in Table 4-A7.
Table 4-A7 The multinuclear metal NMR parameters of Pb-MIL-121 and various metal sources, as obtained from simulations of the corresponding experimental metal SSNMR spectra and from previously reported values in other works (see Figures 4-2 (main text) and 4-A12).a

<table>
<thead>
<tr>
<th>Sample</th>
<th>Site</th>
<th>δ&lt;sub&gt;iso&lt;/sub&gt; (ppm)</th>
<th>Ω (ppm)</th>
<th>κ</th>
<th>C_Q (MHz)</th>
<th>η_Q</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb-MIL-121</td>
<td>Site 1</td>
<td>-2680(15)</td>
<td>346(3)</td>
<td>0.64(2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Site 2</td>
<td>-3100(10)</td>
<td>552(5)</td>
<td>0.64(2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb(OAc)&lt;sub&gt;2&lt;/sub&gt;·3H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>Site 1</td>
<td>-1100(12)</td>
<td>2320(6)</td>
<td>0.75(2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Impurity</td>
<td></td>
<td>-980(10)</td>
<td>1031(7)</td>
<td>0.20(3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na&lt;sub&gt;2&lt;/sub&gt;CO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Site 1</td>
<td>6.0(2)</td>
<td></td>
<td></td>
<td>1.1(1)</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td>Site 2</td>
<td>-1.5(2)</td>
<td></td>
<td></td>
<td>2.4(2)</td>
<td>0.20</td>
</tr>
<tr>
<td>K&lt;sub&gt;2&lt;/sub&gt;CO&lt;sub&gt;3&lt;/sub&gt; (simulation)&lt;sup&gt;17&lt;/sup&gt;</td>
<td></td>
<td>29.2</td>
<td></td>
<td></td>
<td>1.03</td>
<td>0.65</td>
</tr>
<tr>
<td>Mg(OAc)&lt;sub&gt;2&lt;/sub&gt; (simulation)&lt;sup&gt;18&lt;/sup&gt;</td>
<td></td>
<td>5</td>
<td></td>
<td></td>
<td>2.55(5)</td>
<td>0.73(2)</td>
</tr>
<tr>
<td>Ca(OH)&lt;sub&gt;2&lt;/sub&gt; (simulation)&lt;sup&gt;21&lt;/sup&gt;</td>
<td></td>
<td>71.0 (3.0)</td>
<td></td>
<td></td>
<td>2.60(7)</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Zn(OAc)&lt;sub&gt;2&lt;/sub&gt;·2H&lt;sub&gt;2&lt;/sub&gt;O (simulation)&lt;sup&gt;19&lt;/sup&gt;</td>
<td></td>
<td>0</td>
<td></td>
<td></td>
<td>5.3</td>
<td>0.87</td>
</tr>
<tr>
<td>Zn(OAc)&lt;sub&gt;2&lt;/sub&gt; (simulation)&lt;sup&gt;17&lt;/sup&gt;</td>
<td></td>
<td>260</td>
<td>45</td>
<td>1.0</td>
<td>2.42</td>
<td>0</td>
</tr>
<tr>
<td>La(OAc)&lt;sub&gt;3&lt;/sub&gt;·1.5H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td></td>
<td>55(5)</td>
<td>220(7)</td>
<td>1.0(3)</td>
<td>10.5(3)</td>
<td>0.95(3)</td>
</tr>
<tr>
<td>La(OAc)&lt;sub&gt;3&lt;/sub&gt; (simulation)&lt;sup&gt;22&lt;/sup&gt;</td>
<td></td>
<td>-30</td>
<td></td>
<td></td>
<td>11</td>
<td>0.65</td>
</tr>
<tr>
<td>In(OAc)&lt;sub&gt;3&lt;/sub&gt;</td>
<td></td>
<td>0(30)</td>
<td>100(30)</td>
<td>0.5(5)</td>
<td>180(5)</td>
<td>0.22(2)</td>
</tr>
</tbody>
</table>

a These NMR parameters were obtained by analytical simulations of experimental spectra using the WSolids software,<sup>11</sup> which models the NMR spectra of multiple distinct, ordered nuclear environments.

Figure 4-A13 The uncorrected k<sup>2</sup>-weighted Fourier transform of the EXAFS spectra in R-space of Ag-MIL-121 (black) and AgOAc (red), which show peaks at 1.5 (both compounds), 2.2 (Ag-MIL-131), 2.8 (both), and 3.6 Å (both). The two spectra are in close agreement, indicating that the Ag<sup>+</sup> metal in Ag-MIL-121 is of the same oxidation state and has a similar local structure as compared to the Ag<sup>+</sup> metal in AgOAc.
The local environment about the free COOH group of the BTEC linker in MIL-121 is shown in a). The distances between adjacent oxygen atoms in the free COOH group are 2.55 Å for O4···O5 and 3.42 Å for O5···O5. Ag—O bonds that bridge nearby free COOH groups can be formed; the $^{13}$C CP/MAS and $^1$H MAS SSNMR (See Figure 4-1 in main text) spectra of Ag-MIL-121 suggest that Ag is indeed directly bound to these free carboxylate groups. Based on XAS data (Figure 4-1 and Figure 4-A13), the proposed local structure model of Ag$^+$ in Ag-MIL-121 is shown in b).

The Co K-edge EXAFS spectra of Co-MIL-121 (black, top) and Co(OAc)$_2$·4H$_2$O (red, bottom) are illustrated, as recorded in FLY mode. The inflection point of the white line was found to be located at 7721 eV in Co-MIL-121 and 7720 eV in Co(OAc)$_2$·4H$_2$O; the close agreement between these samples indicates that Co within Co-MIL-121 is of the 2$^+$ oxidation state.
Figure 4-A16 The uncorrected $k^2$-weighted Fourier transform of the EXAFS spectra in R-space of Co-MIL-121 (black) and Co(OAc)$_2$$\cdot$4H$_2$O (red). The identical major peaks located at 0.9, 1.4, 1.8, and 2.4 Å indicates that the local structure about Co in Co-MIL-121 should be similar to that of Co within Co(OAc)$_2$$\cdot$4H$_2$O.

Figure 4-A17 The Mn K-edge EXAFS spectra of Mn-MIL-121 (black, top) and Mn(OAc)$_2$$\cdot$4H$_2$O (red, bottom) are shown, as recorded in FLY. The inflection point of the white line was found to be 6547 eV in both samples, indicating that Mn of Mn-MIL-121 is in the 2$^+$ oxidation state.
Figure 4-A18 The uncorrected k²-weighted Fourier transform of the EXAFS spectra in R-space for Mn-MIL-121 (black) and Mn(OAc)₂·4H₂O (red) are shown, which feature peaks at 1, 1.5, 1.9, and 2.3 Å. Although the respective intensities differ slightly, the radial distances are in close agreement, indicating that Mn in Mn-MIL-121 likely has a similar structure to Mn in Mn(OAc)₂·4H₂O.
Figure 4-A19 The PXRD patterns of MIL-121 and Ag-MIL-121 samples synthesized using various concentrations of AgOAc loading source are shown. The red box highlights the extra reflections in the (0.08 M, 1 h) sample of Ag NP@MIL-121 that appear after reduction, which indicates the existence of Ag\(^0\) NPs. When a low concentration of silver acetate and a short time were used in the loading process, the extra reflections in the red box were not observed in the PXRD patterns of Ag NP@MIL-121 samples. The existence of Ag NPs has been confirmed by XPS (Figure 4-2, main text) and visualized by TEM (Figure 4-4, main text).
Figure 4-A20 The CO$_2$ adsorption isotherms for MIL-121 and Li-MIL-121 (loaded with metal guests using various metal source concentrations) at 273 K under 1 atm.

Figure 4-A21 The CO$_2$ adsorption isotherms for MIL-121 and Mg-MIL-121 (loaded using various metal source concentrations) at 273 K under 1 atm.
Figure 4-A22 The CO$_2$ adsorption isotherms for MIL-121 and Ca-MIL-121 (loaded with metal guests using various metal source concentrations) at 273 K under 1 atm.

Figure 4-A23 The CO$_2$ adsorption isotherms for MIL-121 and Ag-MIL-121 (loaded with metal guests using various metal source concentrations) at 273 K under 1 atm.
Table 4-A8 The quantities of H₂, CO₂ and N₂ adsorbed in MIL-121 and the metal-loaded MIL-121 variants shown in Figure 4-3 (a, b, c) of the main text.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Quantity of H₂ adsorbed (^a) (cm³/g, 77 K, 10 bar)</th>
<th>Quantity of CO₂ adsorbed (^a) (cm³/g, 273 K, 1 atm)</th>
<th>Quantity of N₂ adsorbed (^a) (cm³/g, 77 K, 1 bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MIL-121</td>
<td>8.4</td>
<td>55.2</td>
<td>49.3</td>
</tr>
<tr>
<td>Li-MIL-121 (0.74 wt%)</td>
<td>17.0 (102.0%)</td>
<td>83.9 (52%)</td>
<td>20.2 (-59.0%)</td>
</tr>
<tr>
<td>Mg-MIL-121 (0.52 wt%)</td>
<td>15.0 (78.1%)</td>
<td>70.5 (27.7%)</td>
<td>9.4 (-80.9%)</td>
</tr>
<tr>
<td>Ca-MIL-121 (4.01 wt%)</td>
<td>13.1 (56.1%)</td>
<td>69.3 (25.5%)</td>
<td>20.0 (-59.4%)</td>
</tr>
<tr>
<td>Ag NP@MIL-121 (1.8 wt%)</td>
<td>11.3 (34.3%)</td>
<td>93.5 (69.4%)</td>
<td>16.7 (-66.1%)</td>
</tr>
</tbody>
</table>

\(^a\) The percentage values in the brackets are the increase or decrease in the amount of gas adsorbed in metal-loaded MIL-121 compared to that of parent MIL-121.

Figure 4-A24 The PXRD patterns of MIL-121 and Li-MIL-121 samples synthesized for gas adsorption tests using various LiOH reagent concentrations.
Figure 4-A25 The PXRD patterns of MIL-121 and Mg-MIL-121 samples synthesized for gas adsorption tests using different Mg(OAc)$_2$ metal source concentrations.

Figure 4-A26 The PXRD patterns of MIL-121 and Ca-MIL-121 samples synthesized for gas adsorption tests using various concentrations of the loading reagent Ca(OH)$_2$. 
Table 4-A9 The catalytic performance of Ag NP@MIL-121 (1.80 wt %), along with recently reported noble metal based catalysts, in the reduction of 4-NP.

<table>
<thead>
<tr>
<th>Name of Catalyst</th>
<th>Mass of Catalyst used</th>
<th>Rate constant (κ)</th>
<th>κ/m (κ/mass of catalyst used)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag NP@MIL-121</td>
<td>ca. 0.034 mg</td>
<td>5.3 x 10^{-3}</td>
<td>156</td>
<td>This work</td>
</tr>
<tr>
<td>Ag/CTGU-3</td>
<td>1 mg</td>
<td>8.64 x 10^{-3}</td>
<td>8.64</td>
<td>23</td>
</tr>
<tr>
<td>Ag/CTGU-4</td>
<td>1 mg</td>
<td>3.03 x 10^{-3}</td>
<td>3.03</td>
<td>23</td>
</tr>
<tr>
<td>Au@MIL-100(Fe)</td>
<td>3.46 mg</td>
<td>5.5 x 10^{-3}</td>
<td>1.59</td>
<td>24</td>
</tr>
<tr>
<td>Au@Ag-ZIF-8</td>
<td>3.46 mg</td>
<td>4.97 x 10^{-3}</td>
<td>1.44</td>
<td>25</td>
</tr>
<tr>
<td>Au@silica nanotubes</td>
<td>8 mg</td>
<td>10.64 x 10^{-3}</td>
<td>1.33</td>
<td>26</td>
</tr>
<tr>
<td>MCA-Pd/Au</td>
<td>0.0175 mg</td>
<td>4.67 x 10^{-3}</td>
<td>266.9</td>
<td>27</td>
</tr>
<tr>
<td>Au@CPF-1</td>
<td>20 mg</td>
<td>5.05 x 10^{-3}</td>
<td>0.25</td>
<td>28</td>
</tr>
<tr>
<td>Au@CeO2</td>
<td>0.25 mg</td>
<td>32.6 x 10^{-3}</td>
<td>130.4</td>
<td>29</td>
</tr>
<tr>
<td>Au-Fe3O4@MIL-100(Fe)</td>
<td>3.4 mg</td>
<td>92.1 x 10^{-3}</td>
<td>27.1</td>
<td>30</td>
</tr>
<tr>
<td>Ag@BIF-20</td>
<td>5 mg</td>
<td>6.2 x 10^{-3}</td>
<td>1.24</td>
<td>31</td>
</tr>
<tr>
<td>Au@BIF-20</td>
<td>5 mg</td>
<td>3.7 x 10^{-3}</td>
<td>0.74</td>
<td>31</td>
</tr>
<tr>
<td>Ag@CTGU-1</td>
<td>1 mg</td>
<td>2.57 x 10^{-2}</td>
<td>25.7</td>
<td>32</td>
</tr>
<tr>
<td>Py-W/GO/AuNPs</td>
<td>4 mg</td>
<td>1.76 x 10^{-3}</td>
<td>0.44</td>
<td>33</td>
</tr>
<tr>
<td>Pd/CPM-1</td>
<td>2 mg</td>
<td>6.97 x 10^{-2}</td>
<td>34.85</td>
<td>34</td>
</tr>
<tr>
<td>Pd/CPM-2</td>
<td>2 mg</td>
<td>6.77 x 10^{-2}</td>
<td>33.85</td>
<td>34</td>
</tr>
</tbody>
</table>

* Some of the values were calculated based on the information provided in the corresponding literature.

References


Chapter 5

5 Understanding Thermally Triggered Hierarchical Pores in Metal-organic Frameworks

5.1 Introduction

Metal-organic frameworks (MOFs) are highly crystalline porous materials where the metal centers are connected by organic linkers, with various applications in gas storage, gas separation, catalysis, drug delivery and chemical sensing. Most MOFs possess micropores that are smaller than 2 nm, limiting their applications which involve large molecules such as drugs, enzymes and proteins. The introduction of hierarchical pores in MOFs can lead to many advantages since the mesopores and/or macropores allow large molecules to enter and diffuse through the framework channels. MOFs with hierarchical pores have shown improved performance in many aspects, including enhanced catalytic ability, increased gas adsorption and encapsulation of large molecules such as organic dye and biological proteins.

