Sulfur Species Selective Adsorption Using A New Offretite Based Additive

Yira Yorsirys Aponte Torrealba
The University of Western Ontario

Supervisor
Dr. Hugo de Lasa
The University of Western Ontario

Graduate Program in Chemical and Biochemical Engineering

A thesis submitted in partial fulfillment of the requirements for the degree in Doctor of Philosophy

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Abstract

Fluid Catalytic Cracking (FCC) unit is one of the most important conversion processes used in petroleum refineries. Nowadays, petroleum refineries, and specifically FCC units, have to be improved. New technologies must be developed to increase the refineries revenues as well to comply with environmental regulations. One area of significant concern is the necessary in-situ FCC gasoline sulfur reduction.

In this respect, this PhD dissertation proposes a new Zn-Offretite (Zn-OFF) additive for gasoline sulfur reduction via selective adsorption in FCC units. The PhD research developed covers the preparation of the Zn-OFF zeolites and their physicochemical characterization. This physicochemical characterization leads to the demonstration that zinc species are most likely included in the OFF framework. Furthermore, it is also shown that the Zn in the OFF zeolites, may considerably increase acidity as well as the abundance of Lewis acid sites. As a result, it is found that the Zn in the OFF is tailored for thiophenic species selective adsorption.

Regarding the Zn-OFF performance, it is proven in this PhD dissertation, that the Zn-OFF additive displays an excellent performance for 2-methylthiophene (2MTh) selective adsorption. The best sulfur removal was found using the Zn(3.5wt%)-OFF additive and 2MTh at 530 °C and 5 s.

On the basis of the results obtained, it is anticipated that the Zn(3.5wt%)-OFF additive can provide a valuable in-situ sulfur selective adsorption for the thiophenic compounds. It is also established that the used Zn(3.5wt%)-OFF additive, when blended with a FCC commercial catalyst reduces both coke production and sulfur in coke.

It is thus, demonstrated that under typical FCC unit operating conditions, the Zn(3.5wt%)-OFF additive can selectively adsorb sulfur contained species. This additive can also decrease sulfur in coke with this leading to a mitigation of SOx emissions in the FCC regenerator, where coke is combusted and catalyst reactivated.
Keywords

Acknowledgments

I would like to thank all people who helped and inspired me during my PhD study at the University of Western Ontario.

I especially want to express my sincere gratitude to my supervisor, Dr. Hugo de Lasa, for his guidance and support during my research and study at Western Ontario University. His hard work and enthusiasm in research have motivated me.

I wish to specially thank Jose Munoz, the CREC Research Engineer for his support during the operational issues and maintenance of the CREC Riser Simulator. I also wish to thank Pastor Solano for assisting me during my stay in the CREC Lab. I would also like to thank the CREC-Recat Editor, Florencia de Lasa for her assistance in the editing of this manuscript.

I am indebted to my friends and student colleagues at the University of Western Ontario for providing a stimulating and fun environment in which to learn and grow. I am especially grateful to Rezwan Quddus, Ana Maria Aguirre, Isabela Reniati, Fabricio Guayaquil, Saad Al-Bogami, Patricio Valades, Sameer Al-Ghamdi, Ana Giron, Samira Roston, Cristina Salome, Abdulkaber Asaedi and Imtiaz Ahmed. A very special thanks goes out to Gamaliel Che for his help in the adsorption experiments.

I am grateful to Ashley Jokhu and Cole Handsaeme, the Graduate Affairs Coordinators, for assisting me in various administrative matters during my graduate program.

I am also grateful to Dr. Simon Yunez in Micromeritics for providing support in the solid characterization and Dr. Gerardo Vitale for his initial guidance in the synthesis of the materials.

My deepest gratitude goes to my family for their unflagging love and support throughout my life; this thesis would be simply impossible without them. I wish to special thanks to my mother (Zaira Torrealba) and my father (Armando Aponte) for helping me get thought the difficult times, for all emotional support and caring they provided. I would like to express my gratitude to my mother-in-law (Nancy Lanza) for assisting and caring me.
during challenging days. I wish to thank my siblings, Yiza and Yeison Aponte, my cousin Barbara Moreno, and my aunts Luisa and Edita Torrealba who have been a key part in this journey. Lastly, and most importantly, I wish to thank my lovely husband, Angel Lanza, not a single word can fully describe his whole support and love to me; my daughters (Samantha and Victoria), just for being the reason and the love of my life. To them, I would like to dedicate this thesis.
Table of Contents

Abstract ............................................................................................................................................. ii
Acknowledgments ........................................................................................................................... iv
Table of Contents .......................................................................................................................... vi
List of Tables .................................................................................................................................. xi
List of Figures ............................................................................................................................... xiii
List of Appendices ......................................................................................................................... xix
List of Abbreviations ..................................................................................................................... xx
Chapter 1 .......................................................................................................................................... 1
  1 Introduction and Scopes ............................................................................................................... 1
    1.1 Introduction ............................................................................................................................ 1
    1.2 Research Objectives .............................................................................................................. 4
      1.2.1 Overall objective .............................................................................................................. 4
      1.2.2 Specific Objectives .......................................................................................................... 4
Chapter 2 .......................................................................................................................................... 5
  2 Literature Review ....................................................................................................................... 5
    2.1 Introduction ............................................................................................................................ 5
    2.2 Offretite zeolites and their applications ................................................................................ 7
      2.2.1 General Aspect of the Offretite ...................................................................................... 9
      2.2.2 Applications of OFF Zeolites ....................................................................................... 12
      2.2.3 Synthesis Methods of OFF Zeolites .............................................................................. 14
    2.3 Zinc-Modified Zeolites and their Applications ................................................................. 17
      2.3.1 Zinc Loading in Zeolites by Incipient Wet Impregnation and Ion Exchange Method ................................................................. 17
      2.3.2 Zinc Loading in Zeolites by Direct Synthesis ....................................................... 20
### Table of Contents

2.4 FCC Gasoline Sulfur Removal *In-Situ* ................................................................. 22

2.4.1 Gasoline sulfur removal additives ................................................................. 22

2.5 Conclusions ........................................................................................................ 26

Chapter 3 .................................................................................................................. 28

3 Experimental Methodology .................................................................................. 28

3.1 Introduction ......................................................................................................... 28

3.2 Catalytic Systems and Materials ..................................................................... 29

3.2.1 Catalytic Materials: Additives and Commercial Catalyst ......................... 29

3.2.2 Feedstocks for Selective Adsorption Studies .............................................. 30

3.3 Physicochemical Characterization .................................................................. 30

3.3.1 X-Ray Diffraction (XRD) ........................................................................... 31

3.3.2 N2 Isotherms ............................................................................................... 31

3.3.3 Temperature Programmed Studies (TPD, TPR and TPO) ......................... 31

3.3.4 UV-Vis Spectra .......................................................................................... 32

3.3.5 Scanning Electron Microscopy (SEM) ....................................................... 32

3.3.6 Fourier Transform Infrared Spectroscopy (FTIR) ..................................... 32

3.3.7 Chemical Characterizations (XRF and ICP) ............................................. 32

3.3.8 Raman Spectra .......................................................................................... 33

3.4 Reaction system ............................................................................................... 33

3.5 Experimental Procedure .................................................................................. 38

3.5.1 Balance level 2: Reactor Quasi Total Evacuation ....................................... 39

3.5.2 Balance Level 1: Gas Phase Sampling ...................................................... 40

3.6 Products analysis ............................................................................................... 41

3.7 Identification of the compounds retained on the catalytic materials .............. 44

Chapter 4 .................................................................................................................. 45
Quantification of the Selective Adsorption................................................................. 45

4.1 Quantification Method.......................................................................................... 45

4.1.1 Balances Level 1: Gas Phase Sulfur and Carbon Balances ...................... 46

4.1.2 Balances Level 2: Typical Sulfur and Carbon Balances.......................... 47

4.1.3 Balances Level 3. Sulfur and Carbon Balances Based on Solid Residues ................................................................. 48

4.2 Base line and Thermal runs................................................................................. 48

4.3 Adsorption Study: Using Thiophene as Sulfur Containing Species ............. 50

4.3.1 Experimental Runs with Thiophene/TMB Mixture using 10% HIPZ-D Additive +90% FCC Catalyst ................................................................. 50

4.3.2 Experimental Runs with Thiophene/TMB Mixture using HIPZ-D Additive only ................................................................. 52

4.3.3 Experimental Runs with 2-Methylthiophene/TMB using HIPZ-D Additive only ................................................................. 53

4.4 Conclusions........................................................................................................ 56

Chapter 5.................................................................................................................. 58

5 Synthesis and Characterization of OFF and Zn-OFF zeolites and additives ....... 58

5.1 Introduction.......................................................................................................... 58

5.2 Syntheses of Offretite and Zn-Offretite Based Additives............................... 59

5.2.1 Zeolites: Offretite, Zn(2.0wt%)-Offretite and Zn(3.5wt%)-Offretite ......... 59

5.2.2 Additives: OFF, Zn(2.0wt%)-OFF and Zn(3.5wt%)-OFF ....................... 64

5.3 Physicochemical Characterization...................................................................... 65

5.3.1 Pelletization effect over Zeolites: Additives versus Zeolites............... 67

5.3.2 Acidity Characterization: NH$_3$-TPD and Pyridine-FTIR..................... 69

5.3.3 N$_2$ Isotherm.................................................................................................. 78

5.3.4 Zn in OFF Framework....................................................................................... 80

5.4 Conclusions........................................................................................................ 84
8.2 Recommendations ........................................................................................................... 136

References ........................................................................................................................... 137

Appendices ............................................................................................................................ 157

Appendix A: Thiophenic Species Calibration Curves ......................................................... 157
  A.1. Flame Photometric Detector (FPD) .............................................................................. 158
  A.2. Flame Ionized Detector (FID) .................................................................................... 161
  A.3. Mass Spectrometer signal (MS) .................................................................................. 162

Appendix B: Product Distribution GC-MS/FID/FPD reports ........................................... 164

Appendix C: Sulfur and Carbon Elemental Balance Example ........................................ 168
  C.1. Balance Level 1 ........................................................................................................... 168
  C.2. Balance Level 2 ......................................................................................................... 174
  C.3. Balance Level 3 ......................................................................................................... 179
  C.4. Conversions ............................................................................................................... 179

Appendix D: BHJ Method .................................................................................................... 181

Curriculum Vitae .................................................................................................................. 184
List of Tables

Table 2-1. General physicochemical characterization of offretite zeolites .................. 10
Table 2-2. Gel Mixture as reported by Quesada et al. (Quesada and Vitale-Rojas 2006) 16
Table 2-3. Sulfur Species in FCC gasoline (Valla et al. 2004) ................................. 23
Table 3-1. Mass selectivity Detector parameters .................................................... 42
Table 3-2. Gas Chromatography method .............................................................. 43
Table 4-1. Sulfur and Carbon balances evaluated at Balance Level 3 using data from catalytic cracking runs using 10wt% of HIPZ-D additive and 90% of FCC commercial catalyst blends and 1.2wt% of Th in TMB at 530 C and 7s. ................................. 52
Table 5-1. Molar ratio of the zeolite components .................................................. 60
Table 5-2. Physicochemical Properties of the Zeolites, Additives and Matrix ............. 66
Table 5-3. TPD-NH$_3$ Results for the Zeolites and Additives using a $\beta=15^\circ$C/min temperature ramp ................................................................. 68
Table 5-4. NH$_3$-TPD after deconvolution of the peaks using a $\beta=30^\circ$C/min temperature ramp (values are the average of three repetitions) ............................... 72
Table 5-5. Lewis and Brønsted acid sites concentration obtained from the area of the FTIR bands (au/cm). .............................................................. 75
Table 5-6. Mean Electronegativity of the Materials ................................................. 77
Table 5-7. CO$_2$-TPD results for the zeolites at $\beta=20^\circ$C/min ................................ 77
Table 6-1. TMB Conversion and Coke Production using Zn-OFF Additive and FCC Catalyst Blends at 530 °C and 7 s. ...................................................... 96
Table 6-2. Elemental Carbon and Sulfur Balances Comparison ............................... 100
Table 7-1. Desorption Activation Energies \((E_d, \text{kJ/mol})\) and Intrinsic Desorption Rate Constants \((k_{do}, \text{ml/g STP\cdotmin})\) Determined by Linear Regression Eq. (7-11) ............ 122

Table 7-2. Activation Energies \((E_d, \text{kJ/mol})\) and Intrinsic Desorption Rate Constants \((k_{do}, \text{ml/g STP\cdotmin})\) Determined by Nonlinear Regression. .......................................................... 128

Table 7-3. Cross-Correlation Coefficient Matrix for the Desorption Kinetic Constants 130
List of Figures

Figure 2-1. Example of a zeolite structure formation: a) Primary Building Units, b) Secondary Building Units, and c) Composite Building Units ................................................................. 8

Figure 2-2. Offretite Structure (Modeled by Material Studio) ......................................................... 9

Figure 2-3. Simulated XRD pattern for ERI-OFF intergrowth. ERI peaks at 9.3, 16, and 21.5 ° 2Θ (Holmes 2011). ........................................................................................................ 12

Figure 2-4. General mechanism of reaction for gasoline desulfurization in FCC units (adapted from Albemarle commercial information 2011) ............................................................ 24

Figure 2-5. Thiophene selective adsorption process using a sulfur removal additive in FCC units (two vessel) ........................................................................................................... 26

Figure 3-1. Schematic Description of the CREC Riser Simulator, adapted from Ahmed et al. (Ahmed et al. 2016) ........................................................................................................ 33

Figure 3-2. Schematic comparison of the similarity of reaction conditions in a downer catalytic reactor and in the CREC Riser Simulator where both C/O, partial pressures, temperatures and reaction times are matched ................................................................. 35

Figure 3-3. Schematic description of CREC Riser simulator, associated valves and accessories ............................................................................................................................. 36

Figure 4-1. Pressure Data for Balances Levels 1 and 2: a) Balance Level 1: Gas Phase Product Sampling, Vacuum Pressure (▲) and Reactor Pressure (△), b) Balance Level 2: Quasi-Total Product Evacuation, Vacuum Pressure (◼) and Reactor Pressure (□). Run conditions: 0.1 g of Zn(3.5wt%)-OFF Additive at 510 °C and 7 s.............................................. 46

Figure 4-2. Sulfur and Carbon balances calculated with data from thermal runs at 1.2wt% of 2MTh in TMB at 530 C and 7s. Notes: The left hand bars are for Balance Level 1 calculated with Eq. (4-1) and (4-4). The right hand bars are for Balance Level 2: after
quasi total evacuation using Eq. (4-5) and (4-6). Three quantifications were done using MS, FID and FPD for sulfur detection........................................................................................................ 49

Figure 4-3. Sulfur and Carbon balances calculated with data from catalytic cracking runs using 10wt% of HIPZ-D Additive and 90% of FCC catalyst blends. Notes: a) 1.2wt% of Th in TMB at 530 ºC and 7s, b) The left hand bars are for Balance Level 1 calculated with Eqs. (4-1) and (4-4), c) The right hand bars are for Balance Level 2: after quasi total evacuation using Eqs. (4-5) and (4-6). Three quantifications were done using MS, FID and FPD for sulfur detection........................................................................................................ 51

Figure 4-4. Sulfur and Carbon balances calculated with data from runs using 0.1 g of HIPZ-D Additive and 1.2 wt% of Th in TMB at 530 ºC and 7s. Notes: The left hand bars are for Balance Level 1, which is calculated with Eqs. (4-1) and (4-4). The right hand bars are for Balance Level 2, which represents “quasi” total evacuation using Eqs. (4-5) and (4-6)........................................................................................................................................ 53

Figure 4-5. Sulfur and Carbon balances calculated with data from the runs utilizing 0.1g of HIPZ-D Additive and 1.2wt% of 2MTh in TMB at 530 ºC and 7s. Notes: The left hand bars are for Balance Level 1 calculated with Eqs. (4-1) and (4-4). The right hand bars are for Balance Level 2: after “quasi” total evacuation using Eqs. (4-5) and (4-6)............. 54

Figure 4-6. Yield Product Distribution for runs utilizing 0.1g of HIPZ-D Additive at 530 ºC, 7s and using a) 1.2 wt% of Th in TMB, b) 1.2wt% of 2MTh in TMB.............................. 55

Figure 4-7. Schematic sulfur species distribution for 0.1g of HIPZ-D additive using 1.2 wt% of 2MTh in TMB at 530 ºC and 7s............................................................... 56

Figure 5-1. Schematic Description of the OFF and Zn-OFF Zeolite Syntheses. Broken line: reports Zn addition for Zn-OFF zeolite synthesis only. Right hand side: Rx.1) Formation of [Al(OH)₄]⁻ unit; Rx. 2-3) Formation of Zn(OH)₂ and [Zn(OH)₄]²⁻ units.... 61

Figure 5-2. Building Units Formed (PBU and PSU) in the OFF and Zn-OFF Zeolites . 63

Figure 5-3. NH₃-TPD Spectra for the a) OFF Zeolites with and without Zn, and b) OFF Additives with and without Zn (units of concentration in term of zeolite content) .......... 67
Figure 5-4. FTIR Spectra for a) Active Materials (zeolites) and b) Additives and Matrix

Figure 5-5. NH$_3$-TPD profiles at various $\beta$s for one run of: a) the OFF zeolite, b) the Zn(2.0wt%)-OFF zeolite and c) the Zn(3.5wt%)-OFF zeolite

Figure 5-6. Deconvolution of the OFF Sites (Sites I, II and III) for the Zn (3.5wt%)-OFF Zeolite with NH$_3$-TPD using a $\beta$=25°C/min ramp. Notes: a) Inverse Gamma Distribution individual areas are assessed with a $R^2$=0.998. Summation of the 3 peaks areas are calculated with a 0.0623 residual

Figure 5-7. Change in Acid Site Density in the OFF as a Function of the Zn/Al Ratio

Figure 5-8. Pyridine-FTIR spectra of the OFF and Zn-OFF zeolites measured: a) 1400-1800cm$^{-1}$, b) 3590-3790 cm$^{-1}$ and c) 430-1030 cm$^{-1}$

Figure 5-9. Possible Brönsted and Lewis acid sites formed in the Zn-OFF zeolites. (a), (c), (e) and (g) adapted from Meng et al. and Orazov et al. (Meng et al. 2015; Orazov and Davis 2016)

Figure 5-10. N$_2$ Absorption Isotherms at 77 K for OFF and Zn-OFF Zeolites

Figure 5-11. Porosity Distribution calculated by BJH method for a) the OFF zeolite, b) the Zn(2.0wt%)-OFF zeolite and c) the Zn(3.5wt%)-OFF zeolite. Pore distribution is based on N$_2$ adsorption at 77K

Figure 5-12. X-Ray Diffraction Patterns for the Zeolites (a-c), Additives (f-h), Matrix (e) and Fused Alumina (d)

Figure 5-13. Diffuse Reflectance UV-Vis Spectra for the OFF, the Zn(2.0wt%)-OFF, the Zn(3.5wt%)-OFF Zeolites and the ZnO

Figure 5-14. SEM View of the a) OFF, b) Zn(2.0wt%)-OFF and c) Zn(3.5wt%)-OFF. Note: Reference dimension is 6μm
Figure 5-15. Raman Spectra for the OFF, the Zn(2.0wt%)-OFF, the Zn(3.5wt%)-OFF zeolites .......................................................... 84

Figure 6-1. Sulfur and TMB Conversions and Sulfur and Carbon Balances Calculated with Data from Thermal Runs using 1.2 wt% of 2MTh, Th and 25DMTh in TMB at 530 °C and 7 s .......................................................... 88

Figure 6-2. Sulfur Adsorbed ($S_{ads}$) calculated with Eq. (4-1) and Data from Runs in the CREC Riser Simulator using 0.1 g of OFF, Zn(2.0wt%)-OFF and Zn(3.5wt%)-OFF additives and 1.2wt% of Th, 2MTh and 25DMTh in TMB at 530 °C and 7s .................. 89

Figure 6-3. Sulfur Balance ($S_{balance}$) calculated with Eq. (4-5) and Data from Runs in the CREC Riser Simulator using 0.1 g of OFF, Zn(2.0wt%)-OFF and Zn(3.5wt%)-OFF additives and 1.2wt% of Th, 2MTh and 25DMTh in TMB at 530 °C and 7s .................. 90

Figure 6-4. Sulfur as coke ($S_{stripping \ 2}$) calculated with Data from Runs in the CREC Riser Simulator using 0.1 g of OFF, Zn(2.0wt%)-OFF and Zn(3.5wt%)-OFF additives and 1.2wt% of Th, 2MTh and 25DMTh in TMB at 530 °C and 7s .................. 90

Figure 6-5. New total sulfur species formed Runs in the CREC Riser Simulator using 0.1 g of Additive and 1.2wt% of Th, 2MTh and 25DMTh in TMB at 530 °C and 7s..... 92

Figure 6-6. Example of Distribution of Product Species Containing Sulfur after Runs in the CREC Riser Simulator using 0.1 g of Additive and 1.2wt% of 2MTh in TMB at 530 °C and 7s................. 93

Figure 6-7. Offretite Zeolite Framework and Pore Sizes. a) Plane YX and b) Plane YZ. 94

Figure 6-8. Sulfur Balance Level 1 ($S_{ads}$), Sulfur Balance Level 2 ($S_{stripping \ 1}$), and Sulfur Left in Coke -Balance Level 3 ($S_{stripping \ 2}$) Calculated with Eqs. (4-1), (4-5) and (4-7). Conditions: 0.1 g of Zn(3.5wt%)-OFF Additive (additive/HC = 0.6), 1.2 wt% of sulfur species (Th, 2MTh or 25DMTh) in TMB at 530 °C and 7 s. ........................................ 98

Figure 6-9. Distribution of Product Species Containing Sulfur Runs in the CREC Riser Simulator using: a) 0.1 g of Zn(3.5wt%)-OFF Additive (additive/HC = 0.6), b) 1.2 wt%
of sulfur species (Th, 2MTh or 25DMTh) in TMB, c) 530 °C temperature and d) 7s contact time. ................................................................. 99

Figure 6-10. Carbon Balance Level 1 (C_{ads}), Carbon Balance Level 2 (C_{stripping 1}), and Coke Yields - Carbon Balance Level 3 (C_{stripping 2}) Calculated with Eqs. (4-4), (4-6) and (4-8). Conditions: 0.1 g of Zn(3.5wt%)-OFF additive (additive/HC = 0.6), 1.2 wt% of sulfur species (Th, 2MTh or 25DMTh) in TMB at 530 °C and 7 s. ........................................ 100

Figure 6-11. Sulfur Balance Level 1 (S_{ads}), Calculated with Eq. (4-1) as a Function of the Contact Time and Temperature using 1.2 wt% of 2MTh in TMB and 0.1 g of Zn(3.5wt%)-OFF (additive/HC = 0.6). .................................................................................. 101

Figure 6-12. Isomerisation and disproportionation reactions ....................................................... 102

Figure 6-13. Distribution of Product Species Containing Sulfur using 0.1 g of Zn(3.5wt%)-OFF Additive (additive/HC = 0.6), and 1.2 wt% of 2MTh in TMB at 510 °C, 530 °C, 550 °C and 5 s .......................................................................................... 103

Figure 6-14. Coke Yields (C_{stripping 2}) calculated with Eq. (4-8) and Sulfur in Coke (S_{stripping 2}) Calculated with Eq. (4-7), as a Function of Contact Time and Temperature using 1.2 wt% of 2MTh in TMB at 530 °C and 0.1 g of Zn(3.5wt%)-OFF (additive/HC = 0.6). .................................................................................. 104

Figure 6-15. TOC Signal for the Coke Analysis in the Additive at Different Contact Times and Temperatures. Conditions: 0.1 g of Zn(3.5wt%)-OFF and 1.2 wt% 2MTh in TMB and 7s. a) 510-550 °C and 5 s and b) 510-550 °C and 7 s. ......................... 105

Figure 6-16. Adsorption and Reaction Network Taking Place While Using the Zn(3.5wt%)-OFF Additive. .................................................................................................................. 107

Figure 6-17 Carbon Balance Level 1 (C_{ads}) and Carbon Balance Level 2 (C_{stripping 1}). Parameters are calculated with Eqs. (4-4) and (4-6) for different the Zn(3.5wt%)-OFF Additive + FCC Catalyst Blends. Tests performed using a 1.2 wt% 2MTh in TMB at 530 °C and 5 s. .................................................................................. 108
Figure 6-18. Sulfur Balance Level 1 ($S_{ads}$), Sulfur Balance Level 2 ($S_{stripping_1}$), Sulfur Balance Level 3 ($S_{stripping_2}$) Calculated with Eqs. (4-1), (4-5) and (4-7) as a Function of the Percentage of Zn(3.5wt%)-OFF Additive + FCC Catalyst Blends using 1.2 wt% 2MTh in TMB at 530 °C and 5 s................................. 109

Figure 6-19. a) TMB and 2MTh Conversion and b) Coke Yields as functions of the percentage of the Zn-OFF Additive in the Zn(3.5wt%)-OFF Additive + FCC Catalyst Blends using 1.2 wt% 2MTh in TMB at 530 °C and 5 s. ................................................. 111

Figure 7-1. Linear Regression Using Eq. (7-11) for a) OFF, b) Zn(2.0 wt%)-OFF zeolite and c) Zn(3.5 wt%)-OFF zeolite. Horizontal bars represent the standard deviations for 3-5 repeats. .................................................. 121

Figure 7-2. Non-linear Regression for Site I Using Eq. (7-12) for: a) OFF, b) Zn(2.0 wt%)-OFF Zeolite and c) Zn(3.5 wt%)-OFF Zeolite......................................................... 125

Figure 7-3. Non-linear Regression for Site II Using Eq. (7-12) for: a) OFF, b) Zn(2.0 wt%)-OFF Zeolite and c) Zn(3.5 wt%)-OFF Zeolite......................................................... 126

Figure 7-4. Non-linear Regression for Site III Using Eq. (7-12) for: a) OFF, b) Zn(2.0 wt%)-OFF Zeolite and c) Zn(3.5 wt%)-OFF Zeolite......................................................... 127

Figure 7-5. Experimental and Predicted Ammonia Desorption Volume: a) OFF, b) Zn(2.0 wt%)-OFF Zeolite, and c) Zn(3.5 wt%)-OFF Zeolite......................................................... 130
List of Appendices

Appendix A: Thiophenic Species Calibration Curves ....................................................... 157
Appendix B: Product Distribution GC-MS/FID/FPD reports .............................................. 164
Appendix C: Sulfur and Carbon Elemental Balance Example ............................................ 168
Appendix D: BHJ Method ..................................................................................................... 181
List of Abbreviations

Notation

\[ S_{ads} \] Sulfur adsorbed species evaluated in the gas phase, wt%
\[ S_{balance} \] Sulfur Balances after Reactor Evacuation or Stripping 1, wt%
\[ S_{stripping\ 1} = S_{balance} \]
\[ S_{stripping\ 2} \] Sulfur on Solid Residues Left or Stripping 2, wt%
\[ C_{ads} \] Carbon adsorbed species evaluated in the gas phase, wt%
\[ C_{balance} \] Carbon Balances after Reactor Evacuation or Stripping 1, wt%
\[ C_{stripping\ 1} = C_{balance} \]
\[ C_{stripping\ 2} \] Carbon on Solid Residues Left or Stripping 2, wt%
\[ coke\ yield = C_{stripping\ 2} \]
\[ T_p \] Maximum temperature of the peak of NH\textsubscript{3}-TPD
\[ T_M \] Mean temperature of the peak of NH\textsubscript{3}-TPD
\[ E_d \] Desorption energy, kJ/mol
\[ k_{do} \] Intrinsic desorption constant, ml/g STP min