Two traditional strategies have been used to enlarge the pore size in MOFs. One is to use elongated linkers to replace the original organic ligands. This approach can be used to create large pores, but has many drawbacks such as interpenetrated structures, low stability and increased cost. Another method is to create hierarchical pores by templated synthesis where a template is introduced during the synthesis and removed afterwards. However, hierarchical MOFs obtained by template synthesis tend to collapse or lose its crystallinity during the template removal. To create hierarchical pores inside MOFs, another effective strategy is to create crystal “defects” inside the MOFs by targeting the weakness of the MOFs including the sensitivity to water or acid and chemical labile bonds. The introduction of crystal “defects” in MOFs can not only provide hierarchical structure, but also yield extra catalytic performance due to the creation of coordinatively unsaturated metal sites or open metal sites (OMSs). For instance, microporous POST-66(Y) MOF obtains hierarchical pores after a simple water treatment due to the dissolution of yttrium ions. A stepwise transition from microporosity to mesoporosity has also been observed in InOF-2 and MesoMOF-2 by thermal treatment which causes partial
collapse of the crystal structure. The creation of crystal defects in MOFs can also be done by introducing exogenous weaknesses such as the inclusion of defective or pro-labile linker inside chemically stable MOFs.\textsuperscript{6, 14} The mesopores can then be created via acid treatment or linker thermolysis.\textsuperscript{6, 9}

Currently, research on hierarchical MOFs mainly focuses on developing suitable strategies to expand the pore size without total collapse of the framework and expanding their corresponding applications by taking advantage of the enlarged pores. However, a detailed understanding of hierarchical pore formation inside MOFs and their relationship with the enhanced properties are crucial to the development of hierarchical MOFs. Comprehensive and fundamental research addressing these issues are rare. Herein, we report a discovery on the porosity transition in MIL-121 MOF and show that the CO\textsubscript{2} adsorption capability is greatly enhanced after acquiring hierarchical pores. MIL-121 is an aluminum MOF with 1,2,4,5-benzenetetracarboxylic acid (BTEC) as linkers (Figure 5-1a).\textsuperscript{19} The two carboxylic acid groups in BTEC are not connected to the metal centers but are dangling in the channels (insert of Figure 5-1a), which reduces the free pore volume for guest molecule adsorption and results in a dramatically decreased Brunauer-Emmett-Teller (BET) surface area (less than 50 m\textsuperscript{2}/g) in contrast to its analogue MOF MIL-53 (>1000 m\textsuperscript{2}/g).\textsuperscript{19} The small pore size and extremely low BET area of MIL-121 severely restrict its applications, especially in gas adsorption. We discovered that hierarchical pores can be easily created in MIL-121 via the decarboxylation of the BTEC linker by carefully controlling the thermal treatment temperature and duration. After the linker thermolysis, the BET surface area of MIL-121 can be greatly increased from a value of 13.2 m\textsuperscript{2}/g to 887.7 m\textsuperscript{2}/g when the pore size accordingly changes from less than 1 nm to an average value of 3.00 nm (Table 5-1 and Figure 5-1c). Due to the enlarged pore size, the CO\textsubscript{2} gas adsorption in MIL-121 has been increased by 3.89 times (27.1 cm\textsuperscript{3}/g vs 105.3 cm\textsuperscript{3}/g at 1 atm and 273 K). In addition to gas adsorption tests, the existence of hierarchical pores in MIL-121 is unambiguously revealed by scanning electron microscope (SEM). The formation of hierarchical pores inside MIL-121 has been investigated by multinuclear SSNMR spectroscopy in detail. The \textsuperscript{13}C and \textsuperscript{1}H MAS NMR experiments revealed the gradual decomposition of the organic linkers during the thermal treatment. The degeneration of metal centers was directly probed by \textsuperscript{27}Al MAS NMR spectroscopy. Meanwhile, the distinct host-guest interaction between the adsorbed
CO$_2$ and thermally treated MOF is examined by in situ static VT $^{13}$C SSNMR spectroscopy. Finally, a mechanism that describes the formation of hierarchical pores inside MIL-121 is proposed based on the gas adsorption test, SEM images as well as the multinuclear NMR spectroscopy results.

5.2 Results and discussion

Porosity transition in MIL-121.

To eliminate the unreacted ligands in as made MIL-121, a methanol solvent exchanged process has been used on as made MIL-121 (see details in Appendix). The methanol solvent exchanged MIL-121 (termed as Meth-MIL-121) is chosen as the starting material. Meth-MIL-121 was placed in an oven and thermally treated in a temperature range from 250 to 440 °C before gas adsorption tests. The resulting material was termed as MIL-121-xx°C-xxH (xx °C and xx H correspond to the temperature and the duration of the time for thermal treatment). The N$_2$ adsorption isotherms of MIL-121-250°C-16H and MIL-121-380 °C-16H at 77 K show that there are only slight N$_2$ uptake in the two samples, suggesting that these MIL-121 samples have extremely low porosity (<100 m$^2$/g) even after high temperature thermal treatment (Table 5-1). Interestingly, when the thermal treatment temperature is increased to 410 °C, the N$_2$ uptake of MIL-121-410°C-16H is dramatically escalated, which corresponds to a BET surface area of 293.3 m$^2$/g. It is worth noting that the N$_2$ adsorption curve of MIL-121-410°C-16H exhibits a Type IV isotherm with an obvious hysteresis loop (see enlarged picture in Figure 5-A1, Appendix).$^{20}$ The hysteresis loop suggests the existence of mesopores, indicating the formation of hierarchical structure inside MIL-121.$^{9,13}$ With increasing temperature, the existence of hysteresis loop in the N$_2$ adsorption isotherms becomes more pronounced. The corresponding BET surface area of each sample is listed in Table 5-1 and Table 5-A1. Based on these values, it is obvious that the porosity of MIL-121 undergoes a stepwise transition from micropore to mesopore, changing the MIL-121 from an almost nonporous material to a MOF possessing a hierarchical structure.
Figure 5-1 (a) Crystal structure of MIL-121 built from octahedral Al chains and BTEC linkers. (b, c) N₂ adsorption isotherms and pore size distribution of thermally treated MIL-121 samples (solid circles represent adsorption measurement points while open circles are desorption measurement points). (d) PXRD patterns of Meth-MIL-121 and thermally treated MIL-121 samples. (e) CO₂ adsorption isotherms in thermally treated MIL-121 samples at 273 K under 1 atm are illustrated.

MIL-121-440°C-16H has the largest BET surface area, with a value of 887.6 m²/g (623.8 m²/g micropore and 263.8 m²/g mesopore) (Table 5-1). When the thermal treatment time is further increased, the BET surface area of MIL-121 gradually drops to 479.9 m²/g, which mainly arises from the mesopores after 48 H at 440°C (Figure 5-1b, Figure 5-A2, Table 5-
1 and Table 5-A1), indicating that the MOF probably loses its crystallinity after prolonged aging. The pore size distribution in MIL-121-250°C-16H, MIL-121-440°C-16H and MIL-121-440°C-48H clearly reveals the formation and growth of mesoporosity in MIL-121 (Figure 5-1c). MIL-121-250°C-16H consists of only micropores, while the pore size is dramatically increased into the mesopore range for MIL-121-440°C-16H. Compared to MIL-121-440°C-16H, which has mesopore largely in the range of 2-6 nm, the pore size of MIL-121-440°C-48H is extended to 18 nm and centered at around 8 nm, suggesting the existence of abundant mesopores (Figure 5-1c).

Table 5-1 The porosity parameters in thermally treated MIL-121 based on N₂ gas adsorption.

<table>
<thead>
<tr>
<th>MIL-121</th>
<th>( S_{\text{BET}} ) (m²/g)</th>
<th>( S_{\text{BET Micro}} ) (m²/g)</th>
<th>( S_{\text{BET Meso}} ) (m³/g)</th>
<th>Average pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MIL-121-250°C-16H</td>
<td>13.2</td>
<td>8.6</td>
<td>4.6</td>
<td>&lt; 1.00</td>
</tr>
<tr>
<td>MIL-121-380°C-16H</td>
<td>49.4</td>
<td>35.6</td>
<td>13.8</td>
<td>&lt; 1.00</td>
</tr>
<tr>
<td>MIL-121-410°C-16H</td>
<td>293.3</td>
<td>219.9</td>
<td>73.4</td>
<td>2.42</td>
</tr>
<tr>
<td>MIL-121-440°C-5H</td>
<td>398.0</td>
<td>286.9</td>
<td>111.1</td>
<td>2.66</td>
</tr>
<tr>
<td>MIL-121-440°C-9H</td>
<td>659.1</td>
<td>491.2</td>
<td>167.9</td>
<td>2.89</td>
</tr>
<tr>
<td>MIL-121-440°C-16H</td>
<td>887.6</td>
<td>623.8</td>
<td>263.8</td>
<td>3.00</td>
</tr>
<tr>
<td>MIL-121-440°C-48H</td>
<td>479.9</td>
<td>50.5</td>
<td>429.4</td>
<td>8.19</td>
</tr>
</tbody>
</table>

The corresponding PXRD patterns of the samples show that the thermally treated samples still possess high crystallinity and their PXRD patterns are almost the same as the parent MOF, Meth-MIL-121, until aging time was 22 hours at 440 °C (Figure 5-1d, Figure 5-A3). Although some minor peaks of hierarchical samples disappeared after the thermal treatment, the main peaks of parent MIL-121 are still clearly observable, suggesting the topology of MIL-121 are intact. After aging for over 22 hours, the crystallinities of the treated samples gradually decreased, indicating the start of framework degeneration (Figure 5-1d, Figure 5-A3). Further increase in heating time to 48 hours resulted in the disappearance of almost all the diffraction peaks in MIL-121-440°C-48H, hinting that a thermally induced amorphization of MIL-121 has occurred. The retained topology in hierarchical MIL-121 and amorphization in MIL-121-440°C-48H were further confirmed by multinuclear SSNMR experiments, which will be discussed later. With enlarged pore
size and enhanced BET surface areas, the hierarchical MIL-121 sample exhibits a dramatically increased CO$_2$ adsorption in contrast with the micropore MIL-121. The CO$_2$ adsorption data of MIL-121-250ºC-16H, MIL-121-440ºC-16H and MIL-121-440ºC-48H (273K, 1 atm) are given in Figure 5-1e. MIL-121-440ºC-16H sample has the largest CO$_2$ adsorption capacity, with a value of 105.3 cm$^3$/g, which is 288.6% greater than that of MIL-121-250ºC-16H (27.1 cm$^3$/g). The MIL-121-440ºC-48H also showed an enhanced CO$_2$ adsorption capacity compared to MIL-121-250ºC-16H (38.8 vs 27.1 cm$^3$/g, corresponding to a 43% increase). However, the CO$_2$ adsorption capacity of MIL-121-440-48 is still much less than that of MIL-121-440ºC-16H, suggesting that optimized pore size plays a critical role in the CO$_2$ gas adsorption. The different CO$_2$ adsorption capacities in these three samples clearly demonstrate that the interaction between the MOFs and adsorbed gas molecules can be delicately optimized by adjusting the pore size of the host.

**Morphology of MIL-121**

The SEM images of Meth-MIL-121 and thermally treated MIL-121 samples are given in Figure 5-2 and Figure 5-A4. The thermally treated MIL-121 samples, including MIL-121-440ºC-48H, all exhibit parallelepiped-shaped crystals, which are almost the same as Meth-MIL-121 (Figure 5-2). The morphology of MIL-121-440ºC-48H (Figure 5-2e) clearly confirms it is amorphous MIL-121 rather than the MOF-derived aluminum oxide (γ-alumina), which exhibits needle-like alumina sheets. In addition, the formation of hierarchical porosity in MIL-121 is directly validated by the SEM images (Figure 5-2b/d/e), which are in good agreement with N$_2$ sorption analysis. Compared to the relatively smooth surface of Meth-MIL-121 (Figure 5-2b), the surface of MIL-121-440ºC-16H (Figure 5-2d) becomes much rougher with primary mesopores spreading over the crystal. When linker thermolysis continues, the MIL-121-440ºC-48H exhibits a surface decorated with sponge-like pores, indicating rich mesopores with larger sizes were formed.
**Figure 5-2** SEM images of Meth-MIL-121 and thermally treated samples at different scales are shown: (a, b) Meth-MIL-121, (c, d) MIL-121-440ºC-16H, (e, f) MIL-121-440ºC-48H. Scale bar is 1 μm in (a, c, d), 500 nm in (b, d, f) and 200 nm for the inset in (d,e). The formed mesopores are indicated by red circles in the two insets in (d,e).

**Multinuclear SSNMR study on MIL-121**

To reveal the formation mechanism of hierarchical pores in MIL-121, multinuclear SSNMR spectroscopy was employed to probe the linkers and the metal centers during the thermal treatment. $^1$H-$^{13}$C CP/MAS and $^1$H MAS SSNMR spectra of each sample are shown in Figure 5-3 and Figure 5-A5. The $^1$H-$^{13}$C CP and $^1$H MAS SSNMR spectra of MIL-121-250ºC-16H (Figure 5-3a) each feature three resonances, respectively. The $^1$H-$^{13}$C CP/MAS spectrum of MIL-121-250ºC-16H is identical to that of Meth-MIL-121. The $^1$H MAS SSNMR spectra of MIL-121-250ºC-16H is also similar to that of Meth-MIL-121, except the proton signals from solvent molecules like water and/or methanol (Figure 5-A5) are absent, suggesting that there is no change happening to the linker after heating at this temperature. Based on our previous work in chapter 4, the C1 and C2 resonances at ca. 172 ppm in the $^1$H-$^{13}$C CP/MAS spectra of MIL-121 samples (Figure 5-3a) are assigned to free and Al-coordinated carboxylate groups. The resonances at ca. 135 ppm and 130.0 ppm are
assigned to phenyl carbon atoms C3 and C4/5 (Figure 3a). As for the $^1$H MAS NMR spectrum (Figure 5-3b), the H1 resonance at ca. 12 ppm originates from the free COOH group, the H2 resonance at ca. 8 ppm arises from the BTEC phenyl and H3 resonance results from the hydroxyl group that are connected to adjacent Al atoms. The $^1$H-$^{13}$C CP/MAS spectra of thermally treated samples show no difference until the thermolysis temperature reaching 380 ºC – a small resonance located at ca. 163 ppm (denoted in black box, Figure 5-3a) appears in the spectrum of MIL-121-250ºC-16H, suggesting the formation of anhydride due to the condensation between two adjacent free carboxylate groups.\textsuperscript{22-23} When the thermolysis temperature was increased, this anhydride resonance becomes more prominent (Figure 5-3a and Figure 5-A5a), indicating the formation of more anhydride groups. The existence of anhydride groups in the thermally treated MIL-121 can be further confirmed by changes in the corresponding $^1$H MAS SSNMR spectra (Figure 5-3b and Figure 5-A5b) – the H1 which represents the free COOH groups continues to decrease when the temperature is increased and finally completely disappears in the spectrum of MIL-121-410ºC-16H, directly confirming the condensation reaction between adjacent free carboxylate groups. Meanwhile, another $^{13}$C resonance at ca. 120 ppm (denoted as C6) starts to show up in the spectrum of MIL-121-410ºC-16H and continues to increase in those samples as the temperature increases. As mentioned before, the N$_2$ gas adsorption results show that the formation of hierarchical pores starts at the temperature of 410 ºC and the pore size keeps increasing afterwards. Based on the porosity transition in MIL-121 and the chemical shift of C6 which appears in the range of phenyl carbons, this new resonance C6 likely originates from the C5/C4 (see the labels of carbon atoms in Figure 5-3a) after losing the COOH group upon decarboxylation at high temperatures. It is worth noting that the resonances in both $^{13}$C and $^1$H MAS NMR spectra of MIL-121-440ºC-48H are significantly broader compared to the spectra of other samples, suggesting that a substantial amount of highly disordered coordinated linkers still remains inside the MOF, which confirms our previous conclusion that MIL-121-440ºC-48H is the amorphous MOF instead of $\gamma$-alumina.
Figure 5-3 $^1$H–$^{13}$C CP/MAS SSNMR spectra of thermally treated MIL-121 samples are illustrated in (a). (b) The corresponding $^1$H MAS SSNMR spectra of these samples. All spectra were obtained at a magnetic field of 9.4 T using a spinning speed of 14.0 kHz. Notice that the $^{13}$C resonance corresponding to anhydride groups appears in the $^{13}$C spectrum of MIL-121-380°C-16H (black circle in (a)) and at higher temperatures. A depiction of the BTEC linker with corresponding labels for each unique carbon and hydrogen site is shown at the top of each spectral stack.

The decarboxylation process naturally enlarges the pore size and yields a larger free pore volume inside MIL-121. As mentioned above, MIL-121 resembles MOF MIL-53, which has 1,4-benzenedioic acid as linkers. MIL-53 has almost the same topology as MIL-121 but has no extra free carboxylic acid dangling in the channels. Considering that the analogue MOF MIL-53 is still a microporous MOF, a simple decarboxylation in MIL-121
still cannot explain the growing mesopore size observed in the corresponding N\textsubscript{2} gas adsorption and SEM images, which are much larger than 2 nm (Figure 5-1c and Figure 5-2d/f). The collapse of a fragment of the MOF and the concomitant formation of metal oxide aggregates may be the reason for the creation of mesopores.

**Figure 5-4** The $^{27}$Al MAS NMR spectra of Meth-MIL-121 and the thermally treated MIL-121 are shown in (a), as obtained using a spinning speed of 31.25 kHz at a magnetic field of 21.1 T. The labels at top describes the coordination numbers of aluminum based on its CS range. (b) In situ $^{13}$C VT SSNMR experimental spectra of $^{13}$CO\textsubscript{2}-loaded thermally treated MIL-121, as obtained at a magnetic field of 9.4 T. The legend at top describes two different resonances.

To investigate the behaviour of metal centers during the thermolysis, $^{27}$Al MAS SSNMR experiments were performed on Meth-MIL-121 and the thermally treated MIL-121. Selected $^{27}$Al MAS SSNMR spectra at 21.1 T are shown in Figure 5-4a, and the additional spectra acquired at 9.4 T can be found in the Appendix (Figures 5-A6). The $^{27}$Al MAS SSNMR spectrum of Meth-MIL-121 contains two resonances – the main resonance

![Figure 5-4](image-url)
(denoted in green dash line in Figure 5-4a) originates from the metal centers and the second signal is assigned to a minor Al impurity that was probably introduced during the synthesis. Both resonances are in the octahedral Al chemical shift (CS) range, indicating they are all six-coordinated AlO$_6$. The $^{27}$Al MAS SSNMR spectrum of MIL-121-250ºC-16H is identical to that of Meth-MIL-121, suggesting that the removal of adsorbed solvents has no effect on Al local environment. After raising the thermal treatment temperatures to above 395 ºC (Figure 5-A6 and Figure 5-4a), the resonance due to the metal center in crystalline MIL-121 in the $^{27}$Al spectra gradually decreases and totally vanishes in the MIL-121-440ºC-48H spectrum, suggesting that the six-coordinated Al metal centers convert to other Al species during the porosity transition. When the temperature reached 410 ºC, the $^{27}$Al MAS SSNMR spectrum of MIL-121-410ºC-16H features a third resonance which is assigned to crystal “defect” penta-coordinated aluminum (i.e. AlO$_5$) based on its chemical shift. As mention above, MIL-121-410ºC-16H is the first thermally treated sample with obvious hierarchical pores (Figure 5-1b, Figure 5-A1 and Table 5-1) and the corresponding $^{13}$C MAS NMR spectrum also clearly indicates that the decarboxylation phenomenon starts at this temperature (Figure 5-3a). Apparently, the crystal “defect” produced by the thermolysis is the penta-coordinated AlO$_5$, i.e. an OMS or unsaturated metal center. The formation of the OMS results from the six-coordinate Al (metal center of MIL-121) losing one coordinated linker due to the thermally triggered decarboxylation. The appearance of the AlO$_5$ OMS also confirms the previous speculation that the formation of mesopores is directly connected with the defected metal cluster instead of a simple ligand decarboxylation process. In addition, a new resonance in the tetrahedral Al CS range (i.e. AlO$_4$) is observed in the $^{27}$Al spectrum of MIL-121-440ºC-16H and the signal keeps increasing in the subsequent samples until the original metal center resonance totally disappears (Figure 5-4a and Figure 5-A6). It is apparent that more aluminum sites in MIL-121 are converted to tetrahedral aluminum in alumina under the persisting high temperature thermolysis. The appearance of AlO$_4$ resonance suggests that further decomposition happened locally within the structure of MIL-121, which accounts for the enlarged mesopores seen in the corresponding N$_2$ gas adsorption and SEM images (Figure 5-1c and Figure 5-2f). It is interesting to find that the vanished original metal center resonance does not completely convert to AlO$_5$ or AlO$_4$ but also transfers to another form of AlO$_6$ which
is located at around 10 ppm (Figure 5-4a). Considering 10.5 % of the BET surface area of MIL-121-440ºC-48H are still microporous (Table 5-1), the resonance at ca. 10 ppm in $^{27}$Al spectrum of MIL-121-440ºC-48H should be the residue octahedral AlO$_6$ metal centers in the MOF. The introduction of crystal “defect” (i.e. 5-coordinated Al) into MOFs is known to affect the chemical shift of adjacent metal centers in MOFs. Based on the $^{27}$Al MAS spectra of the thermally treated MIL-121, it can be concluded that the transition of the local environments of the aluminum metal centers in MIL-121 has undergone several steps: penta-coordinated AlO$_5$ OMS first forms due to the decarboxylation process at 410 ºC and the formation of tetrahedral AlO$_4$ in aggregated alumina then follows due to partial collapse of the MOF structure when the temperature is increased to 440 ºC. Although most octahedral aluminum metal centers transform into AlO$_5$ or AlO$_4$, some of them still remained, which account for the residual micropore structure in MIL-121-440ºC-48H.

The host-guest interaction between adsorbed CO$_2$ and hierarchical MIL-121 has been investigated by in situ $^{13}$C VT SSNMR spectroscopy. $^{13}$CO$_2$ gas (99% $^{13}$C-labeled) was used, and since the natural abundance of $^{13}$C is just ca. 0.96%, the observed resonances must all originate from $^{13}$CO$_2$. The microporous MIL-121-250ºC-16H, hierarchical MIL-121-440ºC-16H and amorphous MIL-121-440ºC-48H are saturated with $^{13}$CO$_2$ (see details in the Appendix) and the corresponding $^{13}$C NMR spectra are shown in Figure 5-4b. A broad featureless resonance is observed in the $^{13}$C NMR spectrum of MIL-121-250ºC-16H at 293 K. The resonance lacks the typical pattern arising from chemical shift anisotropy (CSA), suggesting a distribution of local environments of adsorbed CO$_2$ molecules. Considering the low adsorption capacity of CO$_2$ in MIL-121-250ºC-16H (27.1 cm$^3$/g, 273K, 1 atm, Figure 5-1e), it seems that the narrow pore size and limited free pore volume of microporous MIL-121-250ºC-16H severely restrict both the adsorption and motion of CO$_2$, resulting in a broad featureless resonance. In contrast, $^{13}$C NMR spectra of hierarchical MIL-121-440ºC-16H features two powder patterns, corresponding to adsorbed CO$_2$ (Figure 5-4b). A relatively narrow resonance (denoted signal 1) is observed in the middle of the spectrum and a broad featureless resonance is found beneath signal 1 (denoted signal 2). The breadth of signal 1 is ca. 60 ppm at 298 K, which is much narrower than the resonance in MIL-121-250ºC-16H (ca.160 ppm). The breadth of the $^{13}$CO$_2$ powder pattern is directly associated with the CO$_2$ motion. A reduced breadth usually corresponds to a
decrease in binding energy between the adsorbed gas and the host, which usually results from elevated temperature or enlarged space, leading to the larger degree of CO$_2$ motion.$^{26-27}$ Considering the existence of hierarchical pores in MIL-121-440°C-16H, signal 1 is assigned to the CO$_2$ in the mesopores which have a larger space for the motion of CO$_2$. Signal 2 is very similar to the featureless resonance in MIL-121-250°C-16H and has a slightly broader breadth (ca. 180 ppm), which indicates that signal 2 also originates from CO$_2$ molecule with limited mobility and located in a microporous environment. The broad breadth and featureless line shape of signal 2 suggest that those adsorbed CO$_2$ molecules are in a disordered environment and interact more strongly with the MOF than the CO$_2$ located at mesopores (i.e. signal 1). The disordered environment probably arises from the decarboxylation process which leads to a distribution of micropores with slightly different pore sizes as well as different degree of decarboxylation in each pore. Meanwhile, the formation of OMSs in MIL-121-440°C-16H should be the reason for the enhanced interaction between CO$_2$ and the host.$^5$ Interestingly, another broad featureless resonance with a narrower breadth of ca.100 ppm is observed in the $^{13}$C NMR spectrum of MIL-121-440°C-48H (Figure 5-4b), implying that this amorphous MOF also has a distribution of weakly absorbed CO$_2$. The amorphous MIL-121-440°C-48H has a much larger average pore size which is commonly regarded as not suitable for small gas molecules adsorption due to the weak interaction between the framework and guest gas.$^3,28$ In addition, the aggregation of AlO$_4$ also reduces the free pore volume for gas adsorption. It seems that the weak host-guest interaction and enlarged pore volume in MIL-121-440°C-48H result in the featureless resonance. The transition from a broad CO$_2$ powder pattern in a microporous MOF to a weak featureless resonance in mesopore MOF was also observed in Mg-MOF-74. When the original ligand, dobdc (2,5-dioxido-1,4-benzenedicarboxylate), of Mg-MOF-74 was replaced by an expanded ligand, dobpd (4,4'-dioxido-3,3'-biphenylidicarboxylate), the resulting analogue MOF, Mg$_2$(dobpd), has a larger pore size (2.5 nm vs 1.5 nm) and the $^{13}$C NMR spectra of the adsorbed CO$_2$ changed from a well-defined broad signal in Mg-MOF-74 into a weak featureless resonance.$^{27}$ During the porosity transition in MIL-121, it is the optimized pore size and pore volume that are responsible for the maximum CO$_2$ adsorption. Existence of both micropores and mesopores which all exhibit strong affinity towards CO$_2$ is the reason for the largely enhanced adsorption capacity in hierarchical MIL-
121-440°C-16H compared to both MIL-121-250°C-16H and MIL-121-440°C-48H.

**Figure 5-5** Schematic illustration of porosity transition in MIL-121.

The combination of gas adsorption data, electron microscopy images and multinuclear NMR studies provides abundant details regarding the porosity transition in MIL-121 which can be described as follows. When temperature reaches 380 ºC, the adjacent free COOH groups in MIL-121 (Figure 5-5a) start to form anhydride by losing water molecules due to the condensation reaction (Figure 5-5b). Once the temperature increases to 410 ºC, a decarboxylation process happens by releasing the CO$_2$, resulting in the five-coordinated AlO$_5$ (i.e. OMS). This is the key step leading to the formation of mesopore inside MIL-121(Figure 5-5c). With a further increase in temperature, alumina with tetrahedral Al forms at 440 ºC inside the mesopores. In the meanwhile, the amount of OMS is also dramatically increased due to the further collapse of local structure in MOFs (Five 5-5d), leading to the expansion of mesopore size and volume, and a gradual loss of the micropore structure.
5.3 Conclusion

We reported that the microporous MIL-121 can be transferred into a hierarchical structure through controlled linker thermolysis. A stepwise transition from microporosity to mesoporosity was found during the thermal treatment. The surface area and pore size/volume of MIL-121 can be delicately tuned, leading to a greatly enhanced CO$_2$ adsorption capacity in the corresponding hierarchical MOF. We comprehensively investigated the formation of hierarchical structure in MOF via the combination of gas adsorption, SEM and multinuclear SSNMR spectroscopy, which is critical to understanding the porosity transition mechanism and its associated properties. This work provides detailed insights regarding the motion of adsorbed gas molecules within a hierarchical micro- and meso-porous MOF, reveling that a strong connection exists between gas adsorption and pore structure in which a suitable pore size plays a key role in determining the final gas capacity. Our work not only illustrates the formation of hierarchical pore in MOFs, but also provides an avenue to investigate the host-guest interaction in hierarchical MOFs, which can be used to guide the optimization of pores structure in various porous materials.

5.4 References

5.5 Appendix

Section A1: Experimental details

Sample preparation

Meth-MIL-121: As made MIL-121 was prepared based on the previously reported procedure with some modifications. A reagent mixture including 1.2 g Al(NO$_3$)$_3$·9H$_2$O (Alfa Aesar, 98%), 0.4 g pyromellitic acid (1,2,4,5-benzenetetracarboxylic acid (BTEC),
Alfa Aesar, 96%), 0.3 ml 4M HCl and 7.0 mL of deionized H2O was added in a Teflon chamber under stirring for 10 minutes. The chamber was then placed within a Teflon-lined stainless steel autoclave and sealed. The autoclave was placed in an oven at 210 °C for 4 h. White powder was obtained by centrifugation and dried in an oven at 90 °C for 5 h. Then 0.20 g as made MIL-121 was immersed in 20 mL of methanol and stored in a Teflon container within a Teflon-lined stainless steel autoclave, which was then heated in an oven at 150 °C for 2 days, during which the methanol was replaced every day. The final product was dried at 90 °C and termed as Meth-MIL-121.

**Thermally treated MIL-121:** Meth-MIL-121 was placed in an oven at a given temperature for a certain period of time under air. The harvest sample was then termed as MIL-121-xx°C-xxH (xx°C and xxH correspond to the given temperature and time of thermal treatment). Before gas adsorption test, the samples were degassed at 200 °C for 8 hours under vacuum.

**N2 and CO2 adsorption measurements:** N2 and CO2 adsorption isotherms were measured by a Micromeritics ASAP 2020 porosity analyzer at separate temperatures of 77 K and 273 K.

**MAS SSNMR measurement.**

13C and 1H SSNMR spectra [ν0(13C) = 100.5 MHz, ν0(1H) = 399.5 MHz] were referenced to TMS using adamantane as a secondary reference: the high-frequency 13C resonance at 38.57 ppm and the 1H resonance at 1.85 ppm were used for the secondary referencing procedure. 1H–13C cross-polarization magic angle spinning (CP/MAS) experiments were performed with proton decoupling at a spinning frequency of 14 kHz using a spectral width of 100 kHz, along with a 1H 90° pulse length of 4.6 μs, contact time of 7 ms and a recycle delay of 2 s. 1H MAS experiments were performed at a spinning frequency of 14 kHz and a spectral width of 100 kHz, utilizing a 90° pulse of 4.4 μs and a recycle delay of 1 s.

27Al MAS SSNMR spectroscopy: 27Al MAS experiments [ν0(27Al) = 104.1 MHz] were referenced to 1.0 M Al(NO3)3 at 0.0 ppm. The experiments were acquired using a 90° - 90° solid echo pulse sequence with proton decoupling, using a 27Al CT-selective 90° pulse
length of 1.58 μs and a recycle delay of 1 s at spinning rate of 15 kHz (9.4 T) and 31.25 kHz (21.1 T).

**Static in situ VT SSNMR.**

Powder samples were packed into an L-shaped glass tube, and then activated using the same vacuum line and procedure as described in chapter 2 and 3. The samples were saturated with the guest gas (¹³CO₂), flame-sealed off from the vacuum line, and brought back to room temperature before SSNMR experiments were performed.
Section A2:

Figure 5-A1 N₂ adsorption isotherms of MIL-121-250°C-16H and MIL-121-410°C-16H (solid circles represent adsorption measurement points while open circles are desorption measurement points). Notice the dramatically increased N₂ uptake and the hysteresis loop in MIL-121-410°C-16H compared with MIL-250°C-16H.

Figure 5-A2 N₂ adsorption isotherms of MIL-121-440°C-15H/17H/22H (solid circles represent adsorption measurement points while open circles are desorption measurement points).
Table 5-A1 The porosity parameters in thermally treated MIL-121 based on N₂ gas adsorption.

<table>
<thead>
<tr>
<th>MIL-121</th>
<th>( S_{\text{BET}} (\text{m}^2/\text{g}) )</th>
<th>( S_{\text{BET Micro}} (\text{m}^2/\text{g}) )</th>
<th>( S_{\text{BET Meso}} (\text{m}^2/\text{g}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>MIL-121-440°C-15H</td>
<td>740.1</td>
<td>527.2</td>
<td>212.9</td>
</tr>
<tr>
<td>MIL-121-440°C-17H</td>
<td>857.0</td>
<td>615.6</td>
<td>241.4</td>
</tr>
<tr>
<td>MIL-121-440°C-22H</td>
<td>778.3</td>
<td>477.2</td>
<td>301.1</td>
</tr>
</tbody>
</table>

Figure 5-A3 PXRD patterns of Meth-MIL-121 and thermally treated MIL-121 samples. Notice that the MIL-121 starts to degenerate after the thermal treatment time was over 22 hours.
Figure 5-A4 SEM images of thermally treated samples at different scales are shown: (a, b): MIL-121-250°C-16H; (c, d): MIL-121-410°C-16H. Scale bar is 2 μm in (a, c) and 500 nm in (b, d).
Figure 5-A5 $^1$H-$^{13}$C CP/MAS and $^1$H SSNMR spectra of Meth-MIL-121 and thermally treated MIL-121 samples are illustrated in (a) and (b). All spectra were obtained at a magnetic field of 9.4 T using a spinning speed (ss) of 14.0 kHz. A depiction of the BTEC linker with corresponding labels for each unique carbon and hydrogen site is shown at the top of each spectral stack.
Figure 5-A6 The $^{27}$Al MAS NMR spectra of Meth-MIL-121 and thermally treated MIL-121 are shown, as obtained using a spinning speed of 15 kHz at a magnetic field of 9.4 T. The asterisk (*) denotes spinning sidebands and the labels at top describes the coordination numbers of aluminum based on its CS range.
Chapter 6

6 Post-synthetic Modification via Anhydride Groups in a Hierarchical Metal-organic Framework: A Novel Efficient “Anchor”

6.1 Introduction

In the past two decades, metal-organic frameworks (MOFs) have emerged and grown as the largest branch of porous materials, leading to tens of thousands of entities and various applications including gas storage, gas separation, catalysis, chemical sensors, drug delivery, electrochemical energy storage and conversion. MOFs are crystalline materials with high porosity, in which metals and organic linkers are covalently connected. The robust structure and organic components of MOFs enable the introduction of abundant chemical functionality into the MOFs by post-synthetic modification (PSM) while the overall topologies of the MOFs remain the same. Currently, PSM has been a very general method to enhance the existing and to introduce new properties to MOFs, such as a higher stability to moisture, an increase in gas uptake, and the introduction of extra catalytic sites with high activities. PSM is mainly based on covalent modification of the organic linkers or formation of metal-ligand bond through the open metal sites. Covalent bonding via the pendant group of the linker or second functional group has been regarded as an efficient way for PSM of MOFs.