Acronyms

C/O Catalyst and feedstock Ratio
CREC Chemical Reaction Engineering Center
DFT Density Functional Theory
ERI Erionite Zeolite
FAU Faujasite Zeolite or Y zeolite
FCC Fluid Catalytic Cracking
FID Flame Ionization Detector
FPD Flame Photometric Detector
FTIR Fourier Transform Infrared Spectroscopy
FXR Fluorescence of X-Ray
GC MS Gas Chromatography/Mass Spectrometer
GSRA Gasoline Sulfur Reduction Additive
GME Gmelinite cages in the zeolite
HIPZ-D Protonated IPZ-D Zeolite, also the name of the GSRA using IPZD
H-OFF Protonated OFF Zeolite
HZSM5 Protonated Zeolite Socony Mobil 5
ICP- AES Inductively coupled Plasma Atomic Emission Spectrometry
IZA International Zeolite Association
Intevep Petroleum Research Institute of Venezuela, branch of PDVSA
<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>K-OFF</td>
<td>OFF zeolite in the cation form</td>
</tr>
<tr>
<td>LPG</td>
<td>Process stream containing a C3 and C4 fraction</td>
</tr>
<tr>
<td>MSD</td>
<td>Mass selective detector</td>
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<tr>
<td>MThs</td>
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<td>Particle Size Distribution</td>
</tr>
<tr>
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<td>Scanning Electron Microscopy</td>
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<td>SSM</td>
<td>Solid Sample Module</td>
</tr>
<tr>
<td>STP</td>
<td>Standard Temperature (0°C) and pressure (1 atm)</td>
</tr>
<tr>
<td>Th</td>
<td>Thiophene</td>
</tr>
<tr>
<td>TMA</td>
<td>Tetra-Methyl-Ammonium</td>
</tr>
<tr>
<td>TMB</td>
<td>1,3,5-Trimethylbenzene or Trimethylbenzene</td>
</tr>
<tr>
<td>TIC TMB</td>
<td>MSD Signal Tri-methyl-benzene</td>
</tr>
<tr>
<td>TOC</td>
<td>Total Organic Carbon</td>
</tr>
<tr>
<td>TPD</td>
<td>Temperature Programmed of Desorption</td>
</tr>
<tr>
<td>TPR</td>
<td>Temperature Programmed Reduction</td>
</tr>
<tr>
<td>TPO</td>
<td>Temperature Programmed Oxidation</td>
</tr>
<tr>
<td>Y</td>
<td>Y Zeolite</td>
</tr>
<tr>
<td>UWO</td>
<td>The University of Western Ontario</td>
</tr>
<tr>
<td>VGO</td>
<td>Vacuum Gas Oil</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>XRF</td>
<td>X-ray fluorescence</td>
</tr>
<tr>
<td>Zn-OFF</td>
<td>Zn loaded OFF zeolite (Zn loaded by direct Synthesis of the OFF)</td>
</tr>
<tr>
<td>Zn(2.0wt%)-OFF</td>
<td>2.0wt% of Zn content loaded in the OFF zeolite</td>
</tr>
<tr>
<td>Zn(3.5wt%)-OFF</td>
<td>3.5wt% of Zn content loaded in the OFF zeolite</td>
</tr>
<tr>
<td>2MTh</td>
<td>2-methylthiophene</td>
</tr>
<tr>
<td>3MTh</td>
<td>3-methylthiophene</td>
</tr>
<tr>
<td>25DMTh</td>
<td>2,5-di- methylthiophene</td>
</tr>
<tr>
<td>24DMTh</td>
<td>2,4-di- methylthiophene</td>
</tr>
<tr>
<td>34DMTh</td>
<td>3,4-di- methylthiophene</td>
</tr>
<tr>
<td>35DMTh</td>
<td>3,5-di- methylthiophene</td>
</tr>
<tr>
<td>4PV</td>
<td>4-port chromatographic valve</td>
</tr>
<tr>
<td>6PV</td>
<td>6-port chromatographic valve</td>
</tr>
</tbody>
</table>
Chapter 1

1 Introduction and Scopes

1.1 Introduction

FCC (Fluidized Catalytic Cracking) unit is the most important conversion process used in petroleum refineries, called the heart of high-conversion refineries. It is a complex process that cracks long chain molecules from vacuum gasoil and residues to produce high value refinery products. These products encompass a high percentage of Liquefied Petroleum Gas (LPG), light and middle distillates (gasoline and diesel) and a low percentage of the heavy cut hydrocarbons and fuel oil (Potapenko et al. 2012; Robinson, Shaheen, and Shaheen 2006; Cuadros et al. 2012). More than 80% of the gasoline in oil refineries is produced by FCC units, with the FCC gasoline being a major sulfur contributor (80-95%) in the final gasoline blend (Wen et al. 2012).

The oil refining industry in North America is still enduring a poor profitability. Several US refineries has been closed since 2012 due to low profit margins. To complicate matters oil refineries are under constant pressure to meet the requested environmental sulfur limits in gasoline and diesel (Wen et al. 2012). Parkinson suggested an optimization which includes in-situ FCC gasoline sulfur reduction and SOx reduction (Parkinson 2012).

In this new economic and regulatory landscape, petroleum refineries, and specifically FCC units, have to improve and develop new technologies to increase their profits. For this reason, new alternatives for the production of FCC gasoline with low sulfur have recently attracted the attention of several groups of researchers. Most of them are looking for alternatives of gasoline sulfur reduction in-situ. In this regard, del Rio et al. (Del Rio, Bastos, and Sedran 2013) reported a study of FCC sulfur reduction additive in order to find an optimum additive + catalyst blend. Karakhanov et al. (Karakhanov et al. 2016) studied mesoporous (La/MCM-41) additives for sulfur removal in FCC, achieving 40% desulfurization in the whole FCC liquid product (Gasoline +).
The reduction of sulfur in FCC gasoline, using sulfur reduction additives is becoming a critical alternative to produce high quality gasoline. Different kinds of FCC sulfur reduction additives for gasoline have been proposed and demonstrated in the last 15 years, with the additive activity being strongly affected by its formulation. Some additives are based on molecular sieve materials. These molecular sieves contain Lewis acid sites which are considered hydrogen transfer promoting centers. With respect to these additives, a Lewis acid site may involve transition metals such as Zn, Cu, Ni, Co, Fe, Mn, and more preferably Zn (Bourane 2014; Dean 2013; Trond Myrstad 2008; Trond Myrstad et al. 1999; Wormsbecher 1994).

Potapenko et al., in 2012, reported that sulfur compounds transformation in FCC units depends on both catalyst and feedstock properties. In fact, sulfur removal can be controlled by changing the catalyst acid-base properties as well as the feedstock hydrogen donor capacity (Potapenko et al. 2012; Potapenko, Doronin, and Sorokina 2012). Moreover, Wen et al. (Wen et al. 2012) describes that gasoline desulfurization is a function of the selected feedstock.

Other approaches also considers; a) alkylation of thiophene and other sulfur compounds to transfer a light hydrocarbon fraction to a heavy fraction (Tang et al. 2015; F. L. Yu et al. 2016), b) pervaporation for thiophene removal from the FCC gasoline (Jain, Attarde, and Gupta 2016).

Recently, CREC Research team has proposed a novel alternative for gasoline sulfur reduction in FCC units using a offretite (OFF) with included Zn (transition metal) additive (Aponte 2011; Aponte, Djaouadi, and de Lasa 2014). This OFF topology with included Zn\(^{+2}\), is envisioned as a good selective adsorption additive, given it enhances Lewis site acidity, as well as the bridging of aluminum ions (Pidko and Van Santen 2007). These two properties are critical to promote sulfur selective adsorption rather than sulfur contained hydrocarbon conversion. It was found that the Zn-OFF has specific advantages with these being its 8 ring small pores. It was observed that sulfur species have a special preference to being adsorbed on the OFF small pores. In this respect, it is assumed that acid sites play
an important role in the sulfur species selective adsorption (Aponte 2011; Aponte and de Lasa 2016; Aponte, Djaouadi, and de Lasa 2014).

FCC gasoline sulfur reduction using additives is still an interesting topic to research. Sulfur reduction additives can be blended to the FCC catalyst. In this respect, additives can be added and/or removed at the discretion of the refiner without requiring a shutdown of the FCC plant. Unfortunately, these additives partially reduce the sulfur content in gasoline up to 20–30 wt% only. It is required however, that sulfur reduction additives to be effective should decrease the total sulfur both in the gasoline and in diesel by more than 50%.

Given the high interest and value of this topic, the present PhD research proposed considers the study gasoline sulfur species selective adsorption in FCC units using a Zn-OFF additives. The demonstration and quantification of this additive is proposed to be developed under fluidized bed conditions as in the industrial FCC unit. The additive to be studied, is constituted by a metalloaluminosilicate (zeolite) with an offretite topology and Zn embedded in its structure. During the preparation process, this zeolite is blended with other materials such as a kaolin filler and a Ludox binder. This PhD research, is especially focused on understanding: a) the additive acid properties, b) the role of zinc, c) the sulfur adsorption mechanism, and d) the optimization and modeling of sulfur selective adsorption in the context of FCC units using Zn-OFF additives.
1.2 Research Objectives

1.2.1 Overall objective

The main objective of the present research is to evaluate the adsorption effectiveness of Zn-OFF additives for gasoline desulfurization. More specifically, the purpose of this research is to understand the key factors affecting the selective adsorption such as shape/selectivity, metal loading, thermodynamic constraints and mechanistic reaction steps.

1.2.2 Specific Objectives

1) To propose and to establish a Zn-OFF additives synthesis method ensuring Zn inclusion in the OFF framework

2) To perform a physicochemical characterization of the synthesized OFF and Zn-OFF additives. The OFF and Zn-OFF characterization should include pyridine desorption and NH$_3$-TPD. NH$_3$-TPD runs should allow evaluation of the OFF and Zn-OFF NH$_3$-TPD desorption kinetic parameters

3) To develop an experimental program using the CREC Riser Simulator reactor allowing quantification of the sulfur species selective adsorption. This program of runs should consider a novel method to evaluate gas phase concentrations and temperatures, cat/oil ratios and initial feed compositions, typical of FCC units

4) To establish the role of Zn in the Zn-OFF additive using thiophene, 2-methylthiophene, 2,5-dimethylthiophene and 1,3,5-trimethylbenzene over different Zn-OFF additives. It is anticipated that these model compounds will provide insights into: a) extent of selective sulfur species adsorption and, b) undesirable sulfur species conversions

5) To understand the sulfur selective adsorption pathways for Zn-OFF additives and the influence of them using concurrently FCC commercial catalysts. The experimental work should include catalyst/additive testing under typical FCC operating conditions
Chapter 2

2 Literature Review

This chapter provides a review of the technical literature concerning the offretite (OFF) zeolite, its synthesis, its modifications and its characterizations. In addition, this chapter considers the zeolites loaded with zinc and more specifically its methods of preparation and its applications.

Furthermore, the last section of this chapter covers the different types of in-situ FCC gasoline sulfur reduction mechanisms currently apply in the oil refining industry.

2.1 Introduction

Zeolites are very stable solids with valuable acidic properties. The zeolite chemical composition can be modified. This has encouraged the development of new zeolites for novel industrial applications in oil refining. In addition to the chemical composition, zeolites can be manufactured with specific pore dimensions and topology of the crystalline structure. These features are key in a catalytic process, with reactions taking place on active sites placed within the zeolite internal pores and cavities (Moliner, Martínez, and Corma 2015; Weitkamp 1991; Ciobanu, Ignat, and Carja 2008). Therefore, the structure of the channels and cavities gives rise to special effects of selectivity. Particularly, the 12 rings channel like OFF has been reported as a strength active centers (Penchev et al. 1983a).

While the offretite zeolite synthesis have been studied by a number of authors (Gorshunova et al. 2016; Howden 1986; Howden 1987a; Yang and Evmiridis 1996; Moudafi et al. 1986; Whyte et al. 1971; Wu et al. 1974; Fernandez, Vedrine, et al. 1986), only a few applications consider the OFF zeolite. This is rather surprising given the advantages of the OFF topology for selective reactivity and adsorption.

In spite of this, the present PhD research proposes a novel application of OFF zeolites for the removal of sulfur containing species from FCC gasoline.
The production of FCC gasoline with low sulfur has recently attracted the attention of several groups of researchers. Potapenko et al. (Potapenko, Doronin, and Sorokina 2012) reported that the transformation of sulfur compounds in FCC is controlled by catalyst acid-base properties and feedstock hydrogen donor capacity. Moreover, Wen et al. (Wen et al. 2012) describes the sensitivity of the gasoline desulfurization to the selected feedstock (residue or reprocessing naphtha) in the FCC process.

FCC gasoline sulfur reduction is still a challenging research topic, specifically using additives. Additives can be added and/or removed at the discretion of the refiners without the need of a shutdown of the FCC plant or the requirement of a large capital investment. It is however, anticipated that a good in-situ sulfur reduction process should achieve a total sulfur species in gasoline and diesel by more than 50%. This still represent nowadays a significant technical challenge.

Many types of FCC sulfur reduction additives have been designed and studied in terms of their performance in the last 10 years. The mechanism of reaction for these additives depends on their chemical and structural formulations. In this respect, there are a number of patents (Wormsbecher 1994; Mystard 2002; Bhore 2003; Turner 2010) based on using materials impregnated with a Lewis acid. The Lewis acids are transition metals such as Zn, Cu, Ni, Co, Fe and Mn, more preferably Zn. It is believed that the Lewis acidity is required to improve hydrogen transfer. However, there are other patents (Chester et al. 2005a; Chester et al. 2005c; Chester et al. 2009a; Chester et al. 2009b; Hu et al. 2005; Cheng et al. 2008) that claim that the additive mechanism takes advantage of the metals contained in zeolites. These zeolites may remove the sulfur species contained in the feed as inorganic sulfur.

Regarding the application of modified zeolites to desulfurization processes, one can notice that the zeolites provide shape selectivity with a controlled pore size distribution. Added metals yield enhanced adsorption for sulfur species (Chester et al. 2005a; Chester et al. 2005c; Chester et al. 2009a; Chester et al. 2009b; Hu et al. 2005; Cheng et al. 2008). As well, vanadium oxide supported on silicoaluminates have been considered for shape selectivity with induced adsorption (Dai, Zheng, and Qian 2009; T Myrstad 2000).
One of the disadvantages of the above reported additives is that they are prone to crack sulfur compounds. Formation of H₂S is limited and more coke is formed (Andersson 1999). This situation unfortunately leads to further conversion of high sulfur coke in the FCC regenerator, contributing to SOₓ emissions.