Even though the reported MOF entries in Cambridge Structural Database (CSD) have surpassed 70000, the available functional groups for PSM study are largely limited to few functional groups including amino, hydroxyl, catechol or thiocatechol and 2,2’-bipyridyl moieties. In addition, in order to keep the topology intact upon incorporation of functionalized linker into MOFs and to avoid the potential damage during PSM, functionalized MOFs for PSM are generally limited to microporous zirconium MOFs such as UiO-66/67 due to their chemical stability. The imbalance between the extremely large community of MOFs and the very limited number of pendant groups and corresponding functionalized MOFs makes it necessary and urgent to explore alternate MOFs with new active and stable functional groups that can be used for PSM.
carboxylic acid groups attract our particularly interest since the carboxyl groups have been widely used in organic reaction to construct covalent bonds. Literature also reports that the free carboxylic acid groups inside MOFs such as UiO-66-(COOH)_x (x = 1 and 2)\(^{17}\) and MIL-53-COOH\(^{18}\) can be converted to anhydride groups after thermal treatment. Anhydrides are well known stable and highly active carboxylate derivatives. In addition to the active functional groups, the pore size of MOFs also plays a key role in PSM. Since most MOFs have micropores with diameters less than 2 nm, this severely limits the mass transfer inside the pores, ruling out the incorporation of large molecules. In our recent study (chapter 5), we have discovered that a stepwise transition from microporosity to mesoporosity can occur in MIL-121 via thermal treatment. In addition, MIL-121, which also features free COOH groups, can form anhydride groups during the thermal treatment. The resulting hierarchical MIL-121 with functionalized anhydride groups gains a great potential for the incorporation of various organic functional groups.

Herein, we present the first PSM study on anhydride-functionalized hierarchical MOF MIL-121 (termed as HMIL-121, Scheme 6-1). MIL-121 is an aluminum-based MOF with inexpensive ligands (1,2,4,5-benzenetetracarboxylic acid, BTEC) as linkers and two of the four COOH groups of BTEC are connected to metal centers, leaving the other two COOH groups dangling in the channels (Scheme 6-1a).\(^{19}\) Due to the dangling, uncoordinated COOH groups, MIL-121 has a limited free aperture of 8.7×5.7 Å\(^{19}\) and extremely small Brunauer-Emmerauer-Teller (BET) surface areas (ca. 13 m\(^2\)/g). A HMIL-121 with BET surface area of 887.6 m\(^2\)/g (average pore size: 3.00 nm, micropore: 623.8 m\(^2\)/g and mesopore: 263.8 m\(^2\)/g, Appendix: Figure 6-A1) is obtained by thermal treatment at 440 °C for 16 hours and used as host for PSM in this work. Our study shows that the HMIL-121 functionalized with anhydride groups exhibits high reactivity towards organic species including alcohols, amines and thiols (Scheme 6-1d) inside the MOF. Surprisingly, Pt salt (tetraamines platinum hydroxide) can also be successfully incorporated into HMIL-121 (Scheme 6-1d). This work demonstrates that the anhydride groups not only can be used to introduce extra organic functional groups into MOFs, but also can be used for metalation of MOFs with noble metals. The resulting Pt modified HMIL-121 is subsequently annealed at a high temperature of 900°C in Ar atmosphere to fabricate the conductive electrocatalyst
and a remarkable catalytic activity towards oxygen reduction reaction (ORR) was demonstrated.

Scheme 6-1 (a) A depiction of MIL-121 with free COOH groups. (b) After thermal treatment at 440 °C for 16 hours, decarboxylation occurs, releasing CO₂ gas and resulting in HMIL-121, which has expanded pore sizes and increased surface areas. (c) The remaining anhydride groups in HMIL-121 show high activity towards various organic compounds and a Pt salt. Color code: black, C; red, O; the center blue octahedron AlO₆.

6.2 Results and discussion

Modification of HMIL-121 with alcohols.
Figure 6-1 (a) An illustration of esterification between alcohols and anhydride groups of the HMIL-121 (O: red, C: grey, Al: blue, H: green). $^1$H–$^{13}$C CP/MAS and $^1$H MAS SSNMR spectra of MIL-121, HMIL-121 and MeO-HMIL-121 are shown in (b) and (c). All MAS spectra were obtained at a magnetic field of 9.4 T using a spinning speed of 14.0 kHz.

The powder X-ray diffraction (PXRD) patterns show that the PSM modified HMIL-121 variants have the same topology as HMIL-121 (Figure 6-A2). Solid-state nuclear magnetic resonance (SSNMR) spectroscopy is sensitive to local structures and can provide element specific information.\textsuperscript{20,21} It has been widely used to examine the PSM process.\textsuperscript{22,23} We have chosen the esterification of methanol and incorporation of Pt into HMIL-121 as two examples to show how anhydride can be used to further functionalize HMIL-121 and the detailed information for the other PSM reaction can be found in the Appendix.
Esterification in industry leads to numerous products including drugs like aspirin, fatty acid esters and macrolides. Esters are usually obtained by the reaction between alcohols and acids or acid derivatives such as anhydride. The utilization of anhydride in esterification always results in two products: the ester and the corresponding acid as by-product (Figure 6-1a). Thus, the confirmation of both ester and corresponding acid groups are necessary to confirm esterification occurred inside HMIL-121.

The esterification between methanol and anhydride group in HMIL-121 was carried at 60 °C for 3 hours with 4 drops of concentrated sulfuric acid as catalyst and the final product is then fully activated and termed as MeO-HMIL-121 (see the Appendix for details). The $^1$H-$^{13}$C cross polarization (CP)/magic angle spinning (MAS) and $^1$H MAS SSNMR spectra of MIL-121, HMIL-121 and MeO-HMIL-121 are shown in Figures 6-1b and 6-1c with the corresponding BTEC linker in MIL-121 placed on top of each spectral stack. The $^1$H-$^{13}$C CP/MAS NMR spectrum of MIL-121 has three resonances – the resonance at ca. 172 ppm originates from C1 and C2, the resonance at ca.134.9 ppm corresponds to phenyl carbon C3, and the resonance at 130.0 results from phenyl carbons C4 and C5 (Figure 6-1b). After thermal treatment, two new resonances appeared. The one at ca. 163.0 ppm is assigned to anhydride groups originating from condensation of two adjacent free carboxylic acid groups (-R-COOH) and the other one at ca. 123.2 ppm corresponds to C6 resulting from C5 and C4 due to the decarboxylation during the thermal treatment (Figure 6-1b). As compared to HMIL-121, the $^{13}$C spectrum of MeO-MIL-121 exhibit two new resonances – one at ca. 168.5 ppm corresponding to the carbonyl moiety in a phenyl ester, suggesting that esterification occurred between anhydride group and methanol molecule; the additional resonance at ca. 51.0 ppm is due to the methoxy group from ester. Since MeO-HMIL-121 is activated at 150 °C under vacuum for 8 hours, the NMR signal of methoxy group should exclusively originate from grafted ester rather than residual methanol. The corresponding $^1$H NMR spectra of three samples are given in Figure 6-1c. There are also three resonances in the spectrum of MIL-121. The resonance at ca. 12 ppm is assigned to the free COOH group on the BTEC linker (labeled H1) and the resonance at ca. 8 ppm originates from BTEC phenyl hydrogens (H2). The relatively broad resonance located between 2-6 ppm consists of several proton signals, including the hydroxyl group connecting adjacent Al metal centers (H3) and water that is adsorbed in the MIL-121
(Figure 6-1c). After the thermal treatment, the H1 resonance completely disappears due to the formation of anhydride, suggesting that there is no more free carboxylate groups inside HMIL-121. In contrast, after the reaction with methanol, the H1 resonance reappears, implying that the free carboxylic acid re-forms in MeO-HMIL-121 due to the esterification between anhydride and methanol. The $^1$H-$^{13}$C CP/MAS and $^1$H MAS SSNMR spectra together unambiguously confirm the esterification of methanol with anhydride group inside HMIL-121. In addition to methanol, other organic molecules including ethanol, aniline, p-toluidine and 1,2-ethanedithiol are also grafted into HMIL-121 via the reactions with anhydride groups. The experimental details and results regarding these modified HMIL-121 variants can be found in the Appendix.

**Modification of HMIL-121 with Pt salt.**

![Figure 6-2](image)

**Figure 6-2** (a) The $^{195}$Pt WURST-CPMG experimental and simulated spectra of Pt(NH$_3$)$_4$(OH)$_2$ and Pt-HMIL-121 at 9.4 T; (b) The XPS analysis of Pt-HMIL-121; (c) The proposed mechanism of incorporation of the Pt species inside HMIL-121.

Pt is one of the most widely used noble metals due to its well-known catalytic properties. In contrast to other noble metals, Pt has particularly important pharmaceutical applications as Pt based drugs are regarded as critical agents in treating cancers.$^{24-25}$ Square-planar Pt(II)-based drugs and the more stable carboxylate platinum (IV) prodrugs based on the
Pt(II) precursor are two main Pt drugs used in both research and clinical therapy.\textsuperscript{26-27} The carboxylate functionalized platinum (IV) prodrugs are usually obtained by the reaction between anhydride and square-planar Pt(II) drugs under oxidizing reagents such as O$_2$, H$_2$O$_2$ or Cl$_2$\textsuperscript{27-28}. Inspired by the synthesis of platinum(IV) prodrug, Pt(II) salt, tetraammineplatinum(II) hydroxide (Pt(NH$_3$)$_4$(OH)$_2$) is successfully introduced into HMIL-121 (termed as Pt-HMIL-121) via acylation, which can be used for drug delivery and/or application in catalysis. The reaction is carried out by mixing HMIL-121 with aqueous Pt(NH$_3$)$_4$(OH)$_2$ at room temperature without using any catalyst. The product is then collected and washed by water to remove the residual Pt precursor (see details in the Appendix).

To characterize the product, the $^{195}$Pt Wideband Uniform Rate Smooth Truncation-Carr-Purcell Meiboom-Gill (WURST-CPMG)\textsuperscript{29-30} experiments were carried out. The experimental and simulated spectra of Pt(NH$_3$)$_4$(OH)$_2$ and Pt-HMIL-121 are shown in Figure 6-2a. The corresponding chemical shift (CP) tensor parameters can be found in Table 6-A1. The $^{195}$Pt NMR spectrum of Pt(NH$_3$)$_4$(OH)$_2$ features a single broad powder pattern, suggesting the presence of one unique platinum site. The CS tensor is also axially symmetric, as indicated by a skew ($\kappa$) value of ca. -1 (Table 6-A1). The axially symmetric tensor observed in the $^{195}$Pt powder pattern of Pt(NH$_3$)$_4$(OH)$_2$ is typical of square-planar Pt(II) salts.\textsuperscript{31-32} In contrast, there are two powder patterns observed in the $^{195}$Pt SSNMR spectrum of Pt-HMIL-121, suggesting two distinct Pt local environments inside the HMIL-121. The simulated spectrum confirms the presence of two Pt sites. The right power pattern in Pt-HMIL-121 (site 1) (Figure 6-2a) has an isotropic chemical shift ($\delta_{iso}$) of -2580 ppm, a span ($\Omega$) of 7161 ppm and a $\kappa$ of -0.90. These values are very similar to that of the Pt site in Pt(NH$_3$)$_4$(OH)$_2$ ($\delta_{iso}$ = -2580 ppm, $\Omega$ = 7091 ppm and $\kappa$ = -0.93, Table 6-A1), suggesting that site 1 arises from a square-planar Pt(II) similar to Pt(NH$_3$)$_4$(OH)$_2$. The CS tensor values of the left resonance (site 2) are 950 ppm, 3090 ppm and 0.12 for $\delta_{iso}$, $\Omega$ and $\kappa$ (Table 6-A1), indicating that site 2 has a distinct local Pt environment compared to site 1 and Pt(NH$_3$)$_4$(OH)$_2$. Although static $^{195}$Pt SSNMR powder patterns of Pt compounds have very large breadth, Pt(IV) resonances trend to appear at a higher frequency compared to Pt(II), with a chemical shift range between approximate +7500 to -7000 ppm.\textsuperscript{32} In contrast, the chemical shifts for Pt(II) resonances are in the range of ca. -500 to -5500 ppm.\textsuperscript{32} Therefore,
it can be concluded that site 1 corresponds to a square-planar Pt(II) specie and site 2 originates from an octahedral Pt(IV) complex. The presence of two different Pt species in Pt-HMIL-121 is further confirmed by X-ray photoelectron spectroscopy (XPS, Figure 6-2b). Two specific peaks with binding energy of 72.72 and 76.05 eV are assigned to the Pt 4f7/2 and Pt 4f5/2 electrons of Pt^{2+}, respectively. The other two peaks with binding energies of 74.75 and 78.08 eV are due to the Pt 4f7/2 and Pt 4f5/2 electrons of Pt^{4+}, respectively.

Based on the multinuclear NMR and XPS studies on Pt(NH\(_3\))\(_4\)(OH)\(_2\) and Pt-HMIL-121, a mechanism can be proposed for how the two Pt species in HMIL-121 arise. Pt(NH\(_3\))\(_4\)(OH)\(_2\) is first oxidized to an octahedral Pt(IV) complex with two coordinated hydroxyl groups by the molecular oxygens dissolved in water (Figure 6-2c). Then, the octahedral Pt(IV) complex is bonded to the carboxylate groups via reacting with anhydride of HMIL-121 (Figure 6-2c). The incorporation of octahedral Pt(IV) complex naturally produces free carboxylate groups, thereby providing acids to react with basic Pt(NH\(_3\))\(_4\)(OH)\(_2\), resulting in the square-planar Pt(II) specie grafted on HMIL-121 (Figure 6-2c). In addition, the acid-base reaction between Pt(NH\(_3\))\(_4\)(OH)\(_2\) and the byproduct free carboxylate groups is directly confirmed by the pH change during the experiment – the aqueous Pt(NH\(_3\))\(_4\)(OH)\(_2\) with a pH value of 10.0 gradually becomes neutral after mixing with HMIL-121, confirming the neutralization reaction.