In addition to this progress, new FCC gasoline sulfur reduction additive compositions are being studied (Bourane 2015; Karakhanyan et al. 2016). In this respect, Aponte et al. (Aponte 2011; Aponte, Djaouadi, and de Lasa 2014) proposed a novel alternative for gasoline sulfur reduction in FCC units using an additive. A thiophene selective adsorption process was demonstrated on this basis, using a gasoline sulfur reduction additive under FCC conditions.

In view of this and the promising results of my MESc (Aponte 2011), the present PhD project considers an OFF zeolite for in-situ FCC gasoline sulfur reduction.

2.2 Offretite zeolites and their applications

The zeolites are formed by tridimensional tetrahedral TO₄ (T=Al, Si, B, Ga, Gr, Fe, P, Co, etc.) joined together for common oxygen atoms. The most common zeolites are composed by silica and alumina tetrahedral, [SiO₄]⁴⁻ and [AlO₄]⁵⁻, respectively, which are called primary building units (refer to Figure 2-1).

These primary building units are assembled together into a secondary building units (SBUs) (refer to Figure 2-1). Following this, these groups are connected together to form an array of interconnected channels. This system is called "a cage-like structure" is known as Composite Building Units (CBUs). The CBUs are connected together to form a framework structure of zeolites (Giannetto 1990; Holmes 2011; IZA 2016).
Currently, there are 232 unique zeolite frameworks identified with the IZA acronym. Each one is formed by different combinations of SBUs (IZA 2016).

Regarding the OFF, it is the result of 6-membered rings (6R) in the pattern AABAAB..., where AA forms a double 6R, and the B are 6-membered rings located at the bottom and top of gmelinite cages (GME). Between the double 6R, there are cancrinite cages and the columns of gmelinite cages are 12-membered ring channels (aperture 6.7 x 6.8 Å) parallel to the z-axis (IZA-SC 2007). Figure 2-1 reports a configuration of the OFF Structure.
The *OFF* main channels (12R) are connected by eight-membered rings with an elliptic cross section (refer to Figure 2-2) of 3.6 Å and 5.2 Å. They are joined to the side cavities of the gmelinite type (Mavrodinova et al. 1985).

Initially, it was believe that the *OFF* 6-membered rings were Al free (Gard and Tait 1972). In 1996-1998, however, it was found that there is a random distribution of Al between both kinds of 6-membered rings, having Al distribution similar to other zeolite structures. One should note that the Si-Al distribution in the *OFF* is essentially disordered on the tetrahedral framework sites (Alberti et al. 1996; Gualtieri et al. 1998).

### 2.2.1 General Aspect of the Offretite

The "offretite" was named in honor of Professor Albert J. J. Offrét in 1890 (IZA 2016; IZA-SC 2007). The first *OFF* characterization of a natural offretite was published at that time. Following this, Sheppard *et al.* (Sheppard and Gude 1969) reported an ungraded characterization for natural offretites. It was the first time that the erionite (*ERI*) and *OFF* zeolites were clearly distinguished.

In 1971, a synthetic *OFF* physiochemical characterization was reported, with BET surface areas of 339-467 m²/g (Whyte *et al.* 1971). Since then, improvements in preparation method have been performed, reaching *OFF* zeolites with 400-670 m²/g of BET surface area, 0.23-0.30 cc/g pore volume. Nowadays, 430-500 m²/g BET surface area is considered...
a typical range for a synthetic OFF (Ocelli and Pollack 1986; Cavalcante et al. 1995; Itakura et al. 2010).

A general physicochemical characterization for a wide range of OFF zeolites, is presented in Table 2-1 (Minerology Database 2016; IZA-SC 2007).

Table 2-1. General physicochemical characterization of offretite zeolites

<table>
<thead>
<tr>
<th>Empirical formula example</th>
<th>$K_{1.1}Ca_{1.1}Mg_{0.7}Al_{5.2}Si_{12.8}O_{36}\cdot15.2(H_2O)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Composition</td>
<td></td>
</tr>
<tr>
<td>SiO$_2$, wt%</td>
<td>52-64</td>
</tr>
<tr>
<td>Al$_2$O$_3$, wt%</td>
<td>15-20</td>
</tr>
<tr>
<td>MgO, wt%</td>
<td>0.3-2.0</td>
</tr>
<tr>
<td>CaO, wt%</td>
<td>3-8</td>
</tr>
<tr>
<td>Na$_2$O, wt%</td>
<td>0.0-1.1</td>
</tr>
<tr>
<td>K$_2$O, wt%</td>
<td>1.5-6.7</td>
</tr>
<tr>
<td>Fe$_2$O$_3$, wt%</td>
<td>0-1</td>
</tr>
<tr>
<td>BET Area, m$^2$/g</td>
<td>339-467</td>
</tr>
<tr>
<td>Pore volume, cc/g</td>
<td>0.23-0.30</td>
</tr>
<tr>
<td>XRD main peaks (Relative intensity $&gt;17%$), 2ϴ</td>
<td>7.66°, 15.35°, 19.31°, 20.35°, 23.11°, 23.51°, 24.68°, 30.98°, 31.23°, 35.64°</td>
</tr>
<tr>
<td>Bulk Density, g/cc</td>
<td>2.13-2.16</td>
</tr>
<tr>
<td>Molecular Weight, g/mol</td>
<td>1453</td>
</tr>
</tbody>
</table>

There are three cations commonly associated with natural offretite. These are: K$^+$, Mg$^{2+}$ and Ca$^{2+}$. These cations can be found in different locations within the structure. K$^+$ ions are located in the center of the cancrinite cages, hydrated Mg$^{2+}$ ions are found in the gmelinite cages and Ca$^{2+}$ ions are located in the 12-membered ring pore (Holmes 2011).

A natural offretite has a very low Si/Al ratio of 2.3 – 2.5 which connects to around 5.5 monovalent cations per unit cell. One of these is the K$^+$ ion in the cancrinite cage, one Mg$^{2+}$ ion in the gmelinite cage, and the remaining contribution from Ca$^{2+}$ ions in the pore. While
The Si/Al ratio for synthetic offretite is around 4, with this corresponding to around 5 cations per unit cell, one K$^+$ ion in the cancrinite cage, one TMA$^+$ (tetramethyl ammonium) or other organic ion in the gmelinite cage and the remaining charge balance by Na$^+$ ions is located in the pores (Holmes 2011).

Regarding the OFF acidity, Bourdillon et al. (Bourdillon et al. 1986) found that OFF has stronger acid sites than Y zeolite. In addition, it is reported that 20% of the acid sites are located in the gmelinite cages, which limited access to small size molecules such as n-hexane. A special feature of this, is that small molecules do not display secondary reactions such as coke formation.

On the other hand, Mirodatos et al. (Mirodatos et al. 1978) reported that the acidic character of OFF became more important as K$^+$ are exchanged by protons. It was found that low K increases the number of acid sites and their strengths. Moreover, it was found that H-OFF has two strong Lewis sites (Mirodatos and Barthomeuf 1979).

In 1982, Penchev et al. (Penchev et al. 1983a) reported a study of the thermochemical and acidic properties of offretites. It was found that acid sites were located in the high-temperature peaks in the NH$_3$-TPD profiles. These peaks were attributed to strong acidic properties. In addition, it was stated that the localization of the acidic centers, their environment and their accessibility contributed to the molecular adsorption on the structure of the zeolites, reporting an OFF acidity higher than ZSM-5 acidity.

Regarding the OFF crystal morphology, it may differ from the synthesis method used (Ocelli and Pollack 1986; Cavalcante et al. 1995; Itakura et al. 2010). However, it can be unmistakably differentiated in all cases by using XRD. The XRD significant peaks of the OFF are commonly in the range of the ones reported in Table 2-1.

X-ray diffraction clearly distinguishes OFF from other zeolites. In this respect, it is well known that OFF crystals may intergrow with ERI crystals. In fact, OFF and ERI can intergrow easily because they share the same hexagonal arrays of 6-member rings within their structures. OFF and ERI also share a hexagonal unit cell with almost identical dimensions. Therefore, and to secure OFF purity, it is important to check the absence of
ERI using XRD. Typical $ERI$ of the 2$\theta$ scale at 9.3, 16, and 21.5° should not be recorded (refer to Figure 2-3).

![XRD pattern](image)

Figure 2-3. Simulated XRD pattern for $ERI$-$OFF$ intergrowth. ERI peaks at 9.3, 16, and 21.5° $2\theta$ (Holmes 2011).

2.2.2 Applications of $OFF$ Zeolites

A few catalytic studies using $OFF$ zeolites are reported in the literature. Examples of the $OFF$ applications can be found in the conversion of toluene and in the isomerization of m-xylene (Mavrodinova et al. 1985; Sastre et al. 1990; Bengoa et al. 1997). These authors reported high isomerization activity. In addition, it is claimed that the $OFF$ prevents coke formation in its narrow channels. The $OFF$ channels are connected by eight-membered rings with elliptic cross sections (refers to Figure 2-2). This allows only small amounts of the benzene, toluene and p-xylene to be transported, with coke formation being very limited.
In addition, and for methanol conversion, a protonic offretite \((H\text{-OFF})\) was studied by Dejaifve et al. (Dejaifve et al. 1981). It was found that coke is formed essentially in the larger pores (12 rings: 6.7x6.8Å), leaving the active acid sites in the smaller pores (8 rings: 3.9x4.9Å) freely accessible to reactant species.

Furthermore, modifications of the \(OFF\) have been studied in order to enhance the \(OFF\) coke resistance for the methanol conversion reaction. These improvements in the \(OFF\) thermal resistance were achieved thanks to increase pore accessibility and by acidity reduction (Fernandez, Vedrine, et al. 1986; Fernandez, Grosmangin, et al. 1986).

The cracking of n-hexane using \(H\text{-OFF}\) is another \(OFF\) application. While comparing the \(OFF\) with a \(Y\) zeolite, it was found that \(OFF\) displays stronger acidity (6 times) than the \(Y\) zeolite. In fact, 20% of the \(OFF\) strong acid sites were located in the gmelinites. Those sites were only accessible to n-hexane, causing a coke formation reduction (Bourdillon et al. 1986). These authors also evaluated xylene conversion in the \(H\text{-OFF}\) zeolites suggesting potential industrial applications.

Furthermore, another \(OFF\) zeolite use was reported for the catalytic reduction of NOx by NH\(_3\). The \(OFF\) was ion exchanged Cu (II) (Arous et al. 2005; Arous et al. 2007). It was found the NO oxidation took place on the copper ions retained in the gmlininites cages.

Most recently, the \(K\text{-OFF}\) was studied (Gorshunova et al. 2015). It was found that \(K\text{-OFF}\) was a promising adsorbent for capturing hydrocarbons from exhaust gas engines and for a \(CO_2\) storage. Offretite has toluene adsorption capability up to 200–400°C. \(CO_2\) adsorption was demonstrated at pressures of 1-30 atm and a temperature of 300 K, with \(CO_2\) adsorption capacities of 4-6.2 mmol/g.

Finally, Aponte et al. (Aponte 2011; Aponte, Djaouadi, and de Lasa 2014) proposed an additive with an \(OFF\) topology for gasoline desulfurization in FCC units. Under these conditions, a selective thiophene adsorption process was observed in the smaller pores (8 rings: 3.9x4.9Å). A promising application in FCC selective removal of sulfur containing species such as thiophene in FCC risers was reported. Using this approach, a significant \(SO_3\) formation in the catalyst regenerator was found, as well as an overall FCC plant sulfur
emission reduction to the environment (Aponte 2011; Aponte, Djaouadi, and de Lasa 2014; Aponte and de Lasa 2016).

2.2.3 Synthesis Methods of OFF Zeolites

2.2.3.1 OFF Zeolite

OFF zeolite synthesis methods have been studied by several authors. A synthetic OFF method of preparation was first reported in 1971 (Jenkins 1971). It was prepared from a mixture of silica, alumina, water, sodium oxide, potassium oxide, and tetra-methyl-ammonium (TMA). The use of TMA: (Na₂O+K₂O) mole ratio of 0.216:1 was proposed.

Furthermore, Howden (Howden 1987a; Howden 1986) found that the use of a TMA template is required for offretite synthesis. It was proven various organic compounds could be used as templates. However, TMA is needed during preparation to avoid erionite intergrowth. They also found that TMA must be located in both the gmelinite cages and the lineal channels. This is important for TMA to act more effectively during synthesis. In addition, the propose gel mixture for the synthesis was prepared with 3.3 mole of TMA cations per unit cell of OFF, Ludox HS-40 and chemically pure Al(OH)₃, NaOH and KOH, and TMA. Once these steps were completed, the OFF synthesis was developed in a non-stirred autoclave.

Other authors proposed other methods for the OFF synthesis using other templates, cations as well as silicate sources (Whyte 1971; Yang and Evmiridis 1996; Wu et al. 1974; Moudafi et al. 1986). For example, Yang et al. (Yang and Evmiridis 1996) proposed a new method which was free of use of template (TMA). A homogeneous water-free gel mixture was prepared under stirring of sodium aluminate, glycerol, sodium hydroxide, precipitated silica, and KCl. The crystallization times in this procedure ranged of 10-70 days, and the temperature used was 120°C.

On the other hand, Moudafi et al. (Moudafi et al. 1986; Moudafi et al. 1987) highlighted the importance of using the proper condition during crystallization to obtain pure OFF. It was also noticed that the morphology of the crystals depended on the crystallization
conditions. For example, \textit{OFF} single hexagonal crystals can be found only when the crystallization occurred either at high temperature or at vigorous shaking.

In addition, researchers have also focused on the stabilization of the \textit{OFF} via dealumination, which yields \textit{OFF} zeolites with an increased stability and pore volume (Fernandez et al. 1986; Carvalho et al. 1993). The dealumination of the \textit{OFF} was effected by steaming treatments followed by HCl extraction of aluminum compounds.

Most recently, an optimization of the synthesis of high pure \textit{OFF} was achieved via magadiite recrystallization. A well-crystallized offretite was prepared from the molar composition: 3.6 K$_2$O: 3.6 Na$_2$O: 1.0 Al$_2$O$_3$:6.5 SiO$_2$: 320 H$_2$O: 1.5 TMA$^+$ by heating it at 140 °C for 3 days (Y. Wang et al. 2010).

In addition, Itakura \textit{et al.} (Itakura et al. 2010) claimed to have developed a method to obtain a high thermal stable \textit{OFF} by hydrothermal conversion of faujasite. The starting FAU was through dealumination treatment involving a combination of steaming at 700 °C and H$_2$SO$_4$ treatment at 75°C for 4 h. The hydrothermal conversion was conducted at 125 °C for 1-21 days in a convection oven. An increase of the Si/Al ratio to almost 8 was achieved by using dealuminated FAU zeolites (Itakura et al. 2010).

Finally, the IZA (International Zeolite Association) reports a synthesis protocol to prepare the \textit{OFF} (Lechert 1992). A gel mixture of: 3.0 Na$_2$O: 1.0 K$_2$O: Al$_2$O$_3$: 20.8 SiO$_2$: 1.73 (TMA)Cl: 324 H$_2$O is crystallized at 160°C during 20h. A careful procedure to mix the reaction gel is described as follows:

Step 1) MIX 1: Sodium hydroxide is mixed with water until it is dissolved

Step 2) MIX 2: MIX 1 is stirred with aluminum tri-isopropylate at 100°C until complete water evaporation takes place

Step 3) MIX3: MIX 2 is blended with water at ambient conditions

Step 4) MIX 4: Water is mixed with sodium hydroxide and potassium hydroxide until complete dissolution takes place

Step 5) MIX 5: MIX 4 is blended with a silica source for 30 minutes
Step 6) MIX 6: MIX 5 is mixed with MIX 3 for 30 minutes

Step 7) MIX 7: MIX 6 is dissolved in water for 30 minutes

Step 8) MIX 8: MIX 7 is blended with TMA-chloride for 30 minutes

Furthermore, and to achieve the OFF prolonged crystallization, extra time is required. The resulting OFF involves: a) a sodium and a potassium cation OFF form, b) a Si/Al ratio in the 3-5 ratio (Itakura et al. 2010).

2.2.3.2 Zinc Loading OFF Zeolite

Quesada et al. (Quesada and Vitale-Rojas 2006) claimed to have developed a method to synthesize a metalloaluminosilicate with an OFF topology. This material, designated IPZ-D, was comprised of Fe, Zn and/or Ni in the OFF framework.

The IPZ-D preparation method involved: 1) dissolving iron nitrate, zinc nitrate, and/or nickel oxide in distilled water, 2) mixing the salt solution (ZO) with sodium silicate, potassium hydroxide, tetramethylammonium chloride, and aluminium hydroxide, in “no preferred blending order”, 3) stirring the mixture until it formed a uniform fluid gel, with molar compositions as reported in Table 2-2, 4) transferring the gel to an autoclave with a stirrer, 5) stirring and heating the autoclave at 160 °C during 38-62 h.

Once the synthesis was completed, the resulting zeolite was treated as follows: a) filtered, b) washed with distilled water, c) dried at 120°C for 12 h, d) calcined at 500 °C during 6 h under air flow, and f) ion exchanged with NH$_4^+$ ions and calcined again at 550 °C.

Table 2-2. Gel Mixture as reported by Quesada et al. (Quesada and Vitale-Rojas 2006)

<table>
<thead>
<tr>
<th>Mole Ratio of Reactant</th>
<th>Preferred Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$_2$O$_3$/SiO$_2$</td>
<td>0.02-0.25</td>
</tr>
<tr>
<td>Fe$_2$O$_3$/SiO$_2$</td>
<td>0.01-0.25</td>
</tr>
<tr>
<td>ZO/SiO$_2$</td>
<td>0-0.5</td>
</tr>
<tr>
<td>(K+Na)$_2$O/SiO$_2$</td>
<td>0.2-0.8</td>
</tr>
<tr>
<td>TMA/SiO$_2$</td>
<td>0-0.3</td>
</tr>
<tr>
<td>H$_2$O/SiO$_2$</td>
<td>5-30</td>
</tr>
</tbody>
</table>
However and in spite of this data, Aponte et al. (Aponte and de Lasa 2016) established a methodology for the direct synthesis Zn-\textit{OFF}. It was found that the sequence, that the materials were added to form the gel mixture, was critical to introduce the zinc into the framework of the \textit{OFF}. This method is reported in Chapter 5 of the present PhD dissertation.

### 2.3 Zinc-Modified Zeolites and their Applications

Zinc-loaded zeolites are suitable catalysts for different processes. The preparation of the zinc-loaded zeolite is crucial to control the nature and the location of Zn cations. The specific zinc location produces different acid sites causing diverse activities and selectivity of the catalysts. Zinc species can be introduced into zeolites by various methods. Some of the methods are: a) ion exchange, b) incipient wet impregnation, c) \textit{ZnCl}_2 sublimation, d) solid-state ion exchange with ZnO or metallic zinc, and e) direct hydrothermal synthesis (Niu et al. 2014).

Most of the zinc in zeolites are loaded by two methods: incipient wet impregnation and ion exchange method. It is important to mention that recently, the zinc loaded by “direct synthesis” has gained more interest. It is claimed to be the best option, in terms of stability and selectivity (Niu et al. 2014; L. Wang et al. 2007; Orazov and Davis 2016; Aponte and de Lasa 2016; Ni et al. 2011). The inclusion of zinc in the framework gives special catalytic properties such as acidity and shape-selectivity (L. Wang et al. 2007).

In the following sections, a brief discussion of the applications for different zinc-loaded zeolites is provided.

#### 2.3.1 Zinc Loading in Zeolites by Incipient Wet Impregnation and Ion Exchange Method

Most of metal-containing zeolites are prepared by indirect methods. They are made by wet impregnation or ion-exchange (in solution or solid state).

Zinc can be loaded in the zeolite by ion exchange using a small zinc cation amount in aqueous zeolite suspension. Following this, a Zn\textsuperscript{2+} exchange occurs. Upon thermal
decomposition of the complex zinc species used (mostly in air or oxygen) or the reduction of the metal ion with hydrogen, very small clusters of the zinc are formed inside the zeolite channels.

Regarding incipient wet impregnation, zinc is dissolved in an aqueous or organic solution. Then, the Zn solution is added to a zeolite containing the same pore volume as the volume of the solution that was added. Following this, the resulting cake is dried and calcined to drive off the volatile components within the solution, depositing the metal on the zeolite.

Some examples of Zn-loaded zeolite applications are mention as follows:

1) The propane aromatization processes (Biscardi, Meitzner, and Iglesia 1998) using Zn/ZSM-5 prepared by zinc wet impregnation over ZSM-5. Exchanged Zn cations increase propane conversion turnover rates, hydrogen formation rates, and selectivity to aromatics on H-ZSM5.

2) The dehydrogenation and cracking of paraffins (Ono 1980; Ono et al. 1994) using Zn-ZSM-5. It was found that Zn-ZSM-5 showed an enhanced activity for the C-C and C-H bond cleavages versus ZSM-5 free of zinc.

3) The hydroamination processes (Penzien, Su, and Müller 2002; Penzien, Müller, and Lercher 2001; Penzien et al. 2004) using Zn/H-BEA synthetized by zinc ion-exchange. These Zn ion-exchanged zeolites were shown to be excellent catalysts for the intramolecular hydroamination of alkenes and alkynes. In particular, the cyclisation of 3-(aminopropyl)-vinyl-ether and 6-aminohex-1-yne was found to be dominant.

4) The aromatization of ethane and butane (Hagen and Roessner 1995; N. Kumar et al. 2002; Roessner, Hagen, and Heemsoth 2000) using Zn/ZSM-5 and Zn-Pt/ZSM-5 prepared by zinc wet impregnation. These authors reported that Zn-H-ZSM-5 catalysts exhibit very high n-butane conversion and selectivity to aromatic hydrocarbons under the reaction temperatures 713 - 803 K and the space velocities 1.5 - 5.5 h⁻¹.
5) The aromatization of light paraffins (Ciobanu, Ignat, and Carja 2008; Biscardi, Meitzner, and Iglesia 1998) using Zn/H-ZSM-5 and Zn/HY prepared by zinc wet impregnation. It was found that the introduction of zinc into ZSM-5 and Y samples led to a series of promising catalysts, with high activity and a good selectivity.

6) The alkylation of toluene with methanol (Hattori et al. 2016) using Zn/Cs-X prepared by zinc ion exchange. It is observed that ZnO was the promoter for the conversion of methanol into formaldehyde.

7) The synthesis of glycerol carbonate from glycerol carbonylation (Vijaykumar and Halgeri 2015) using Zn-ZSM5, Zn-MOR, Zn-Y and Zn-beta. These catalysts prepared by zinc ion exchange. It was found that the glycerol carbonate yield increased using the Zn-exchanged zeolites in the following order: Zn-MOR < Zn-ZSM-5 < Zn-beta < Zn-FAU. It was noticed the use of the Zn$^{2+}$ exchanged HY zeolite was relatively inexpensive, yielding a highly active catalyst for glycerol carbonylation to produce glycerol carbonate.

8) NOx removal (Iwamoto, Yahiro, and Mizuno 1993) using Zn/ZSM5 synthetized by zinc ion-exchange. It was reported that the maximum activity and the active temperature of the Zn/ZSM5 were 44% and 873 K, respectively.

9) The hydration of acetylene (Onystyáck and Kalló 2003) using Zn/MFI zeolite prepared by ion exchange. These authors reported a Zn-MFI stable up to 500 °C.

10) Water treatment processes (L. Wang et al. 2016) using ZnO coated in 4A commercial zeolite. It was found that ZnO-coated zeolite adsorbents display a high adsorption capacity to remove humid acids from aqueous solutions. The adsorption was carried out given the strong electrostatic interactions between negative functional groups of humid acids and the positive charges of ZnO-coated zeolite adsorbents.

11) Antibacterial activity (Alswat et al. 2016) using ZnO-nanoparticles loaded on the surface of a commercial catalyst obtained by co-precipitation method. A 87%
antibacterial efficiency enhancement was observed when ZnO increases from 3 to 8 wt%.

12) Antimicrobial activity (Tekin and Bac 2016) using Zn on X zeolite prepared by zinc ion exchange. It was reported that a Zn$^{2+}$ loaded zeolite showed an excellent antimicrobial activity for escherichia coli, staphylococcus aureus, pseudomonas aeruginosa, a candida albicans yeast and aspergillus niger fungus.

2.3.2 Zinc Loading in Zeolites by Direct Synthesis

The zinc direct synthesis method is based on incorporating metal ions into the zeolite during synthesis. It is reported that this is a superior method, given that it provides better dispersion and stability of metal species in zeolite.

Regarding the metal in zeolites using this method, they can be located in the zeolite framework and/or in the extra framework (L. Wang et al. 2007; Ni et al. 2011). One should notice, however, that catalytically active sites may have a special role when incorporated into the framework.

In this type of preparation, the precursors of the metal active sites (e.g. salts and alkoxides) are added to the synthesis gel of the inorganic support, with part of the zeolite framework atoms being iso-morphously substituted by metal species.

Alongside of zeolite applications, direct synthesis is largely used to develop microporous AlPOs, SAPOs and other zeolite frameworks. Different metals (such as Co, Mg, Zn, Ti, etc.) can be iso-morphously substituted into the zeolite framework which include Al, Si or P atoms (Dal Santo et al. 2012).

One should note that there are only a few research studies that are reported in this area (Quesada and Vitale-Rojas 2006; L. Wang et al. 2007; J. Gao et al. 2009; Ni et al. 2011; Niu et al. 2014; Meng et al. 2015; Aponte and de Lasa 2016). Some of these studies only consider zeolite synthesis without providing reactivity. In this respect, Wang et al. (L. Wang et al. 2007) reported a novel material preparation method of Zn-ZSM-5.
Recently, Niu et al. (Niu et al. 2014) reported the comparison between four synthesis methods. Zn-containing HZSM-5 zeolites were prepared by impregnation, ion exchange, and physical mixing with ZnO, as well as by direct synthesis. The influence of preparation method on the Zn/ZSM-5 catalytic performance in the methanol-to-aromatic conversion was reported. These authors stated that the acid site distribution, the nature of zinc species, and the catalytic performance are significantly influenced by the Zn zeolite preparation method. It was also mentioned that the Zn-ZSM-5 zeolite prepared by direct synthesis, displayed the longest catalytic usage time given the special pores for coke, which prevent micropore blocking. The Zn-ZSM-5 prepared by ion exchange provided however, the highest selectivity to aromatics.

In this respect, Ni et al. (Ni et al. 2011) described a nano-sized Zn-ZSM-5 zeolite, prepared by direct synthesis, for the aromatization of methanol. The high resistant of the zeolite to coke formation was observed. It was specified that the Zn-ZSM-5 can control the decomposition of methanol and avoid deep aromatization.

Another application of Zn-ZSM5 prepared by direct synthesis was studied by Gao et al. (J. Gao et al. 2009). These authors described catalytic studies for the alkylation of benzene with ethanol. A high ethylbenzene selectivity and good alkylation activities were reported. The enhanced of the Zn-ZSM-5 was assigned to the increase of the Lewis/Brönsted acid site ratio and the crystallite size reduction. Both the acid properties and crystallite size have an in influence on the benzene conversion.

Furthermore, Zn loaded by direct synthesis in ZSM-11 was studied in the methanol-to-olefin reactions (Meng et al. 2015). It was stated that Zn-ZSM-11 generated new Brönsted acid sites favoring propene and butane formation. It was found that there was a structural damage in the zeolite due to the zinc species incorporation. This crystallite damage reduced the formation of aromatics, hydrogen, and carbon oxides.