**ORR activity**

Pt is well known for its excellent catalytic activity in various applications. Therefore, modified Pt-HMIL-121 was used to fabricate MOF-derived Pt containing electrocatalyst for ORR. Fuel cells and metal-air batteries are very promising candidates for environmentally sustainable energy sources, where the ORR plays a key role in determining their electrical energy conversion.\(^{33-34}\) Currently, Pt based cathode is still the most efficient materials in catalyzing ORR.\(^ {34}\) Due to the high cost of Pt, constructing low Pt containing electrocatalyst without losing the performance is critical to achieving large scale industrial production for electric vehicles and equipment involving ORR.\(^ {34}\) Recently, MOF-derived carbon materials have attracted tremendous attention due to the inheritance of high surface area and porosity from their parent MOF precursors, leading to high
exposure and easy accessibility of the active sites.\textsuperscript{11, 35} In addition, the resulting MOF-derived carbon materials eliminate the poor electrical conductivity and have higher thermal/chemical stability compared to their parent MOFs, making them an ideal host for fabricating highly dispersed metal doped electrocatalyst.\textsuperscript{11, 36}

![Figure 6-3](image)

**Figure 6-3** (a) SEM images of Pt-HMIL-121; (b, c, d) Pt-HMIL-121-900 samples at different scales. Scale bar: 5 \( \mu \)m in (a, b), 500 nm in (b) and 100 nm in (d)

Pt-HMIL-121 was pyrolyzed by heat treatment at 900\(^\circ\)C under Ar atmosphere, followed by hydrochloric acid leaching (see details in the Appendix). The resulting catalyst is termed as Pt-HMIL-121-900. During the pyrolysis, the grafted Pt complex decomposed, generating the reduced metallic Pt nanoparticles (NPs). Meanwhile, the HMIL-121 substrate was carbonized and converted into the conductive Al-doped porous carbon. The Pt-HMIL-121-900 with highly dispersed Pt NPs was thus fabricated. Before testing the electrochemical catalytic performance, the morphology of precursor Pt-HMIL-121 and catalyst Pt-HMIL-121-900 were carefully investigated by scanning electron microscopy (SEM). As shown in Figure 6-3, the SEM images at different scales indicate that the Pt-HMIL-121-900 remains as parallelepiped shaped crystals which are almost the same as the
parent Pt-HMIL-121. After high temperature treatment at 900 °C, the size of Pt-HMIL-121-900 crystals are a bit smaller than those of HMIL-121-900 (Figures 6-3a/b), which is a common phenomenon in carbonized MOFs due to the loss of most H and O elements.37 The crystal face of Pt-HMIL-121-900 is decorated with dominant mesopores, suggesting the existence of a hierarchical structure with large average pore size. The differences in surface area and hierarchical pores in Pt-HMIL-121 and Pt-HMIL-121-900 were further characterized by N2 sorption tests. The two samples show the same type IV isotherms with hysteresis loops which are similar to that of HMIL-121 (Figure 6-A4), suggesting the existence of both mesopores and micropores. The calculated BET surface area for Pt-HMIL-121 is 411.0 m²/g which is less than that of HMIL-121 (887.6 m²/g) due to the steric hindrance of the incorporated Pt species within the pore channels. In contrast, the BET surface area for Pt-HMIL-121-900 is as high as 2866 m²/g (Figure 6-A4). This value is one of the highest reported BET surface area among pyrolytic MOFs, suggesting Pt-HMIL-121-900 has the potential to provide sufficient exposure of the Pt sites and facilitate mass transport during ORR.

Transmission electron microscopy (TEM) images show more details of Pt-HMIL-121-900 sample. From Figure 6-4a, it can be seen that Pt-HMIL-121 is converted into the porous carbon decorated with Pt NPs that are dispersing on both the surface and in the pores of Pt-HMIL-121-900 substrate. Figure 6-4b shows the high-resolution TEM (HRTEM) image of the Pt-HMIL-121-900, revealing the crystalline Pt NPs are uniformly distributed in the Pt-HMIL-121-900 matrix after carbonation. The particle size of Pt NPs is within 2-3 nm, suggesting the absence of obvious aggregation. The lattice distance of crystalline Pt NPs in HRTEM image is measured and given in the insert of Figure 6-4b. A value of 0.225 nm was obtained, which is in good agreement with the interplanar distance of d111 in a Pt crystal.38 The element maps of C and Pt are illustrated in Figures 6-4 c/d, demonstrating that the Pt NPs are uniformly dispersed throughout the porous carbon matrix and no obvious aggregate crystalline Pt NPs are observed.
Figure 6-4 TEM and HRTEM images of Pt-HMIL-121-900. Scale bars are 100 nm in (a), 5 nm in (b) and 2 nm for the insert in (b). STEM element maps of C and Pt for Pt-HMIL-121-900 at 100 nm are given in (c) and (d), respectively.

The XRD patterns of Pt-HMIL-121 and Pt-HMIL-121-900 samples are illustrated in Figure 6-A5. After pyrolysis, there is a significant difference in XRD patterns of Pt-HMIL-121-900 and Pt-HMIL-121. The reflections of HMIL-121 disappeared, and well-defined Pt and carbon crystalline peaks formed in Pt-HMIL-121-900 (Figure 6-A5). The crystalline carbon is generated from the decomposition of the host HMIL-121. During the high temperature pyrolysis, most of the hydrogen, oxygen and carbon elements are evaporated, resulting in Pt-doped hierarchically porous carbon particles. The Pt loading of Pt-HMIL-121-900 is 7.0 wt%, as determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES), and thus the Pt-HMIL-121-900 is now referred as 7%Pt-HMIL-121-900.
Figure 6-5 (a) ORR curves for the electrocatalysts of 7.0%Pt-HMIL-121-900, HMIL-121-900, and 40.0%Pt/C catalysts in O₂-saturated 0.1 M HClO₄ solution at room temperature (1600 rpm, sweep rate 10mV·s⁻¹). (b) The mass activity at 0.9 V for 7.0%Pt-HMIL-121-900 and commercial 40%Pt/C catalysts. The electrochemical performance of 7.0%Pt-HMIL-121-900 is evaluated for ORR and compared with the performances of pyrolytic HMIL-121 (termed as HMIL-121-900) and the state-of-the-art commercial Pt/C catalyst (40.0 wt% Pt and termed as 40%Pt/C catalyst). Figure 6-5a presents the linear-scanning voltammogram curves for the 7.0%Pt-HMIL-121-900, HMIL-121-900 and 40% Pt/C catalysts obtained in a O₂-saturated 0.1M HClO₄ electrolyte at a rotating speed of 1600 rpm. The 7%Pt-HMIL-121-900 displays a much positively-shifted ORR onset potential (1.04 V vs. RHE) and a higher current density (5.3 mA·cm⁻²) compared to the corresponding values of HMIL-121-900. The kinetic currents at 0.9 V for the 7.0%Pt-HMIL-121-900 and commercial 40%Pt/C electrocatalysts obtained from the Koutecký-Levich equation are used to get the mass activity based on the Pt loading (Figure 6-5b). For the fresh catalysts, the 7.0%Pt-HMIL-121-900 exhibits a mass activity of 0.35 A·mg⁻¹Pt at 0.9 V, which is around two times higher than that of commercial 40%Pt/C catalyst (0.18 A·mg⁻¹Pt). Based on these results, it is apparent that 7.0%Pt-HMIL-121-900 shows excellent catalytic performance in ORR with a relatively lower Pt loading and have much higher ORR mass activity compared to that of commercial Pt/C catalyst. The uniformly dispersed Pt NPs on the hierarchical carbon matrix of HMIL-121 enable high electrochemical active surface area of Pt catalyst, revealing that the anhydride
functionalized hierarchical HMIL-121 has a great potential to fabricate efficient Pt doped electrocatalyst for ORR as well as other Pt related energy conversions.

6.3 Conclusion

In conclusion, the hierarchical HMIL-121 with anhydride groups exhibit high activity towards covalently grafting various organic species as well as Pt(IV)/Pt(II) complexes on the pore wall of HMIL-121. The resulting Pt doped HMIL-121 is used to fabricate electrocatalyst via pyrolysis, which achieved high ORR activity. Our work not only opens a novel avenue to introduce multiple chemical functionality inside anhydride-functionalized MOFs, but also offers a tunable catalyst platform for Pt related electrochemical energy conversion. We also showed that multinuclear SSNMR spectroscopy is a highly effective method to follow the PSM processes which are critical to understanding the mechanisms during the modification. It is hoped that this work will inspire those working in the fields of MOFs, COFs and porous organic polymers to continue seeking high active and stable pendant groups for future PSM studies.

6.4 References


6.5 Appendix

Section A: Experimental details.
**MIL-121 and Solvent exchanged MIL-121:** These samples were prepared following the same method described in chapter 5.

**Hierarchical MIL-121:** The hierarchical MIL-121 was obtained based on our previous work in chapter 5: Meth-MIL-121 was placed in an oven at 440 °C for 16 h. During this process, a decarboxylation occurred and part of the structure collapsed, creating hierarchical pores inside the MOF. The resulting MOF is termed as HMIL-121, which was then used as the starting material for PSM.

The obtained PSM product was termed as **XX-HMIL-121** where XX stands for the corresponding incorporated species.

**Esterification by alcohols:**

**MeO-HMIL-121:** A mixture of 200.0 mg HMIL-121 and 10.0 ml 99.9% MeOH was placed in a 25 ml round-bottom flask and then 3 drops of concentrated H$_2$SO$_4$ (98%) was added. The reagent mixture was then put in an oil bath at 60 °C. The reaction was held for 5 h under magnetic stirring. The product was then isolated by centrifugation. To remove residual MeOH, the product was immersed within 25 mL of DI water and stirred for 5 min in a 50.0 ml centrifuge tube. This washing process was repeated three times before the collected product was dried at 90 °C. The dried sample was then completely activated at 150 °C under a dynamic vacuum (≤1 mbar) for ca. 8 h. The final fully activated product is termed as MeO-HMIL-121.

**EtO-HMIL-121:** The esterification of ethanol (EtOH) inside HMIL-121 is similar to methanol. 20.0 mg of 4-Dimethylaminopyridine (DMAP) was used as catalyst instead of concentrated H$_2$SO$_4$ while the rest of the reaction condition is the same as MeO-MIL-121.

**Amidation by amino:**

**Aniline-HMIL-121:** 200 mg HMIL-121 and 10 mg DMAP were added into 10.0 ml aniline. The reagent mixture was placed in a 25 ml round-bottom flask. The flask was then put into an oil bath at 80 °C. The reaction was held for 8 hours under magnetic stirring. The product was then isolated by centrifugation. To remove residual aniline and DMAP,
the product was immersed within 25 mL of DMF and stirred for 5 min. This DMF washing process was repeated three times. To remove residue DMF, the obtained product was mixed with 25 mL of DI water and stirred for 5 min in a 50.0 ml centrifuge tube. This water wash procedure was also repeated three times. The collected product was then dried at 90 °C. The dried sample was completely activated at 150 °C under a dynamic vacuum (≤1 mbar) for ca. 8 h. The final fully activated product is termed as Aniline-HMIL-121.

**p-Toluidine-HMIL-121**: 1.000 g of p-Toluidine, 200 mg HMIL-121 and 10 mg DMAP were added into 20.0 ml dimethylformamide (DMF). The reagent mixture was placed in a 50 ml round-bottom flask. The flask was then put into an oil bath at 80 °C. The reaction was held for 8 hours under magnetic stirring. The product was then isolated by centrifugation, followed by the same DMF and DI water wash process and activation as Aniline-HMIL-121. The final fully activated product is termed as p-Toluidine-HMIL-121.

**Thiolation by thiols:**

EDT-HMIL-121: 1.0 ml 1,2-Ethanedithiol (EDT) was diluted by 9.0 ml dichloromethane. The diluted EDT solution was then mixed with 200 mg HMIL-121 in a 50.0 ml centrifuge tube for 40 minutes at room temperature under magnet stirring. The product was then isolated by centrifugation and followed by the dichloromethane wash process to remove residue EDT (each wash time lasted for 3 minutes with 25.0 ml dichloromethane in a 50.0 ml centrifuge tube). The collected product was then dried at 60 °C. The dried sample was completely activated at 90 °C under a dynamic vacuum (≤1 mbar) for ca. 6 h. The final fully activated product is termed as EDT-HMIL-121.

**Metalation of Pt complexes:**

**Pt-HMIL-121**: a general metalation of Pt complex into HMIL-121 follows a reaction between aqueous Pt(NH₃)₄(OH)₂ and HMIL-121 in a 50.0 ml centrifuge tube at room temperature under magnet stirring. 60.0 mg Pt(NH₃)₄(OH)₂ and 300.0 mg HMIL-121 were mixed with 15 mL of DI water for 40 min in a 50 mL centrifugation tube at room temperature under magnet stirring. The product was then collected by centrifugation, followed by 4 times DI water wash process to remove residue Pt precursor (each wash time
lasted for 5 minutes with 25.0 ml DI water in a 50.0 ml centrifuge tube). The collected product was then dried at room temperature overnight inside a fume hood. The dried sample was completely dehydrated at 100 °C under a dynamic vacuum (≤1 mbar) for ca. 6 h.

**SSNMR measurement:**

All $^1$H, $^{13}$C, and $^{195}$Pt SSNMR experiments were acquired at a magnetic field of 9.4 T using a Varian InfinityPlus wide-bore NMR spectrometer.

$^{13}$C and $^1$H SSNMR spectroscopy: the set up for $^{13}$C and $^1$H SSNMR spectroscopy is the same as that described in chapter 5.

$^{195}$Pt static SSNMR spectroscopy: A 1.0 M aqueous Na$_2$PtC$_4$ solution was used as a chemical shift reference ($v_0^{(195}\text{Pt}) = 85.59$ MHz, $\delta_{iso} = 0.0$ ppm). The Pt spectra of two samples (Pt salt and Pt-HMIL-121) were acquired using WURST-CPMG pulse sequence with a WUST-80 pulse and $^1$H decoupling. The Pt spectra of two samples are produced from coaddition of several individual sub-spectra due to the wide breadth of the resonance. The Pt spectrum of Pt salt contains 8 sub-spectra which have $^{195}$Pt frequency ranging from 85.05 to 86.25 MHz. For each sub-spectrum, the pulse delay is 3 second, spectral window is 1000 kHz, spikelet separation in the frequency domain is 5000 Hz and scan number is 500. The Pt spectrum of Pt-HMIL-121 contains 3 sub-spectra which have $^{195}$Pt frequency of 85.6, 85.745 and 85.89 MHz respectively and for each sub-spectrum, the pulse delay is 0.165 second, spectral window is 1000 kHz, spikelet separation in the frequency domain is 9090 Hz and scan number is 219992.

**Preparation of Pt-MIL-121-900**

The powder of Pt-HMIL-121 was placed into a quartz boat and then heat-treated at the 900 °C (3°C·min$^{-1}$) for 1 h under Ar gas in a tube furnace. The pyrolysis product of Pt-HMIL-121-900 was acid-washed with 1M HCl solution overnight under magnetic stirring and then filtered and washed with plenty of deionized water. The final catalyst of Pt-HMIL-121-900 was obtained by vacuum drying.
Electrochemical measurements

The electrochemical characterizations were performed in a three-electrode system using a rotating-disk electrode (RDE) setup with an Autolab electrochemistry station and rotation control (Pine Instruments). The ink was prepared by mixing 3.0 mg of catalyst in 3.0 ml of aqueous solution containing 0.6 mL of isopropyl alcohol and 30 µL of Nafion (5.0 wt%). 30 min sonication was then conducted to ensure good dispersion and wetting of the catalyst. 60 µL of the catalyst ink was pipetted onto a polished glassy carbon electrode (Pine, 5.0 mm dia., 0.196 cm²) and allowed to dry at room temperature. All electrochemical measurements were carried out in 0.1 M HClO₄ electrolyte using a Pt wire as a counter electrode and reversible hydrogen electrode (RHE) as a reference electrode. All potentials reported henceforth are vs. RHE. Each electrode was activated by scanning from 0.05 to 1.1 V at 50 mV·s⁻¹ in N₂-saturated 0.1 M HClO₄ until no changes were observed in the cyclic voltammetry (CV) curves. O₂ was then bubbled into HClO₄ for 30 min to achieve an O₂-saturated electrolyte. ORR linear sweep voltammetry (LSV, 10 mV·s⁻¹) was then conducted in O₂-saturated 0.1 M HClO₄ on the RDE system with a rotation speed of 1600 rpm. The LSV curves obtained under N₂ were subtracted from the LSV curves obtained under O₂ to remove the non-Faradaic current. For comparison, the commercial 40% Pt/C is prepared on the electrode using a similar procedure as described above with a Pt loading of 10 µg·cm⁻².

The kinetic current was calculated from the ORR polarization curves by using mass-transport correction and normalized to the loading amount of Pt, in order to compare the mass activity of different catalysts. According to the Levich−Koutecky equation²:

\[
\frac{1}{i} = \frac{1}{i_k} + \frac{1}{i_d}
\]

Where \(i_k\) is the kinetic current and \(i_d\) is the diffusion-limiting current.