Finally, a Zn-OFF prepared by direct synthesis, was reported suitable to remove sulfur for gasoline, mitigating as well SOx emission in the FCC regenerator (Aponte and de Lasa 2016). It was stated that the Zn in the OFF zeolites increased the total acidity as well as the acid site strength, with more Lewis acidity being promoted. The authors reported that
the Zn-OFF Additives promoted unimolecular reactions such as sulfur adsorption rather than bimolecular reactions leading to coke formation.

In summary, only few applications of Zn included in the zeolite framework via direct synthesis have been described in the technical literature, with this being an area of research that deserved much more attention.

2.4 FCC Gasoline Sulfur Removal *In-Situ*

There are different options to reduce sulfur in FCC gasoline as follows: 1) Gasoline post-hydrotreating, 2) VGO pre-hydrotreating, 3) Optimization of the FCC operating conditions, 4) Use of gasoline sulfur reduction additives or FCC catalysts enhancing high hydrogen transfer and. The last two options are considered relevant in this review because they involve FCC sulfur removal *in-situ*.

2.4.1 Gasoline sulfur removal additives

Different kinds of FCC sulfur reduction additives for gasoline have been proposed and demonstrated in the last 20 years, with the additive activity being strongly affected by their formulation.

Some additives are based on molecular sieve materials. Molecular sieves contain Lewis acid sites which are considered hydrogen transfer promoting centers. For these additives, a Lewis acid site may involve transition metals such as Zn, Cu, Ni, Co, Fe, and Mn (Bourane 2014; Dean 2013; Bhore 2003; Mystard 2002; Bourane 2015; Kowalczyk et al. 2003; Wormsbecher and Kim 1996).

On the other hand, other additives for sulfur removal can be based on a metal function contained in zeolites. Metallic sites remove sulfur species from the feed, via the transformation of the sulfur organic species into inorganic sulfides. It is believed that molecular sieve components of the additive provides shape selectivity (pore size constrain) while the metallic species on the zeolite provide adsorption sites for sulfur species (Gokak et al. 2013; X. Gao 2013; Turner 2010; Chester et al. 2005d; Chester et al. 2005b; Chester et al. 2009b; Chester et al. 2009a; Hu et al. 2005; Cheng et al. 2008).
A number of companies including Grace Davison, Albemarle, Marathon Oil, ExxonMobil, Statoil, Intercat JM and even joint venture companies have proposed those additives for sulfur removal in FCCs. The share aim is to reduce sulfur species contained in the gasoline boiling range (Table 2-3). One can notice that proposed additives are based on different formulations; promoting different reaction pathways.

Corma et al., (Corma et al. 2001) postulated that thiophene is mainly converted into coke, with some other species being converted into gasoline and light gases. For example, 2-methylthiophene is more easily cracked to form gasoline and gases. It is also pointed out that thiophene and 2-methylthiophene can hardly crack as a direct pathway. However, they can be cracked only after a previous partial saturation of these molecules via hydrogen transfer. On the other hand, large chains of alkylthiophenes, with an alkyl chain of more than three carbon atoms, may lead to cyclization with the side chains yielding monoalkylbenzothiophene. Thus, introduction of a solid promoting hydrogen transfer may lead to formation of alkylbenzothiophene and coke.

<table>
<thead>
<tr>
<th>Sulfur compounds in FCC gasoline</th>
<th>Boiling range (°F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mercaptans</td>
<td>&lt;150 (65.5 °C)</td>
</tr>
<tr>
<td>Thiophene</td>
<td>150-200 (65.5-93.0 °C)</td>
</tr>
<tr>
<td>C₁ thiophenes, tetrahydrothiophene</td>
<td>200-250 (93-121 °C)</td>
</tr>
<tr>
<td>C₂ thiophenes</td>
<td>250-300 (121-149 °C)</td>
</tr>
<tr>
<td>C₃ thiophenes, thiophenol</td>
<td>300-375 (149-190 °C)</td>
</tr>
<tr>
<td>C₄ thiophenes, C₁ thiophenol</td>
<td>350+ (177 °C)</td>
</tr>
<tr>
<td>Benzothiophene, C₂ thiophenol</td>
<td>375+ (190 °C)</td>
</tr>
</tbody>
</table>

Moreover, it was observed that there is also the possible competitive adsorption of sulfur contained species and other aromatics for the same active sites. This competitive adsorption lowers cracking rates. The reverse is also true. For instance, toluene reduces the cracking of mercaptans of tetrahydrothiophene and increases the yield of alkyl-thiophene and benzothiophenes. As a result the vacuum gas oil with increased content of aromatics may lead to a gasoline with higher sulfur content (Corma et al. 2001).
Shan et al. (Shan et al. 2002) conducted mechanistic studies on thiophene species over USY zeolites under mild conditions (460 °C and C/O: 2.5). It was found that thiophene crack over Y-zeolite producing propylene, butane, butane and H₂S. Furthermore, alkylthiophenes and benzothiophene are produced via cracking of polymerized thiophene derivatives.

Figure 2-4 reports a general pathway of the possible reaction mechanism in FCC gasoline sulfur removal using additives. It can be observed that the desired pathway for gasoline sulfur removal additive is the one highlighted in yellow, where mercaptans and mainly thiophene species are converted into H₂S. A big challenge is to avoid coke formation and thiophene alkylation, because those alkyl thiophene species still in the boiling point range of gasoline and sulfur in coke burn in the regenerator increasing the SOx emission (refer to Table 2-3).

Figure 2-4. General mechanism of reaction for gasoline desulfurization in FCC units (adapted from Albemarle commercial information 2011)

Regarding feedstock quality, Corma et al. (Corma et al. 2001) reported that a high olefin content in the feed increases alkylthiophene conversion. In fact, it appears that adding
olefins in the feed decreases both light gases and coke formation increasing the gasoline fraction. This behavior can be justified given the positive effect of olefins on cracking initiation via the formation of carbenium ions on the catalyst surface.

In reference to aromatic feedstocks, Corma et al. (Corma et al. 2001) showed that the high content of monoaromatics such as toluene reduces both mercaptan and tetrahydrothiophene cracking while increasing the yield of alkylthiophenes and benzo thiophenes. Thus, and as a result of toluene addition in the feed, a gasoline with higher sulfur content is produced. It is hypothesized that the strong adsorption affinity of toluene in the feed is the responsible for the cracking rate reduction.

Furthermore, it has been reported that the vanadium in the feedstock enhances the sulfur reduction in FCC. Roberie et al. (Roberie et al. 2006) claimed that addition of vanadium species in the VGO feedstock favors deposition of vanadium species on the catalyst. For instance, vanadium content up to 500-2000 ppm, reduces organic sulfur species by 25 wt% under FCC conditions.

It appears in this respect, that the deposition of both nickel and vanadium species on the FCC catalyst, could have beneficial effects on sulfur reduction in FCC gasoline. In fact, taking advantage of the metal content in the VGO could be a possible approach to reduce sulfur in FCC gasoline (Lappas et al. 2002; Lappas et al. 2004).

The reaction mechanisms described by Figure 2-4 only apply for conventional additives. It is important to mention that a novel approach was proposed by Aponte et al. (Aponte 2011; Aponte, Djaouadi, and de Lasa 2014), focusing on in-situ sulfur removal via selective adsorption. On this basis, gasoline sulfur removal via strong selective adsorption using an additive was proposed. It is found in this respect, that thiophene selective adsorption on the HIPZ-D occurs for reaction times smaller than 7 seconds. It was also observed that a 10wt% HIPZ-D and 90wt% FCC catalyst blends provide both a valuable and a practical approach to implement the HIPZ-D additive in FCC.

Using this method sulfur species can be left adsorbed on the HIPZ-D surface (additive), at the time of leaving the riser cracker. Hydrocarbons and particles can be separated in the cyclones from light gases, gasoline and light cycle oil (refer to Figure 2-5). Following solid
separation in the unit cyclones, the HIPZ-D adsorbed sulfur species could be desorbed in FCC stripper unit and recovered as a separate gas product stream (thiophenic species) together with the adsorbed VGO fraction. Thiophenic species in the C6-C8 range could be easily separated from gasoline.

Figure 2-5. Thiophene selective adsorption process using a sulfur removal additive in FCC units (two vessel)

As a result, the sulfur species could be safely released before the FCC catalyst and HIPZ-D additive reaches the FCC regenerator. This may significantly; a) reduce the SOX formation in the catalyst regenerator, mitigating the overall FCC plant sulfur emissions to the environment, b) reduce the content of sulfur species in the gasoline fraction.

2.5 Conclusions

- The desulfurization of gasoline in FCC using conventional additive is based on the cracking and the hydrogenation of organic sulfur species into H2S and hydrocarbons. This mechanism also favors the coke formation. The properties of a FCC catalyst have as well a great influence on the performance of the additive.
- Contaminants in the feed such as V and Ni can also improve the desulfurization in the FCC unit. On the other hand, the high olefin content in the feedstock may increase the sulfur content given that olefins may react with H₂S.

- The synthesis of pure OFF has been widely reported. The most accepted synthesis method involves the use of TMA as a template and the use of both cations: sodium and potassium. The OFF crystallization usually requires prolonged time (3-21 days). The Si/Al molar ratio obtained in the OFF is in the range of 3-5.

- The zinc-loaded zeolite synthesis method is critical to control the nature and the location of Zn cations. Most of the zinc-loaded on zeolites have been prepared by incipient wet impregnation and ion exchange method.

- A promising novel method for loading zinc on a zeolite, is reported as “direct synthesis”. Zn-loaded zeolites prepared by direct synthesis have been reported for the Zn-ZSM-5 and Zn-ZSM-11 synthesis and only recently for Zn-OFF. This method provides in principle a best option in terms of zeolite stability, better metal dispersion and reaction selectivity. Using this “direct synthesis”, Zn can be incorporated in the OFF lattice framework as shown in this PhD dissertation, following the “required sequence” of reagents mixing.

- There are only a few catalytic studies using OFF zeolites in the literature. Despite this, offretite has a particular parallel system of channels with 8- and 12-membered ring windows, which makes this material attractive as a catalyst and as an adsorbent for chemical processes.

- Zinc loaded zeolites have been considered for different applications such as: a) dehydrogenation, b) aromatization, c) cracking, d) alkylation, e) hydroammination, f) water treatment, g) glycerol synthesis, h) antibacterial, k) antimicrobial, and i) NOx removal. The zinc location in the zeolite framework yields diverse acid sites causing enhanced catalytic activity and selectivity. None of the proposed applications considers Zn in the OFF framework for gasoline desulfurization.
Chapter 3

3 Experimental Methodology

This chapter reports the different experimental activities of the present study. The catalytic systems and feedstocks used during the research are summarized. The characterization techniques used to evaluate the physicochemical properties of the catalytic materials are also discussed. The experimental equipment and procedures established to perform the tests along with the outlet analysis techniques for the products are also described.

3.1 Introduction

Sulfur content in FCC gasoline depends on different variables such as the source of the VGO. Typically, in FCC between 2-20% of the feed sulfur ends up in the gasoline fraction (C5+ to 221 °C) (Siddiqui et al. 2007). The main sulfur components of FCC gasoline are thiophene or alkylthiophenes (50-60 wt%) and benzothiophene (30 wt%) (Valla et al. 2004). On this basis, model compounds such as thiophene, 2-methylthiophene, and 2,5-di-methylthiophene were selected as sulfur key species in gasoline. In addition, it was judged that a good model compound for the gasoline species is 1,3,5-trimethylbenzene.

The sulfur selective adsorption additives prepared for this study and the commercial additive were evaluated individually. In addition, these materials were evaluated together with a Y zeolite (commercial catalysts).

The experiments were developed using the CREC (Chemical Reactor Engineering Center) fluidized Riser Simulator (de Lasa 1992). The CREC “Riser Simulator” is a laboratory scale mini-fluidized bed unit with 60 cm³ and 1 g of catalyst capacity. It simulates the operating conditions of an industrial unit in terms of reaction time, temperature, hydrocarbon partial pressures and catalyst/oil (C/O) ratios.

Thermal and two kind of catalytic runs were performed in the CREC Riser Simulator described above. All the three prepared additives and the commercial additive were evaluated with thiophene, 2-methylthiophene and 2,5-dimethylthiophene blended with
1,3,5-trimethylbenzene. Selected experimental conditions were as follows: a) Total initial pressure: 25 psi, b) Temperatures: 510, 530 and 550°C, c) Contact times: 3, 5 and 7s, d) Additive to oil mass ratio: 0.3, 0.6 and 0.9, e) Additive and FCC commercial catalyst blends mass ratios at: 0/100, 10/90, 20/80, 30/70 and 100/0 (total C/O = 6), f) Impeller velocity to secure good fluidization: 5700 rpm. To ensure the validity and reproducibility of the data, at least 3 repeats for each one of the experiments were performed for every condition studied.

The identification and quantification of products were done using 6890N gas chromatograph (GC), connected to an Agilent 5973N mass selective detector (MSD). The MSD was used to identify the reaction products. The GC was also connected to a flame photometric detector (FPD) and flame ionization detector (FID), allowing product quantification. The FPD was the one specifically utilized for detection of sulfur species.

Prior to the experimental runs, calibration curves were developed to correlate the calculated GC areas and concentrations of sulfur in the hydrocarbon mixture. In addition, the FID was employed to quantify the hydrocarbon and sulfur species as well.

The amount of coke in the used catalyst and additives was measured by the Total Organic Carbon Analyzer (TOC-V CPH) from the SHIMADZU Company using the solid sample module (SSM-5000A).

3.2 Catalytic Systems and Materials

3.2.1 Catalytic Materials: Additives and Commercial Catalyst

In these study a total of 4 additives and a FCC commercial catalyst were evaluated:

- Three additives were synthesized called OFF, Zn(2.0wt%)-OFF and Zn(3.5wt%)-OFF. These materials are described in Chapter 5.
- One additive for thiophene removal via selective adsorption under FCC condition, designed as HIPZ-D, was used to validate the quantification method of sulfur and carbon adsorption. Chapter 4 describes the experimental method. HIPZ-D is a
aluminosilicate with an \textit{OFF} topology and Fe and Zn included in its structure. The HIPZ-D additive was mixed during the fluidizable pellet manufacturing process with other materials such as kaolin and Ludox (Quesada and Vitale-Rojas 2006).