Section A2:
**Figure 6-A1** The adsorption-desorption isotherms for N\textsubscript{2} in MIL-121, HMIL-121 and modified HMIL-121 variants by PSM at 77 K under 1 bar are depicted. In these diagrams, solid circles represent adsorption measurement points while open circles are desorption measurement points. Compared to HMIL-121, the N\textsubscript{2} adsorption of modified HMIL-121 variants all significantly decreased. The decrease originates from the reduced pore size/space due to the existence of those incorporated organic species and Pt complexes, hinting the successful introduction of them into HMIL-121 via reaction with anhydride groups.
Figure 6-A2 The PXRD patterns of MIL-121, HMIL-121 and modified HMIL-121 variants by PSM are shown. Few peaks in the PXRD pattern of HMIL-121 disappeared in contrast with that of MIL-121 due to the decarboxylation process during thermal treatment. However, the main peaks of the PXRD pattern remain, suggesting the topology of MIL-121 are not changed in HMIL-121. After PSM, the main peaks of HMIL-121 are remained in those of the modified HMIL-121 variants, revealing that the topology of HMIL-121 is not altered during the modification.
Figure 6-A3 (a) The $^{1}$H–$^{13}$C CP/MAS NMR spectra of MIL-121, HMIL-121 and modified HMIL-121 variants by PSM obtained at a spinning speed of 14 kHz are shown. The vertical pink dashed line denotes the resonance assigned to anhydride groups in HMIL-121 framework. Multiple additional resonances can be observed in the spectra of modified HMIL-121 variants compared to that of HMIL-121, originating from the incorporated organic species. (b) The $^{1}$H MAS NMR spectra of MIL-121 HMIL-121 and modified HMIL-121 variants by PSM are illustrated, as obtained at a spinning speed of 14 kHz. Notice that the resonance belong to H1 that is absent in HMIL-121 appears in the spectra of the modified HMIL-121 variants, suggesting that free carboxylic acid formed after the PSM. The $^{1}$H–$^{13}$C CP/MAS NMR spectra and $^{1}$H MAS NMR spectra together confirm that the organic species have been covalently bonded to the frameworks via reacting with anhydride groups.
Table 6-A1. The $^{195}$Pt SSNMR parameters of Pt(NH$_3$)$_4$(OH)$_2$ and Pt-HMIL-121, as obtained from simulations of the $^{195}$Pt SSNMR spectra shown in Figure 6-2 (main text).

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\delta_{iso}$ (ppm)</th>
<th>$\Omega$ (ppm)</th>
<th>$\kappa$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(NH$_3$)$_4$(OH)$_2$</td>
<td>-2580(40)</td>
<td>7091(60)</td>
<td>-0.93(2)</td>
</tr>
<tr>
<td>Pt-HMIL-121 Site 1</td>
<td>-2580(62)</td>
<td>7161(80)</td>
<td>-0.90(4)</td>
</tr>
<tr>
<td>Site 2</td>
<td>950(23)</td>
<td>3080(40)</td>
<td>0.12 (2)</td>
</tr>
</tbody>
</table>

Figure 6-A4 N$_2$ adsorption–desorption isotherms and pore size distribution of Pt-HMIL-121-900 and Pt-HMIL-121.
Figure 6-A5 The PXRD patterns of Pt-HMIL-121 and Pt-HMIL-121-900.

References


Chapter 7

7 Probing Calcium-Based Metal-Organic Frameworks via Natural Abundance $^{43}$Ca Solid-State NMR

7.1 Introduction

Metal-organic frameworks (MOFs) are porous materials composed of metal centres and organic linkers\textsuperscript{1} with diverse applications in fields including gas storage, gas separation, and catalysis.\textsuperscript{2-4} Within many applications, such as in biomedicine or the food industry, the cost and toxicity of MOFs is of very high importance.\textsuperscript{5-6} Many MOFs are based on transition metals (e.g., Co, Cu, Cr), which are toxic to humans and the environment.\textsuperscript{7-8} Calcium is a “green” and cost-efficient metal due to its excellent biocompatibility and relatively high abundance on Earth. Several Ca-based MOFs have exhibited promising properties. For example, the CaSDB (SDB: 4,4′-sulfonyldibenoic acid) MOF has a high selectivity for CO$_2$/N$_2$ adsorption and excellent Xe uptake capacity,\textsuperscript{9-10} while the calcium MOF-1201 and MOF-1203\textsuperscript{11} frameworks are able to encapsulate the agricultural fumigant cis-1,3-dichloropropene.

Structural characterization is critical to understanding the origins of MOF properties. Solid-state NMR is a powerful probe of local structure in MOFs, and is particularly useful when a single crystal for X-ray diffraction (XRD) cannot be obtained.\textsuperscript{12-13} The metal ions in MOFs play a key role in structure and function; NMR can unravel the local structure about metal centers, and investigate metal-guest interactions.\textsuperscript{12, 14-17} Due to the closed Ca$^{2+}$ electronic configuration, NMR is one of the few spectroscopic techniques that can directly interrogate Ca$^{2+}$.\textsuperscript{18-19} Solid-state $^{43}$Ca NMR experiments on MOFs are rare; there are only two $^{43}$Ca NMR studies on the bioMIL-3/4 MOF, which yielded spectra of low signal-to-noise ratios (S/Ns).\textsuperscript{20-21} $^{43}$Ca has unfavorable NMR properties: it is a quadrupolar nucleus ($I = 7/2$) with a relatively small quadrupole moment (Q) of -40.8 mb,\textsuperscript{22} a low gyromagnetic ratio ($\gamma = -1.8028 \times 10^7$ rad s$^{-1}$ T$^{-1}$) and an extremely low natural abundance of 0.135 %.\textsuperscript{23} The very low natural abundance of $^{43}$Ca is problematic in porous MOFs, which dilute the metal concentration. For comparison, there are 3.67x10$^{-3}$ $^{43}$Ca atoms/nm$^3$ in the CaSDB MOF, which is more than an order of magnitude less than the 4.86x10$^{-2}$ $^{43}$Ca atoms/nm$^3$ in
CaO. \(^{43}\)Ca enrichment is very expensive.\(^{18,24}\) The \(^{43}\)Ca isotropic chemical shift (\(\delta_{\text{iso}}\)) range is a narrow 40 ppm (ca. +20 ppm to -20 ppm) for calcium bound to organic ligands; in contrast, the \(\delta_{\text{iso}}(^{43}\text{Ca})\) range is ca. 300 ppm within inorganic Ca-based materials.\(^{18,25}\) These challenges raise the question: can \(^{43}\)Ca NMR spectra of MOFs be obtained with sufficient quality to provide direct information on Ca metal centers?

We have performed a natural abundance \(^{43}\)Ca magic-angle spinning (MAS) NMR study on four Ca based MOFs of varying composition and topology: CaBDC (H\(_2\)BDC = terephthalic acid),\(^{26}\) CaPDC\(^{27}\) (H\(_2\)PDC = 2,5-pyridinedicarboxylic acid), CaSDB,\(^{28}\) and CaBTC\(^{29}\) (H\(_3\)BTC = trimesic acid)]. The advent of high magnetic fields has resulted in sensitivity enhancements for low-\(\gamma\) unreceptive quadrupolar nuclei, including \(^{43}\)Ca.\(^{30-31}\) The quadrupolar interaction (QI) broadens \(^{43}\)Ca resonances and imparts a characteristic lineshape, however, broad resonances are difficult to detect due to their low S/N. In order to partially remove the QI, narrow resonances, and render \(^{43}\)Ca signals detectable, MAS techniques are employed. Due to the relatively small Q of \(^{43}\)Ca, MAS techniques typically remove a large degree of spectral features associated with the QI, with \(^{43}\)Ca MAS NMR spectra consisting of relatively symmetrical resonances. These MAS-narrowed resonances are easier to detect but the lack of a characteristic QI-dominated lineshape renders the extraction of an accurate quadrupolar coupling constant (C\(Q\)) and asymmetry parameter (\(\eta_Q\)) difficult.\(^{19,32}\) Accurate \(\delta_{\text{iso}}\) values can be obtained, but since the QI has been significantly reduced, only upper limit estimates of C\(Q\) are possible and \(\eta_Q\) values are often unclear. However, there is remarkable agreement between experimental and DFT-calculated C\(Q\) values (Table 7-1, Figures 7-A1 and 7-A2), hinting that the quadrupolar interaction is the primary source of resonance broadening. In this study, \(\delta_{\text{iso}}\) is chiefly relied upon to provide insight into the local environment about Ca sites in these MOFs, with C\(Q\) and \(\eta_Q\) values discussed where possible. We demonstrate that acquiring \(^{43}\)Ca spectra at a high magnetic field of 21.1 T and performing plane-wave density functional theory (DFT) calculations can probe the local structure about Ca metal centers in MOFs and detect the changes resulting from the Ca coordination environment during structural transformations and guest incorporation or removal.
7.2 Results and discussion

Structural changes in CaBDC and CaPDC

Figure 7-1 $^{43}$Ca MAS NMR spectra (solid lines) and simulations (broken red lines) of three CaBDC phases are shown in (a), (b) and (c), along with those of (d) CaPDC-H$_2$O and (e) CaPDC-DMF. The minor resonance in (e) marked by the dashed black circle originates from residual CaPDC-H$_2$O. Carbon is colored gray, oxygen is red, nitrogen is blue, hydrogen is cyan and calcium is green.

The structure of as-made CaBDC MOF (Figure 7-A3) is altered during heating, forming a nonporous phase termed “desolvated CaBDC” at 400 °C.$^{26}$ When desolvated CaBDC is exposed to water, it forms the hydrated phase “hydrated CaBDC.”$^{26}$ The phase changes between as-made, desolvated, and hydrated CaBDC have previously been studied using a
combination of XRD, X-ray adsorption spectroscopy, and $^1$H/$^{13}$C MAS NMR,\textsuperscript{26} however, the local environment about Ca during the structural changes remains uninvestigated. The coordination about Ca is shown in Figure 1 and the extended frameworks are depicted in Figure 7-A3. As-made CaBDC features edge-sharing CaO$_8$ polyhedra, with six oxygens from BDC linker groups and the other two oxygen atoms from water and DMF (Figure 7-1a). Ca loses the coordinated water and DMF molecules after desolvation, yielding six-coordinate CaO$_6$ with all oxygen atoms originating from linkers (Figure 7-1b). Hydrated CaBDC contains eight-coordinate CaO$_8$ (Figure 7-1c), with four oxygen atoms from water molecules and four oxygen atoms from three BDC linkers.

Table 7-1 Experimental and calculated $^{43}$Ca MAS NMR parameters for calcium based MOFs.

<table>
<thead>
<tr>
<th>Ca MOF</th>
<th>$^{43}$Ca MAS NMR parameters</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$</td>
<td>C_Q</td>
<td>$ (MHz)</td>
<td>$\delta_{iso}$ (ppm)</td>
<td>$\eta_Q$</td>
</tr>
<tr>
<td>As made CaBDC</td>
<td>1.40 (5)$^a$</td>
<td>-4.2 (1)</td>
<td>N/A</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>Calculated</td>
<td>1.57</td>
<td>N/A</td>
<td>0.42</td>
<td>1132.2</td>
<td></td>
</tr>
<tr>
<td>Desolvated CaBDC</td>
<td>2.30 (5)$^a$</td>
<td>-5.9 (3)</td>
<td>N/A</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>Calculated</td>
<td>2.00</td>
<td>N/A</td>
<td>0.56</td>
<td>1137.9</td>
<td></td>
</tr>
<tr>
<td>Hydrated CaBDC</td>
<td>1.10 (4)$^a$</td>
<td>-2.5 (0.8)</td>
<td>N/A</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>Calculated</td>
<td>0.90</td>
<td>N/A</td>
<td>0.48</td>
<td>1129.2</td>
<td></td>
</tr>
<tr>
<td>CaPDC-H$_2$O</td>
<td>1.25 (5)$^a$</td>
<td>-4.3 (3)</td>
<td>N/A</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>Calculated</td>
<td>1.16</td>
<td>N/A</td>
<td>0.82</td>
<td>1134.3</td>
<td></td>
</tr>
<tr>
<td>CaPDC-DMF</td>
<td>1.30 (6)$^a$</td>
<td>-11.9 (2)</td>
<td>N/A</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>Calculated</td>
<td>1.58</td>
<td>N/A</td>
<td>0.24</td>
<td>1136.8</td>
<td></td>
</tr>
<tr>
<td>As made CaSDB</td>
<td>3.10 (10)</td>
<td>-12.9 (5)</td>
<td>0.90 (3)</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>Calculated</td>
<td>3.29</td>
<td>N/A</td>
<td>0.89</td>
<td>1140.1</td>
<td></td>
</tr>
<tr>
<td>Activated CaSDB</td>
<td>3.18 (14)</td>
<td>-12.3 (9)</td>
<td>0.90 (7)</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>Calculated</td>
<td>2.75</td>
<td>N/A</td>
<td>0.88</td>
<td>1138.0</td>
<td></td>
</tr>
<tr>
<td>As made CaBTC</td>
<td>1.50 (6)$^a$</td>
<td>-1.7 (2)</td>
<td>N/A</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>Calculated</td>
<td>1.61</td>
<td>N/A</td>
<td>0.31</td>
<td>1125.4</td>
<td></td>
</tr>
<tr>
<td>Activated CaBTC</td>
<td>1.20 (7)$^a$</td>
<td>-4.9 (1)</td>
<td>N/A</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>Calculated</td>
<td>1.06</td>
<td>N/A</td>
<td>0.35</td>
<td>1130.5</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Experimental $C_Q$ values are an upper limit estimate, since the breadth of the sharp and featureless resonances arises mainly from the quadrupolar interaction ($i.e., C_Q$).

Each $^{43}$Ca MAS NMR spectrum of the three CaBDC phases features a single $^{43}$Ca resonance, in good agreement with the sole Ca site in the corresponding crystal structures.\textsuperscript{26} The structural change from eight-coordinate as-made CaBDC to six-coordinate desolvated CaBDC causes a decrease in $\delta_{iso}$ from -4.2(1) ppm to -5.9(3) ppm (Table 7-1). Ca transitions back to eight-coordinate in hydrated CaBDC (Figure 7-1c), leading to a +3.4
ppm increase in $\delta_{\text{iso}}$. Plane-wave DFT calculations of chemical shielding ($\sigma_{\text{iso}}$) values (Table 7-1) accurately model the observed changes in $\delta_{\text{iso}}$ (Table 7-2). The experimentally observed $\delta_{\text{iso}}$ and the DFT-calculated $\sigma_{\text{iso}}$ move in opposite directions (i.e., a more negative $\delta_{\text{iso}}$ corresponds to a more positive $\sigma_{\text{iso}}$, and vice versa, see Table 7-A1). Calculations of $\sigma_{\text{iso}}$ indicate that $\delta_{\text{iso}}$(desolvated) should be 5.75 ppm less than $\delta_{\text{iso}}$(as made), in agreement with the observed decrease of 1.7 ppm. Calculations also successfully predict that $\delta_{\text{iso}}$(hydrated) is greater than $\delta_{\text{iso}}$(desolvated) and $\delta_{\text{iso}}$(as made), although the difference between $\delta_{\text{iso}}$(hydrated) and $\delta_{\text{iso}}$(desolvated) is slightly overestimated (Table 7-2). These are small changes in $\delta_{\text{iso}}$, yet are still modeled accurately by calculations.

**Table 7-2** The experimentally observed and calculated differences in $\delta_{\text{iso}}$(

<table>
<thead>
<tr>
<th>Ca MOF (form A – form B)</th>
<th>$\delta_2$-$\delta_1$ (ppm)</th>
<th>Experimental</th>
<th>Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaBDC (desolvated – as made)</td>
<td>-1.7</td>
<td>-5.75</td>
<td></td>
</tr>
<tr>
<td>CaBDC (hydrated – desolvated)</td>
<td>+3.4</td>
<td>+8.77</td>
<td></td>
</tr>
<tr>
<td>CaBDC (hydrated – as made)</td>
<td>+1.7</td>
<td>+3.02</td>
<td></td>
</tr>
<tr>
<td>CaPDC (DMF – H$_2$O)</td>
<td>-7.6</td>
<td>-2.48</td>
<td></td>
</tr>
<tr>
<td>CaSDB (activated – as made)</td>
<td>+0.6</td>
<td>+2.15</td>
<td></td>
</tr>
<tr>
<td>CaBTC (activated – as made)</td>
<td>-3.2</td>
<td>-5.17</td>
<td></td>
</tr>
</tbody>
</table>

[a] Calculated $\sigma_{\text{iso}}$ differences have been converted to calculated $\delta_{\text{iso}}$ differences. See Table 7-A1 for calculated changes in $\sigma_{\text{iso}}$.