- A FCC commercial catalyst composed of a Y zeolite and a matrix. For the adsorption-reactivity studies, the FCC commercial catalyst was deactivated hydrothermally with steam during 7 h in a steam deactivation plant.

### 3.2.2 Feedstocks for Selective Adsorption Studies

Thiophene (C\(_4\)H\(_4\)S, Aldrich 99+% purity), 2-methylthiophene (C\(_5\)H\(_6\)S, Aldrich 98+% purity), 2,5-dimethylthiophene (C\(_6\)H\(_8\)S, Aldrich 98+% purity) species, were selected as key sulfur containing species in gasoline. 1,3,5-trimethylbenzene (C\(_9\)H\(_{12}\), Sigma Aldrich 98% purity, Mesitylene) was employed to model gasoline components. 1.2 wt% of thiophene, 1.2 wt% of 2-methylthiophene and 1.2 wt% of 2,5-dimethylthiophene were used to establish sulfur selective adsorption.

### 3.3 Physicochemical Characterization

The physical chemical characterization of the FCC catalyst and the additive were performed using the following analysis:

- X-ray diffraction (XRD)
- N\(_2\) adsorption isotherm (BET, t-plot and DFT porosity distribution)
- Temperature programmed of desorption (TPD)
- Temperature Programmed Reduction (TPR)
- Temperature Programmed Oxidation (TPO)
- Fourier Transform Infrared Spectroscopy (FTIR)
- Scanning Electron Microscopy (SEM)
- UV–vis spectra (UV-vis)
- Fluoroscence of X-Ray (XRF) to detect the metals the composed the solids
- Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) to quantify Zn content in the solids
- Raman spectroscopy
3.3.1 X-Ray Diffraction (XRD)

The XRD analysis was effected by using Cu as an anode material, and by using Ni filtered CuK$_\alpha$ radiation ($\lambda = 0.15406$nm) in an Ultima IV X-Ray diffractometer from Rigaku. The XRD analyses were performed in the 5° to 60° of the 2$\theta$ range.

3.3.2 N$_2$ Isotherms

BET was used to evaluate the specific surface area and pore size distribution. Nitrogen adsorption was carried out at 77.818 K using a 3 Flex 3.02 Analyzer Model from Micromeritics. The materials were degassed at 300 °C for 4 h. Nitrogen adsorption covered the 10$^{-8}$ to 1 relative partial pressure range.

Pore size distributions were calculated using BHJ method (Webb and Orr 1997). The pore radio distribution was established using the N$_2$ isotherm data for each material. Appendix D reports in detail the equations used to asses this parameter.

3.3.3 Temperature Programmed Studies (TPD, TPR and TPO)

The TPD NH$_3$ analysis was carried out using an AutoChem II 2920 Analyzer from Micromeritics. Samples were pretreated using helium gas for 2 h at 500 °C. Following this, ammonia was adsorbed for 1 h at 100 °C using a NH$_3$/He gas mixture (4.52 % ammonia, 95.58 % helium) at a 50.3 STP cc/min. Then, the sample temperature was increased linearly using a 15 °C/ min ramp until 580 °C was reached. The resulting desorption peaks were recorded using the instrument thermal conductivity detector (TCD).

In addition, CO$_2$-TPD was implemented in the AutoChem II 2920 Analyzer from Micromeritics as follows: 1) Samples were preheated under helium gas flow for 1 h at 550 °C, 2) CO$_2$ was adsorbed for 1 h at 50 °C using a CO$_2$/He gas mixture (9.89 v% of CO$_2$ in He), and 3) CO$_2$ was desorbed using a 20 °C/ min temperature ramp until 680 °C was reached.

Furthermore, and before proceeding to the TPR and TPO analyses, the Zn-OFF zeolites were calcined at 550°C for 7 h under an air flow. Furthermore, and during the TPR and
TPO analyses, the temperature was increased linearly by a 10 °C/min ramp until 680 °C was reached. TPR and TPO used an H₂/Ar gas mixture (9.89% Hydrogen) for zinc oxide reduction and an O₂/He mixture (5.0% Oxygen) for zinc oxidization.

3.3.4 UV-Vis Spectra

The UV–Vis spectra were obtained using a Shimadzu UV-Vis-NIR Spectrometer UV-3600. During the analyses, barium sulfate was used as reflectance standard. The OFF samples were diluted with barium sulphate to obtain a 5wt% zeolite solid mixture.

3.3.5 Scanning Electron Microscopy (SEM)

SEM analyses were carried out using a Hitachi S-4500 Field Emission SEM Instrument with a Quartz PCI XOne SSD X-Ray Analyzer. The zeolite crystallites were dispersed using sonication in methanol, with platinum oxide glass used as conductive substrate during SEM analyses.

3.3.6 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR measurements were run in a Bruker IFS55 FTIR Spectrometer with a 4 cm⁻¹ resolution and 100 scans. The samples were diluted as 50 vol% of additive in KBr, approximately. The KBr was used to obtain the FTIR spectrum background. Prior to the analysis, samples were saturated with pyridine at 120 ºC for one hour using a N₂-pyridine stream. Then, the unbounded pyridine was flushed using a N₂ flow at 120 ºC for one hour. After this, the adsorbed pyridine was analyzed using a Diffuse Reflectance Fourier-Transform Infrared Spectrometer (DRIFTS).

3.3.7 Chemical Characterizations (XRF and ICP)

The Zn chemical content was determined by using Inductively Coupled Plasma Atomic Emission Spectroscopy at the Biotron at the University of Western Ontario (ICP-AES; Perkin Elmer Optima 3300 Dual View). Al, Si, Fe, and Na contents were established using XRF from a Bruker Analyzer at the Biotron at the University of Western Ontario. Prior to the XRD analysis, all samples were dissolved in aqua regia.
3.3.8 Raman Spectra

Raman spectra were obtained using a Renishaw Model 2000-Laser Raman Spectrometer. Excitation of the samples was carried out with a 633nm wave of Ar ion laser.

3.4 Reaction system

Experiments were carried out using the CREC Riser Simulator (de Las a 1992). A schematic diagram of CREC Riser Simulator is shown in the Figure 3-1. The hearth of the set up consists of an upper and lower shell that allows the catalyst to be loaded and unloaded easily into a basket. This basket is located in the lower reactor shell.

The catalyst basket is contained in between by two grids, which trap the catalyst and restrict its mobility within the basket.

![Figure 3-1. Schematic Description of the CREC Riser Simulator, adapted from Ahmed et al. (Ahmed et al. 2016)](image-url)

The CREC Riser Simulator reactor is designed to create an annular space between the outer portion of the basket and the inner walls of the bottom shell. This space allows the recirculation of chemical species in the reactor by the rotation of an impeller positioned above the catalyst basket. A metallic gasket is used to seal the two chambers. Additionally,
a packing gland assembly with a cooling jacket supports and seals the impeller shaft. As the impeller rotates, a low-pressure region is formed in the center region of the impeller blades. As a result, gas introduced into the bottom shell of the reactor is induced to move upwards through the catalyst basket. Upon entering the basket, the gas mixes with the catalyst and causes the solid particles to fluidize, improving the contact between the gas and solid phases. Gas mixing patterns in a CREC Riser Simulator can be represented as ideal batch well-mixed unit.

The reactor volume is found to be 60.1±0.8 cm$^3$. This volume includes the reactor and the connecting lines within the reactor and the 4-port valve (4PV). A detailed explanation of the procedure followed to measure the reactor volume is reported in the appendix A of Aponte’s M.E.Sc. dissertation (Aponte 2011).

It is important to highlight that the CREC Riser Simulator provides a close mathematical analogy of continuous riser and downer units (refer to Figure 3-2). Various significant reactivity conditions such as C/O, partial pressures, temperatures and reaction times are closely matched to the ones of the larger scale unit.
Figure 3-2. Schematic comparison of the similarity of reaction conditions in a downer catalytic reactor and in the CREC Riser Simulator where both C/O, partial pressures, temperatures and reaction times are matched.

The CREC Riser Simulator operates in conjunction with: a) a four-port valve, which enables the connection and isolation of the reactor, b) a vacuum box, and c) a series of sampling valves (six-port valve) that allow the withdrawal of reaction products in short periods of time. The sampling system also allows sending the reaction product sample to the analytical system. Figure 3-3 reports a schematic diagram of the CREC riser simulator experimental setup.

All the connections and vacuum box of the CREC riser simulator were replaced by Sulfinert™ coated tubing in order to avoid adsorption and desorption of sulfur compounds in the lines.
The CREC Riser Simulator is equipped as well with three ways valves: $V_1$ and $V_2$ valves. $V_1$ valve is used to select the gas carrier (air or argon) fed to the reactor and vacuum system. Argon is used during reaction period as an inert gas while air for coke combustion during catalyst regeneration. $V_2$ valve is used to vent the system or create vacuum in the system or help to connect the vacuum box with vacuum pump.

Valves $V_{3a}$ and $V_{3b}$ are on-off valves which separate the vacuum box from the vacuum pump. All valves are of the solenoid type and are controlled from the control panel.
The 4-port chromatographic valve (4PV) connects the reactor with the air/argon supply at one end, as well as with the vacuum system at the other end. In the open position, the following is accomplish: a) the gases (Ar or reaction products) flow in entering to the reactor through the inlet port and out of the reactor through the outlet port, b) the gases (Ar or reaction products) leaving the reactor are transferred to the vacuum box. In the 4PV closed position, the reactor is isolated from the rest of the sampling system, while the argon carrier gas bypasses the reactor and flows directly into the vacuum chamber.

A Sulfinert™ coated vacuum chamber is connected to the 4PV. This vacuum box volume is 1175 ± 3 cm³ as reported in Aponte’s M.E.Sc. dissertation (Aponte 2011). This volume includes the vacuum chamber, connecting lines, 6PV and sample loop. This large volume allows quick and easy removal of reactor content from the smaller volume of the CREC Riser Simulator.

Additionally, a large pressure difference is obtained using a vacuum pump in order to remove the reactor contents effectively (45-47 psi). Pressure traducers connected to both the riser and vacuum box allow one the measure the pressures in both systems. The reaction time is set with a timer connected to the actuator of the 4PV. This timer is linked to a micro switch located in the manual injector. When the plunger of the syringe is pushed all the way forward to deliver its contents to the reactor, the injector switch is pressed and the timer is started. Once the required reaction time is reached, the actuator opens the 4PV and the reactor is emptied due to the pressure difference between the reactor and the vacuum box. As a result, these two chambers causes reaction products to be evacuated from the reactor towards the vacuum box. This evacuation, which occurs almost instantaneously, leads to a sudden drop in the reactor pressure.

A 6-port chromatographic valve (6PV) is installed after the vacuum box. This valve has two allowed positions: load and inject. These two valve positions provide two independent paths for the gases. The “load” position allowed the sample loop to be filled with a product sample. The “inject” position connects the sample loop with the helium carrier gas line, allowing the product sample to be directed to the GC.
The chromatographic valves (4PV and 6PV) and vacuum chamber are located inside of the heated box. A thermocouple placed inside the heated box is used to measure and control the temperature of the vacuum system. The vacuum box temperature is always set at 250°C to avoid condensation of products. The temperature of the line connecting the 6PV and GC was also kept at 250-270 °C, using a heating tape.

Pressure transducers are installed in both reactor and vacuum box chambers to monitor the progress of each experiment.

One should notice that any further chemical species reaction in the vacuum box is prevented given the low temperature of the vacuum box (250 °C) and absence of the catalyst.

3.5 Experimental Procedure

Thermal and catalytic runs were performed in the above described reactor set-up. Fluidizable solid samples of the above mentioned additive and/or catalyst were contacted in the CREC Fluidized Simulator with thiophene, 2-methylthiophene and 2,5-dimethylthiophene blended with 1,3,5-trimethylbenzene. Selected experimental conditions were as follows: a) Total initial pressure: 25 psi, b) Temperatures: 510, 530 and 550 °C, c) Contact times: 3, 5 and 7 s, d) Additive to oil mass ratio: 0.3, 0.6 and 0.9, e) Additive and FCC commercial catalyst blends mass ratios at: 0/100, 10/90, 20/80, 30/70 and 100/0 (total C/O = 6), f) Impeller velocity to secure good fluidization: 5700 rpm. At least 3 repeats for each one of the experiments and for every condition studied were performed.

Thus, each injection into the GC gave three chromatographic signals. The combined information of these three GC analyses allowed both the identification and the quantification of various hydrocarbons free of sulfur species, as well as of the quantification of sulfur containing species (refer to Appendix B).

The coke formed on the additive was measured using a Total Organic Carbon Analyzer (TOC V) with a Solid Sample Module (SSM 5000A) from Shimadzu. The TOC analysis
was performed once every run completed and following the total evacuation of the reactor contents.

Moreover, in the runs with the additive and the FCC catalyst blends, a separation of these two components was performed prior to the TOC analysis, using standard screen meshes. This was possible given that the FCC catalyst particles were all larger than 53 μm and the additive particles in the 45-53 μm range. The TOC analysis of these two particle fractions allowed determining the coke formed on both the FCC catalyst and the additive.

One gram of the mixture of additive and FCC catalyst was loaded in the catalyst basket. The reaction system was sealed, leak tested and heated to the reaction temperature in argon atmosphere. Then, the feed was injected, and once the preselected reaction time was reached, the reaction products were evacuated from the reactor and sent to the analytical system via the heated transfer line.

A number of systematic steps were involved in each run in the CREC Riser Simulator. These various steps were followed with pressure changes as recorded by the pressure transducer. As explained in the in the below Section 4.1 two different experimental set up were performed in each operation condition.

### 3.5.1 Balance level 2: Reactor Quasi Total Evacuation

Regarding the Balance level 2 - Reactor quasi total evacuation, it is a typical perform with “quasi” complete evacuation of CREC Riser Simulator contents. One specific example of this, is reported in the M.E.Sc. thesis (Aponte 2011). For instance, for 0.1 g of Zn(3.5wt%)-OFF additive at 530 °C and 5 s is presented in the following steps:

**Step 1)** The reactor was loaded with 0.100 ± 0.001 g of a Zn(3.5wt%)-OFF additive.

**Step 2)** The CREC Riser Simulator at 530 °C, was purged with an inert gas (argon) and the reactor pressure (P_r) was set at 25.1 psi.