There are different $C_Q$ values for each CaBDC phase, which are strongly supported by calculations. $C_Q$(

There are different $C_Q$ values for each CaBDC phase, which are strongly supported by calculations. $C_Q$(

The CaPDC MOF also exhibits a solvent-related phase change. There is one seven-coordinate Ca site in as-made CaPDC (denoted CaPDC-H$_2$O), which is bound to five oxygen atoms from PDC linkers, one linker nitrogen atom, and one water oxygen atom. After immersing CaPDC-H$_2$O in DMF for 48 h, the coordinated water is replaced by one
O-bound DMF ligand, yielding CaPDC-DMF. In this new phase, the single unique Ca metal center is eight-coordinate, bound to six oxygen atoms from PDC linkers, one linker nitrogen atom, and one DMF oxygen atom. The structures of CaPDC-H$_2$O and CaPDC-DMF are shown in Figure 7-1 and Figure 7-A5, respectively.

The transition from seven-coordinate CaPDC-H$_2$O to eight-coordinate CaPDC-DMF decreases $\delta_{\text{iso}}$ of the single $^{43}$Ca resonance by 7.6 ppm (Figures 7-1d, 1e). This contrasts with the trend in CaBDC, where a higher Ca coordination number results in a more positive $\delta_{\text{iso}}$. These opposing trends are less surprising in light of a recent review that indicated there is no straightforward relationship between Ca coordination number and $\delta_{\text{iso}}$, particularly when different ligands are present. Calculated $\sigma_{\text{iso}}$ values correctly indicate that $\delta_{\text{iso}}$ of CaPDC-DMF is lower than that of CaPDC-H$_2$O (Table 7-2), but underestimate the difference by ca. 5 ppm. The change in Ca coordination has a negligible impact on linewidth and $C_Q(^{43}\text{Ca})$ in CaPDC-H$_2$O versus CaPDC-DMF, unlike the significant $C_Q$ changes in CaBDC. DFT calculations on the two CaPDC phases produce $C_Q$ values that match well with experiments (Table 7-1). There is a small additional $^{43}$Ca resonance in the CaPDC-DMF spectrum (Figure 7-1e) which originates from CaPDC-H$_2$O remaining after solvent exchange, which was verified by PXRD (Figure 7-A6).

**Structural changes in CaSDB and CaBTC**

CaSDB is a stable microporous Ca MOF with zig-zag channels oriented along the $b$ axis (Figure 7-A7a). In as-made CaSDB, octahedral CaO$_6$ coordination units are bound solely to SDB linkers (Figure 7-2a). Activated CaSDB (Figure 7-A7b) features edge-sharing CaO$_6$ octahedra, with Ca bound to SDB linkers that were repacked after activation (Figure 7-2b). The $^{43}$Ca MAS NMR spectra of as-made and activated CaSDB (Figure 7-2a,b) are of relatively lower S/N due to the breadth of the signals. A single $^{43}$Ca resonance exists in as-made CaSDB at $\delta_{\text{iso}} = -12.9(5)$ ppm (Table 7-1), in agreement with the crystal structure. Unlike the featureless $^{43}$Ca resonances of CaBDC and CaPDC, as-made CaSDB gives rise to a $^{43}$Ca resonance with quadrupolar features, yielding a $C_Q$ value of 3.10(10) MHz and $\eta_Q$ value of 0.90(3). Activated CaSDB yields similar parameters, with a resonance at $\delta_{\text{iso}} = -12.3(9)$ ppm that corresponds to a $C_Q(^{43}\text{Ca})$ of 3.18(14) MHz and a $\eta_Q$
value of 0.90(7). The similarity in all three NMR parameters indicates that the local Ca environment is essentially preserved from as-made to activated CaSDB. Plane-wave DFT calculations of NMR parameters in CaSDB are in reasonable agreement with experimentally observed values. Calculations correctly predict that activated CaSDB is more chemically shifted than as-made CaSDB, with the predicted shift of 2.15 ppm slightly overestimating the experimental difference of 0.6 ppm (Table 7-2). Calculated $C_Q^{(43\text{Ca})}$ values for as-made and activated CaSDB are both near the relatively large experimental values, inferring that structural distortion of CaO$_6$ octahedra is responsible. The calculated $\eta_Q$ values of 0.89 for as-made CaSDB and 0.88 for activated CaSDB match the experimental values well (Table 7-1).

Figure 7-2 The experimental (solid lines) and simulated (red broken lines) $^{43}\text{Ca}$ MAS NMR spectra of (a) as made CaSDB, (b) activated CaSDB, (c) as made CaBTC and (d) activated CaBTC. On the right side is an illustration of the Ca local environment.

CaBTC is another stable porous Ca MOF. As-made CaBTC, contains a single eight-
coordinate Ca metal center bound to seven BTC oxygen atoms and one water oxygen (Figure 7-2b/c, Figure 7-A9). There is also a non-coordinated lattice water molecule present. In accordance with the crystal structure, only one resonance was observed in the as-made CaBTC $^{43}$Ca MAS NMR spectrum. The lattice water can be removed via activation, yielding activated CaBTC (Figure 7-A10), which remains eight-coordinate and bound to a single water molecule. The low-angle PXRD reflections of as-made and activated CaBTC are nearly identical (Figure 7-A11), but there are slight differences among high-angle reflections, indicating that their crystal structures are slightly dissimilar. In agreement, their $^{43}$Ca NMR parameters diverge. $\delta_{\text{iso}}$ decreases 3.2 ppm from -1.7(2) ppm in as-made CaBTC to -4.9(1) ppm in activated CaBTC. In good agreement, the calculated decrease in $\delta_{\text{iso}}$ is -5.2 ppm (Table 7-2). $C_Q^{(43}\text{Ca})$ changes from 1.50(6) MHz in as-made CaBTC to 1.20(7) MHz after activation, with calculations accurately predicting both values.

To the best of our knowledge, gas adsorption in CaBTC has not been explored. Accordingly, we performed CO$_2$ and N$_2$ adsorption tests (Figure 7-A12). After the removal of lattice water, activated CaBTC does not adsorb significant amounts of N$_2$, but shows a high affinity for CO$_2$; this MOF exhibits highly selective adsorption of CO$_2$ over N$_2$. Considering the green and cheap nature of Ca metal and Ca-containing precursors, along with the low cost of the H$_3$BTC linker, activated CaBTC is a very promising material for gas separation. The gas adsorption properties of CaBTC are currently being studied in our lab and will be described elsewhere in the future.

Despite the fact that only lattice water has been removed in activated CaBTC and there is no change in coordination, the relatively large difference in $\delta_{\text{iso}}$ of CaBTC and the large magnitude of changes in $C_Q$ between as-made and activated CaBTC were observed. It appears that $^{43}$Ca MAS NMR is very sensitive not only to the changes in the Ca coordination sphere, but also to the presence of guest species in the pore not directly bound to the Ca.

### 7.3 Conclusion

In summary, natural abundance $^{43}$Ca MAS NMR has been employed to examine low metal density MOFs at a high magnetic field of 21.1 T. $^{43}$Ca $\delta_{\text{iso}}$ and $C_Q$ values are highly
dependent on local structure and differences within the Ca coordination sphere. The presence of guests in the local Ca environment can also be detected by $^{43}\text{Ca}$ NMR. Calcium typically has a high coordination number and Ca centers in MOFs are usually found coordinated to at least one solvent molecule; this work shows that $^{43}\text{Ca}$ NMR is an effective tool for monitoring local environment changes in favourable cases. All $\delta_{\text{iso}}$ values of Ca MOFs lie within the range associated with Ca-organic compounds, which is logical given the common Ca-O and Ca-N binding motifs. DFT calculations of $^{43}\text{Ca}$ NMR parameters in MOFs strongly agree with experimental data, and can predict the direction of change in $\delta_{\text{iso}}$ after guest solvent removal/exchange and between different MOF phases. This work demonstrates that $^{43}\text{Ca}$ MAS NMR and DFT calculations can be used to investigate Ca MOFs and that natural abundance solid-state NMR studies are feasible to perform on other challenging metal nuclei in low density MOF systems. It is hoped that this work will inspire the community to explore the local structure of calcium in many other MOFs.

7.4 References


### 7.5 Appendix

**Section A1: Experimental details**

**CaBDC**

As made CaBDC was prepared following the previously reported procedure with some
modifications. One reagent solution was made by dissolving 0.260 g of Ca(NO$_3$)$_2$·6H$_2$O in 2.0 mL of deionized (DI) water, while a second reagent solution was prepared by adding 0.180 g of benzenedicarboxylate (BDC) linker to a mixture of 8.0 mL N,N’-dimethylformamide (DMF) and 0.25 mL triethylamine (TEA). The two reagent solutions were then mixed together and magnetically stirred for 5 min, after which the resulting reagent mixture was placed in a Teflon chamber within a Teflon-lined stainless steel autoclave. The autoclave was then sealed and heated at 125 °C in an oven for 3 days. After removing the autoclave from heat and letting it cool to room temperature, the product was obtained as a crystalline white powder, which was isolated by vacuum filtration and washed with DMF three times.

**Desolvated CaBDC** was obtained by thermal treatment of as made CaBDC. A sample of as made CaBDC was placed into a glass vial, put into an oven and heated at 400 °C for 6 h. After thermal treatment, the obtained desolvated CaBDC product was brown.

**Hydrated CaBDC** was obtained by immersing a sample of desolvated CaBDC in DI water for two weeks. Hydrated CaBDC was obtained as white crystalline powder after vacuum filtration.

**CaPDC**

**CaPDC-H$_2$O** (named [Ca(2,5-PDC)(H$_2$O)]$_n$ in the first instance it was reported) was prepared following literature procedures with some modifications. To begin, 0.1670 g of 2,5-pyridinedicarboxylic acid and 0.1110 g of CaCl$_2$ were dissolved in a solution consisting of 3.6 g DMF and 1.9 g of H$_2$O. The resulting mixture was magnetically stirred for 10 min and then placed in a Teflon chamber within a Teflon-lined stainless steel autoclave, which was sealed and heated in an oven at 180 °C for 3 days. The product was obtained as colorless needle-shaped crystals after vacuum filtration, and was washed three times with ethanol.

**CaPDC-DMF** (termed [Ca(2,5-PDC)(DMF)]$_n$ in the first instance it was reported) was obtained by immersing 0.50 g of CaPDC-H$_2$O in 20.0 mL of DMF for two days, after which colorless needle-shaped crystals of CaPDC-DMF were obtained by vacuum filtration.
CaSDB

As made CaSDB was prepared according to the previously reported procedure with some modifications.² 0.198 g of 4,4-sulfonyldibenzoic acid and 0.074 g of CaCl₂ were dissolved in 10.0 mL of 95 % (v/v) ethanol. The resulting mixture was magnetically stirred for 10 minutes and then placed in a Teflon chamber within a Teflon-lined stainless steel autoclave, which was sealed and heated in a 180 °C oven for 3 days. The product was obtained via vacuum filtration as colorless needle-shaped crystals and was washed with ethanol three times.

Activated CaSDB was obtained by heating as made CaSDB at 180 °C for 8 hours under dynamic vacuum (≤ 1 mbar) to evacuate all guest molecules.

CaBTC

As made CaBTC was prepared using a modified version of the reported procedure.³ 0.0420 g of trimesic acid and 0.0316 g of Ca(OAc)₂ were dissolved in a mixture of 3.0 mL DI H₂O and 1.0 mL 95 % (v/v) ethanol. The resulting mixture was stirred for 10 min and then transferred to a 25 mL glass vial, which was sealed and heated in a 90 °C oven for 24 h. After vacuum filtration, the product was obtained as colorless needle-shaped crystals and was washed with ethanol three times.

Activated CaBTC was obtained by heating as made CaBTC at 125 °C for 8 h under dynamic vacuum (≤ 1 mbar).

NMR measurements

All NMR experiments were acquired at a magnetic field of 21.1 T using a Bruker Avance II NMR spectrometer located at the National Ultrahigh-Field NMR Facility for Solids (Ottawa, ON, Canada). A 7 mm single-channel Bruker MAS probe was used to acquire ⁴³Ca MAS spectra \( \nu_0(⁴³Ca) = 60.5 \text{ MHz} \) at a spinning rate of 5 kHz. All ⁴³Ca chemical shifts were referenced to a solution of 2.0 M CaCl₂/H₂O (δiso = 0.0 ppm). All activated or desolvated Ca MOF samples were packed into NMR rotors under an argon atmosphere in
a glove box. The spectra were acquired using a one-pulse sequence with a ca. 45° pulse length of 1.0 μs and a recycle delay of 2 s that was found sufficient for complete relaxation. The spectral width was 20 kHz and the number of scans for each spectrum were 12 000 for as made CaBDC, 72 000 for desolvated CaBDC, 32 000 for hydrated CaBDC, 36 000 for CaPDC-H₂O, 36 000 for CaPDC-DMF, 66 000 for as made CaSDB, 66 000 for activated CaSDB, 36 000 for as made CaBTC, and 36 000 for activated CaBTC, which required 6.5 to 40 hours of experimental time per spectrum.

**Details of theoretical calculations**

All calculations were performed using the CASTEP software package⁶ in the Materials Studio 4.4 environment. The unit cell parameters and atomic coordinates were obtained from the reported structures of the corresponding Ca MOFs.¹⁻⁴ CASTEP, which uses the gauge-including projector-augmented wave (GIPAW) method, pseudopotentials, and plane-wave basis sets, was employed to calculate the $^{43}$Ca CS and EFG NMR parameters.⁶⁻⁷ These calculations also employed the generalized gradient approximation (GGA) along with the Perdew–Burke–Ernzerhof (PBE) functional.⁸ In all instances, a plane-wave cut off energy of 500 eV was used.

**Experimental details for all other instrumentation**

**Powder XRD (PXRD).** The PXRD patterns of the CaBDC, CaPDC and CaSDB MOFs were recorded using a high resolution Rigaku powder X-ray diffractometer operating using Co Kα radiation ($\lambda = 1.7902$ Å). Reflections were collected at 20 values between 5 and 45°. For the CaBTC MOF, the PXRD were performed on an Inel CPS powder diffractometer operating with Cu Kα radiation ($\lambda = 1.5406$ Å). Reflections were collected at 20 values ranging from 5 to 45°.

**Gas adsorption.** The CO₂ adsorption isotherm of CaBTC was measured using a Micromeritics ASAP 2020 porosity analyzer at a temperature of 273 K. The sample was first degassed under vacuum at 125 °C for 8 h.

**Thermogravimetric analysis (TGA).** TGA of CaBTC was measured on a TA Instruments Q50 thermogravimetric instrument under N₂ flow (40 mL·min⁻¹) and heated from 40 to
550 °C at a rate of 10 °C·min⁻¹.

**Table 7-A1.** The experimentally observed changes in \(^{43}\text{Ca}\) isotropic chemical shift, along with the calculated differences in isotropic chemical shielding, between two different forms of each Ca MOF.

<table>
<thead>
<tr>
<th>Ca MOF (form A – form B)</th>
<th>(\delta_2-\delta_1) (ppm) (Experimental)</th>
<th>(\sigma_2-\sigma_1) (ppm) (Calculated)</th>
<th>(\delta_2-\delta_1) (ppm) (Calculated)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaBDC (desolvated – as made)</td>
<td>-1.7</td>
<td>+5.75</td>
<td>-5.75</td>
</tr>
<tr>
<td>CaBDC (hydrated – desolvated)</td>
<td>+3.4</td>
<td>-8.77</td>
<td>+8.77</td>
</tr>
<tr>
<td>CaBDC (hydrated – as made)</td>
<td>+1.7</td>
<td>-3.02</td>
<td>+3.02</td>
</tr>
<tr>
<td>CaPDC (DMF – H₂O)</td>
<td>-7.6</td>
<td>+2.48</td>
<td>-2.48</td>
</tr>
<tr>
<td>CaSDB (activated – as made)</td>
<td>+0.6</td>
<td>-2.15</td>
<td>+2.15</td>
</tr>
<tr>
<td>CaBTC (activated – as made)</td>
<td>-3.2</td>
<td>+5.17</td>
<td>-5.17</td>
</tr>
</tbody>
</table>

*Note that the changes in experimental chemical shift are opposite in sign from the changes in calculated chemical shielding.*
Figure 7-A1 Experimental (blue lines) $^{43}$Ca MAS NMR spectra at 21.1 T are shown, along with simulations (red broken lines) based on plane wave DFT calculations. The simulations were constructed using calculated $^{43}$Ca $\zeta_Q$ and $\eta_Q$ values along with the experimentally determined $\delta_{iso}$ values. Note the striking similarity in resonance widths between experimental and DFT-calculated spectra, suggesting that despite the lack of lineshape features or details, the main source of experimental resonance broadening is the $^{43}$Ca quadrupolar interaction.
Figure 7-A2 Experimental $^{43}$Ca MAS NMR spectra at 21.1 T are shown (blue lines) along with simulations (red broken lines) based on plane wave DFT calculations. The simulations were constructed using calculated $^{43}$Ca $C_Q$ and $\eta_Q$ values with experimentally determined $\delta_{iso}$ values. As stated in the caption of Figure 7-A1, note the striking similarity in resonance widths between experimental and DFT-calculated spectra, suggesting that despite the lack of lineshape features, the main source of experimental resonance broadening is the $^{43}$Ca quadrupolar interaction. The case of CaSDB is especially illustrative of this point.
Figure 7-A3 (a) The extended lattice of the as made CaBDC crystal structure; (b) the extended lattice of the desolvated CaBDC crystal structure; and (c) the extended lattice of the hydrated CaBDC crystal structure. In this diagram, carbon is colored gray, oxygen is red, nitrogen is blue, hydrogen is cyan and calcium is green.
Figure 7-A4 The simulated (i.e., calculated from the known crystal structure) and experimental PXRD patterns of the three phases of CaBDC.
Figure 7-A5 (a) The extended lattice of the CaPDC-H$_2$O crystal structure is shown, along with (b) the extended lattice of the CaPDC-DMF crystal structure. In this diagram, carbon is colored gray, oxygen is red, nitrogen is blue, hydrogen is cyan and calcium is green.
Figure 7-A6 The simulated (i.e., calculated) and experimental PXRD patterns of CaPDC-H$_2$O and CaPDC-DMF. The PXRD pattern of CaPDC-DMF features reflections not included in the calculated pattern, indicating that a small amount of residual CaPDC-H$_2$O did not convert to CaPDC-DMF after solvent exchange.
Figure 7-A7 (a) The extended lattice of the as made CaSDB crystal structure is shown, along with (b) the extended lattice of the activated CaSDB crystal structure. In this diagram, carbon is colored gray, oxygen is red, hydrogen is cyan, sulfur is yellow and calcium is green.
Figure 7-A8 The simulated and experimental PXRD patterns of as made and activated CaSDB.
Figure 7-A9 (a) The extended lattice of the as made CaBTC crystal structure is illustrated, along with (b) the local coordination environment of Ca in CaBTC. In this diagram, carbon is colored gray, oxygen is red, hydrogen is cyan and calcium is green.
Figure 7-A10 The TGA graph of as made CaBTC. The weight loss of approximately 10% between 40 and 125 °C is due to the removal of lattice water.

Figure 7-A11 The simulated and experimental PXRD patterns of as made and activated CaBTC.
Figure 7-A12 The measured CO$_2$ adsorption isotherm in activated CaBTC at 273 K and 1 atm. The quantity of adsorbed CO$_2$ was found to be 60.3 cm$^3$/g, and no significant adsorption of N$_2$ was observed at 77 K and 1 bar.

References


Chapter 8

8 Summary and Future Work

8.1 Summary

A brief summary of previous chapters is discussed in this chapter, and some directions for future work are also described.

In chapter 2, the CO$_2$ adsorption and dynamics in two SDB-based MOFs (PbSDB and CdSDB) have been investigated by a combination of solid state NMR (SSNMR) spectroscopy and single crystal X-ray diffraction (SCXRD). Multinuclear VT SSNMR experiments provide abundant information regarding the CO$_2$ adsorption in the two MOFs, including number of adsorption sites, dynamic motion of CO$_2$ at different temperatures and the gas-MOF interaction. For CO$_2$ adsorption, a combination of a localized motion and a nonlocalized hopping is found in both MOFs. The subsequent SCXRD experiments supported the SSNMR findings and revealed the exact locations of CO$_2$ adsorption sites and their occupancies. In addition, the formation of a second CO$_2$ adsorption site in CdSDB has been clearly elucidated by SSNMR spectroscopy and SCXRD. This work shows that a combination of SSNMR spectroscopy and SCXRD can be a powerful tool to investigate the gas adsorption mechanism in MOFs.

In chapter 3, a combination of SCXRD, SSNMR, and computational methods have been employed to investigate CO$_2$, C$_2$H$_2$ and CH$_4$ adsorption within the amide-functionalized Cu(INAIP) MOF. Amide functional groups are often used to enhance the affinity of MOFs towards small gas molecules. Unfortunately, the guest binding sites and corresponding adsorption mechanisms remain unclear in amide-functionalized MOFs. In this work, SCXRD was used to reveal the exact gas adsorption sites and VT SSNMR spectroscopy was employed to probe the dynamic behavior of adsorbed gases at various temperatures. In addition, computational methods provide detailed information about the host-gas interactions, which cannot be obtained by direct experimental measurement. We unambiguously show that the carbonyl group of the amide group is the guest adsorption site, rather than the amine portion.
In chapter 4, fourteen metal ions (Li$^+$, Na$^+$, K$^+$, Mg$^{2+}$, Ca$^{2+}$, Ba$^{2+}$, Zn$^{2+}$, Co$^{2+}$, Mn$^{2+}$, Ag$^+$, Cd$^{2+}$, La$^{3+}$, In$^{3+}$, and Pb$^{2+}$) have been successfully introduced within the MIL-121 MOF using a cost-efficient route involving free carboxylic groups on the linker. The local and long-range structure of the metal-loaded MOFs is characterized using multinuclear SSNMR and X-ray methods. Li/Mg/Ca-loaded MIL-121 and Ag nanoparticle-loaded MIL-121 exhibited enhanced H$_2$ and CO$_2$ adsorption. Ag nanoparticle-loaded MIL-121 also demonstrated remarkable catalytic activity in the reduction of 4-nitrophenol. Our work shows that the free carboxylic acid groups on MOF linkers are an ideal anchor site for loading guest metal ions, and this route also provides a facile route for constructing single-site catalysts in porous materials.

In chapter 5, we report a thermally triggered porosity transition in microporous MIL-121. By carefully controlling linker thermolysis at different temperatures, hierarchical pores can be created in MIL-121 (termed as HMIL-121), resulting in a dramatically increased BET surface area, enlarged average pore size and enhanced CO$_2$ adsorption capability. The formation of hierarchical pores has been investigated by a combination of gas adsorption test, SEM and multinuclear SSNMR spectroscopy. Based on the results of those experiments, several key steps in the porosity transition were discussed. In addition, static VT $^{13}$C SSNMR experiments on $^{13}$CO$_2$ loaded MIL-121 and HMIL-121 yielded some direct information about CO$_2$ adsorption behavior in those samples, which is important for optimizing CO$_2$ adsorption in this MOF.

In chapter 6, we find that the HMIL-121 can be functionalized by forming anhydride groups on the pore walls. The reactive anhydride groups can be used as an ideal “anchor” site for further post-synthetic modification (i.e. drafting various functional groups) while the hierarchical structure in HMIL-121 permits the incorporation of large molecules. Our results show that the anhydride functionalized HMIL-121 exhibits high reactivity towards covalently grafting with various organic molecules including methanol, ethanol, aniline, p-toluidine and 1,2-ethanedithiol. In addition, noble metal Pt complexes were also successfully introduced into HMIL-121 and the Pt doped HMIL-121 was used to fabricate an electrocatalyst, which showed high ORR activity.
In chapter 7, natural abundance $^{43}$Ca SSNMR spectroscopy at a high magnetic field of 21.1 T has been employed to characterize several calcium-based MOFs. Understanding the local environment of calcium in these materials is critical for unraveling the origins of specific MOF properties. $^{43}$Ca SSNMR spectroscopy is one of the very few techniques that can directly characterize calcium metal centers, however, the $^{43}$Ca nucleus is a very challenging target for SSNMR spectroscopy due to its extremely low natural abundance and resonant frequency. We demonstrate that $^{43}$Ca NMR and quantum chemical calculations can probe the local structure of calcium metal centers within MOFs, investigate the effect of guest molecules on MOF structure, and monitor phase changes.

8.2 Future work

Chapter 2 and 3 demonstrate that a combination of SCXRD and SSNMR spectroscopy is a powerful tool to investigate gas adsorption mechanism in MOFs. We hope this combination of characterization techniques can be extended to study the structural changes in MOFs. Currently, we have found that a porous Zn based MOF is unstable in water, which degenerates into a nonporous phase. Many MOFs, especially those based on divalent metals such as Zn$^{2+}$, are unstable towards humidity and/or liquid water, which severely restricts their applications in research fields such as drug delivery or gas adsorption. We are going to use SCXRD and SSNMR spectroscopy to characterize this water-induced structure change, which can shed light on the mechanism of MOF degeneration.

Our work in chapter 4, 5 and 6 show that the free carboxylic acid group in MIL-121 have many promising applications. Constructing MOFs functionalized with free carboxylic acid will be our next step. We have tried to use 1,2,4-Benzene-1,2,4-tricarboxylic acid (1,2,4-BTC) to replace the 1,2,4,5-Benzene-1,2,4,5-tetracarboxylic acid (BTEC) in MIL-121, and a 1,2,4-BTC based Al MOF has been harvested with high crystallinity. This new MOF has a very similar PXRD pattern to MIL-121, suggesting its structure is analogue to MIL-121 and probably also featuring a free carboxylic acid. A single crystal of this MOF has been cultivated and its crystal structure will be solved soon.

In chapter 7, we mentioned that one of the MOF, CaBTC, has a great potential in selective gas adsorption. We are now working with Professor Mike Zaworotko’s group from
University of Limerick to test the adsorption of CO$_2$ over other small gas molecules on CaBTC. So far, CaBTC exhibits super high selectivity in adsorption of CO$_2$ over N$_2$ and CH$_4$. A more detailed study including breakthrough experiments and theoretical calculation is on the way.
Appendices: Copyright Permission

PERMISSION/LICENSE IS GRANTED FOR YOUR ORDER AT NO CHARGE

This type of permission/license, instead of the standard Terms & Conditions, is sent to you because no fee is being charged for your order. Please note the following:

- Permission is granted for your request in both print and electronic formats, and translations.
- If figures and/or tables were requested, they may be adapted or used in part.
- Please print this page for your records and send a copy of it to your publisher/graduate school.
- Appropriate credit for the requested material should be given as follows: "Reprinted (adapted) with permission from (COMPLETE REFERENCE CITATION). Copyright (YEAR) American Chemical Society." Insert appropriate information in place of the capitalized words.
- One-time permission is granted only for the use specified in your request. No additional uses are granted (such as derivative works or other editions). For any other uses, please submit a new request.
PERMISSION/LICENSE IS GRANTED FOR YOUR ORDER AT NO CHARGE

This type of permission/license, instead of the standard Terms & Conditions, is sent to you because no fee is being charged for your order. Please note the following:

- Permission is granted for your request in both print and electronic formats, and translations.
- If figures and/or tables were requested, they may be adapted or used in part.
- Please print this page for your records and send a copy of it to your publisher/graduate school.
- Appropriate credit for the requested material should be given as follows: "Reprinted (adapted) with permission from (COMPLETE REFERENCE CITATION). Copyright (YEAR) American Chemical Society." Insert appropriate information in place of the capitalized words.
- One-time permission is granted only for the use specified in your request. No additional uses are granted (such as derivative works or other editions). For any other uses, please submit a new request.

If credit is given to another source for the material you requested, permission must be obtained from that source.
PERMISSION/LICENSE IS GRANTED FOR YOUR ORDER AT NO CHARGE

This type of permission/license, instead of the standard Terms & Conditions, is sent to you because no fee is being charged for your order. Please note the following:

- Permission is granted for your request in both print and electronic formats, and translations.
- If figures and/or tables were requested, they may be adapted or used in part.
- Please print this page for your records and send a copy of it to your publisher/graduate school.
- Appropriate credit for the requested material should be given as follows: "Reprinted (adapted) with permission from (COMPLETE REFERENCE CITATION). Copyright (YEAR) American Chemical Society." Insert appropriate information in place of the capitalized words.
- One-time permission is granted only for the use specified in your request. No additional uses are granted (such as derivative works or other editions). For any other uses, please submit a new request.
Order Completed
Thank you for your order.

This Agreement between Mr. Shoushun Chen ("You") and John Wiley and Sons ("John Wiley and Sons") consists of your license details and the terms and conditions provided by John Wiley and Sons and Copyright Clearance Center.

Your confirmation email will contain your order number for future reference.

License Details:
- License Number: 4413701246633
- License date: Aug 21, 2018
- Licensed Content Publisher: John Wiley and Sons
- Licensed Content Publication: Chemistry - A European Journal
- Licensed Content Title: Probing Calcium-Based Metal-Organic Frameworks via Natural Abundance 43Ca Solid-State NMR Spectroscopy
- Licensed Content Author: Shoushun Chen, Bryan E.G. Lucier, Mansheng Chen, et al
- Licensed Content Date: Jun 8, 2018
- Licensed Content Volume: 24
- Licensed Content Issue: 35
- Licensed Content Pages: 5
- Type of use: Dissertation/Thesis
- Requestor type: Author of this Wiley article
- Format: Print and electronic
- Portion: Full article
- Will you be translating?: No
- Title of your thesis / dissertation: Investigating gas adsorption mechanisms, post-synthetic modification and molecular-level structure in MOFs

Expected completion date: Aug 2018
Expected size (number of pages): 260
Requestor Location: Mr. Shoushun Chen

Publisher Tax ID: EUR25007151
Total: 0.00 CAD

Would you like to purchase the full text of this article? If so, please continue on to the content ordering system located here: Purchase PDF

If you click on the buttons below or close this window, you will not be able to return to the content ordering system.
Curriculum Vitae

Name: Shoushun Chen

Post-secondary Education and Degrees:

<table>
<thead>
<tr>
<th>Institution</th>
<th>Year</th>
<th>Degree</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liaoning University</td>
<td>2006-2010</td>
<td>B.E.</td>
</tr>
<tr>
<td>Shenyang, Liaoning, China</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Xiamen University</td>
<td>2010-2013</td>
<td>M.S.</td>
</tr>
<tr>
<td>Xiamen, Fujian, China</td>
<td></td>
<td></td>
</tr>
<tr>
<td>The University of Western Ontario</td>
<td>2013-2018</td>
<td>Ph.D.</td>
</tr>
</tbody>
</table>

Honours and Awards:

<table>
<thead>
<tr>
<th>Award</th>
<th>Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Western Graduate Research Scholarship (UWO)</td>
<td>2013-2018</td>
</tr>
<tr>
<td>International Graduate Student Scholarship (UWO)</td>
<td>2013-2018</td>
</tr>
</tbody>
</table>

Related Work Experience

<table>
<thead>
<tr>
<th>Role</th>
<th>Institution</th>
<th>Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Teaching Assistant</td>
<td>The University of Western Ontario</td>
<td>2013-2018</td>
</tr>
<tr>
<td>Research Assistant</td>
<td>The University of Western Ontario</td>
<td>2013-2018</td>
</tr>
</tbody>
</table>

Publications:


**Presentations:**


3. (Poster) “Doping across the Periodic Table: Loading Metals within MIL-121” 100th Canadian Chemistry Conference and Exhibition, Toronto, ON, Canada, May 28th-June 1st, 2017.


5. (Poster) “Doping Metals Within the MIL-121 MOF via a Greener, One-step Route” Nanoporous Materials-8, Ottawa, On, Canada July 9-12, 2017