**Step 3)** The vacuum box at 250°C is evacuated until the vacuum box pressure (P_vb) reached a desired vacuum pressure value, in this case 1.44 psi.
Step 4) Following this, a 0.1686 g liquid reactant amount is injected. This time is \( t = 0 \) s for the experiment. Then, the reactant sample is vaporized and reacted with the catalyst section.

Step 5) Once the desired reaction time elapsed (\( t = 5 \) s), most of reactor contents were transferred towards the vacuum box with both the pressure of the reactor and vacuum box reaching an equilibrium level.

Step 6) Once the previous steps were completed, the recorded information with \( P_{vbf}-P_{vbi}=1.46 \) psi is used to calculate the carbon and sulfur elemental balances as reported in Appendix C.

After the run was completed, the reactor was cooled down. The additive was discharged from the reactor. Thus, coke was measure in the spent additive. For those cases that involved a mixture of additive and FCC commercial catalyst, following the discharge a separation of the two material was affected by sieving the particle fractions. Then, coke and sulfur were measured separately for both the FCC catalyst and for the additive.

Regeneration conditions were set at 580 °C and 30 min of air flow. Under these conditions coke is expected to be fully removed from both FCC catalyst and additives.

### 3.5.2 Balance Level 1: Gas Phase Sampling

A modification in the experimental steps were established when Balance Level 1- Gas Phase was studied (refer to Chapter 4). In this case, the vacuum box was operated at pressure conditions relatively close to the one of the reactor. To develop these runs, new MS, FID and FPD calibrations (base line) were adopted.

The upcoming paragraphs describe an example, of a run for Balance Leve 1- Gas Phase using: 0.1 g of Zn(3.5wt%)-OFF Additive at 530 °C and 5 s as follows:

Step 1) The reactor was loaded with a 0.100± 0.001 g of additive particle.

Step 2) At 530 °C, The CREC Riser Simulator was purged with an inert gas (argon) and the reactor pressure (\( P_{ri} \)) was set at 25.5 psi.
Step 3) The vacuum box was set at 250°C and 39.4 psi. Then, $P_{vb}$ reached a desired delta pressures of 8-9 psi, between the reactor and vacuum box. This allowed the transfer of a reactor gas sample to the vacuum box. One can thus, notice that under these conditions, a sample coming essentially from the gas phase is transferred to the vacuum box for further analysis (refer to red trace in Figure 4-1).

Step 4) Following this, a 0.171 g liquid reactant amount was injected. This time ($t = 0$ s for the experiment) is reported as point A in Figure 4-1. Then, the reactant sample was vaporized as reported in Figure 4-1 at point A-B. Then, it reacted with the catalyst section (point C-B in Figure 4-1).

Step 5) Once the desired reaction time elapsed ($t = 5$ s), or point C in Figure 4-1 was reached, a limited fraction of reactor products (e.g. about 20-30% of all chemical) were transferred from the reactor to the vacuum box. Then, the reactor and the vacuum box pressures reached equilibrium (e.g. 40 psi, refer to point D in the Figure 4-1).

Step 6) Once the previous steps were completed, the recorded information (reported in Figure 4-1) with a $P_{vbr} - P_{vb} = 0.26$ psi was used to calculate carbon and sulfur elemental balances reported in Appendix C. It is important to highlight that for this example, the carbon balance closure was 0.77%, which represent an excellent result.

3.6 Products analysis

Identification and quantification of chemical species were performed in 6890N gas chromatograph (GC) connected to an Agilent 5973N mass selective detector (MSD). The MSD was used to identify the reaction products. The GC was also connected to a flame photometric detector (FPD) and flame ionization detector (FID), which allowed the quantification of the products. More specifically the FPD was used for detection of sulfur compounds. Prior to the experimental runs calibration curves correlating calculated areas and concentrations of sulfur in hydrocarbon mixtures were developed (refer to Appendix A). In addition, the FID was employed to quantify the hydrocarbon species as well as the sulfur species.
The MSD was operated in the scan mode using the parameters detailed in the Table 3-1. The reaction products were identified. The retention times of the peaks found with the MSD ion detector and the retention times of the peaks in the FID/FPD chromatograms were compared.

### Table 3-1. Mass selectivity Detector parameters

<table>
<thead>
<tr>
<th>Parameters/Setting</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transfer Temperature</td>
<td>280°C</td>
</tr>
<tr>
<td>Tune File</td>
<td>ATUNE2.U</td>
</tr>
<tr>
<td>EM Voltage</td>
<td>0</td>
</tr>
<tr>
<td>Solvent delay</td>
<td>0 min</td>
</tr>
<tr>
<td>Acquisition mode</td>
<td>SCAN</td>
</tr>
<tr>
<td>Threshold</td>
<td>150counts</td>
</tr>
<tr>
<td>Sample rate 2nd</td>
<td>2</td>
</tr>
<tr>
<td>Mass range</td>
<td>5-500</td>
</tr>
<tr>
<td>Scan/sec</td>
<td>2.97</td>
</tr>
</tbody>
</table>

The GC used was equipped with two columns: 1) Shimadzu SHRXI-5MS and 2) HP-5. They were dimethylpolysiloxane capillary columns with a length of 30 m and a nominal film thickness of 0.25 µm. They permitted the separation of the various chemical species present in the samples. Both columns were connected to the back inlet of the GC. While one of the column ends was linked to an MSD directly, the other one was equipped with a splitter and coupled to both FID and FPD detectors. In this manner, each single injection produces three signals, one per detector. Detector configurations allowed identification and quantification of various hydrocarbon species as well as sulfur containing species in the hydrocarbon mixture. Table 3-2 provides a detailed description of the method used for each detector.

The GC oven program was run using the following thermal ramp: a) Initially the oven temperature was set at 40 °C for 10 min, b) Following this, the temperature was increased at 8 °C/min to 70 °C, and c) Finally, and once 70 °C was reached, the temperature was raised at 15 °C/min to 250 °C.
Table 3-2. Gas Chromatography method

<table>
<thead>
<tr>
<th>Parameter/Setting</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Inlet</strong></td>
<td></td>
</tr>
<tr>
<td>Mode</td>
<td>Split</td>
</tr>
<tr>
<td>Gas</td>
<td>He</td>
</tr>
<tr>
<td>Temperature</td>
<td>310 °C</td>
</tr>
<tr>
<td>Pressure</td>
<td>8.13 psi</td>
</tr>
<tr>
<td>Split ratio</td>
<td>25:1</td>
</tr>
<tr>
<td>Total Flow</td>
<td>76.3 ml/min</td>
</tr>
<tr>
<td><strong>Column 1</strong></td>
<td></td>
</tr>
<tr>
<td>Detector</td>
<td>MSD</td>
</tr>
<tr>
<td>Outlet</td>
<td>Vacuum</td>
</tr>
<tr>
<td>Mode</td>
<td>Constant Flow</td>
</tr>
<tr>
<td>Inlet Back Flow</td>
<td>1.1 ml/min</td>
</tr>
<tr>
<td><strong>Column 2</strong></td>
<td></td>
</tr>
<tr>
<td>Detector</td>
<td>FID/FPD</td>
</tr>
<tr>
<td>Outlet</td>
<td>Ambient</td>
</tr>
<tr>
<td>Mode</td>
<td>Constant Flow</td>
</tr>
<tr>
<td>Inlet Back Flow</td>
<td>1.7 ml/min</td>
</tr>
<tr>
<td><strong>Detector</strong></td>
<td>FID</td>
</tr>
<tr>
<td>Temperature</td>
<td>310 °C</td>
</tr>
<tr>
<td>Hydrogen Flow</td>
<td>40 ml/min</td>
</tr>
<tr>
<td>Air Flow</td>
<td>450 ml/min</td>
</tr>
<tr>
<td>Makeup gas type</td>
<td>N₂</td>
</tr>
<tr>
<td>Makeup flow</td>
<td>45 ml/min</td>
</tr>
<tr>
<td>Lit offset</td>
<td>2.0</td>
</tr>
<tr>
<td>Type</td>
<td>Front detector</td>
</tr>
</tbody>
</table>

The GC/MSD analytical system was operated using the MSD Productivity ChemStation, which is an integrated GC/MS software application for all the tasks associated with GC/MS data acquisition, data processing, and reporting.
3.7 Identification of the compounds retained on the catalytic materials

The coke deposited on the FCC catalyst and on the additives was measured as CO\textsubscript{2} formed using the Shimadzu Total Organic Carbon Analyzer (TOC-V) with a solid sample module (SSM-5000A). This equipment was previously calibrated using glucose to quantify the mass of carbon.

It has to be mentioned that coke was measured independently in both the FCC catalyst (> 53 μm) and in the additive (45-53 μm). A separation of these two components was performed prior to the TOC analysis, using standard screen meshes. This method was established by Aponte (Aponte 2011).
Chapter 4

4 Quantification of the Selective Adsorption

Aponte et al. (Aponte 2011; Aponte, Djaouadi, and de Lasa 2014) proposed a novel additive for gasoline sulfur reduction in FCC units. Thiophene selective adsorption, was demonstrated using a CREC Riser Simulator. The additive was designated as HIPZ-D. Its demonstrated performance was based on chemical species recovered, resulting from the fast evacuation from the reactor (refer to section 3.5.1). Selected operating conditions of the study did not allow one to distinguish between adsorbed species and species in the gas phase.

Thus, and to provide an accurate quantification of selective adsorption, a modified experimental method was developed in the context of the present PhD research. The proposed method considers sampling the CREC Riser Simulator atmosphere under controlled pressure conditions. Chemical species sampled represent those contained in the gas phase only. This additional information allowed quantification of the sulfur species adsorption in the additive.

The proposed methodology allowed performing carbon and sulfur balances.

4.1 Quantification Method

The selective adsorption and quantification of adsorbed sulfur species were established developing experiments in the CREC Riser Simulator with two types of evacuations as described Figure 4-1:

a) *Gas Phase Product Sampling.* This was accomplished having a limited total pressure difference (8-9 psi) between the reactor and the vacuum box prior to sampling. When the vacuum box and the reactor were connected, only gas phase species were transferred.

b) *Quasi Total Reactor Evacuation.* This was effected having a significant total pressure difference between the reactor and the vacuum box (e.g. 46-47 psi) prior to evacuation.
When the vacuum box and the reactor chambers were connected, a quasi total removal of the chemical species from the CREC Riser Simulator reactor was achieved.

Figure 4-1. Pressure Data for Balances Levels 1 and 2: a) Balance Level 1: Gas Phase Product Sampling, Vacuum Pressure (▲) and Reactor Pressure (△), b) Balance Level 2: Quasi-Total Product Evacuation, Vacuum Pressure (■) and Reactor Pressure (□). Run conditions: 0.1 g of Zn(3.5wt%)-OFF Additive at 510 ºC and 7 s.

On the basis of the above and of the GC analysis of samples, the following carbon and sulfur balances were established:

4.1.1 Balances Level 1: Gas Phase Sulfur and Carbon Balances

The Balance Level 1 involved the gas phase sulfur and carbon balances. As stated above, a controlled total pressure difference of 8-9 psi was kept between the reactor and the vacuum box prior to reactor sampling. By using this data, one is able to quantify both the sulfur \( \left( S_{ads} \right) \) as well as the carbon \( \left( C_{ads} \right) \) contained in the adsorbed species as follows:

\[
S_{ads} = \frac{S_{in} - S_{out \ gas \ phase}}{S_{in}} \times 100 \tag{4-1}
\]
\[ S_{in} = X_{\text{injected}} m_{\text{injected}} \]  
\[ S_{out} = \sum_{i=1}^{n} Y_{i,sp} m_p \]  
\[ C_{\text{ads}} = \frac{c_{\text{in}} - c_{\text{out, gas phase}}}{c_{\text{in}}} \times 100 \]

where \( S_{in} \) represents the total sulfur species fed to reactor (sulfur in thiophene or 2-methylthiophene or 2,5-dimethylthiophene), \( X_{\text{injected}} \) stands for the sulfur mass fraction for thiophenic species, \( m_{\text{injected}} \) denotes the hydrocarbon mass fed to the reactor, \( S_{out} \) is the total sulfur amount element in the gas phase, \( Y_{i,sp} \) refers to the fraction of sulfur containing species, \( m_p \) represents the total mass of products, \( C_{\text{in}} \) stands for the total elemental carbon fed to the reactor, \( C_{\text{out, gas phase}} \) denotes the total elemental carbon in the gas phase species after a set reaction time.

Regarding \( m_p \), it was determined by establishing the total moles of product species including those in the reactor and in the vacuum box. In addition, these calculations involved the ideal gas law and the average molecular weight of the product mixture on an argon free basis (refer to Appendix C).

### 4.1.2 Balances Level 2: Typical Sulfur and Carbon Balances

The Balance Level 2 considers sulfur and carbon balances following reactor evacuation or Stripping 1. To accomplish this, the vacuum box was kept at 1.6 psi prior to reactor evacuation. The connection of the reactor with the vacuum box allowed evacuating of “weakly adsorbed” sulfur and hydrocarbon species from the Zn-OFF additive or/and the FCC catalyst. On this basis, a \( C_{\text{balance}} \) and a \( S_{\text{balance}} \) (elemental carbon and sulfur balances) also designated as \( C_{\text{stripping 1}} \) and \( S_{\text{stripping 1}} \) were effected as follows:

\[ S_{\text{stripping 1}} = S_{\text{balance}} = \frac{S_{\text{in}} - S_{\text{out, total}}}{S_{\text{in}}} \times 100 \]

where \( S_{\text{in}} \) (refer to Eq. 4-2) represents the total sulfur species fed to the reactor, and \( S_{\text{out, total}} \) (refer to Eq. 4-3) denotes the sulfur species recovered after quasi-total evacuation of product species.
\[ C_{\text{stripping 1}} = C_{\text{balance}} = \frac{C_{\text{in}} - C_{\text{out, total}}}{C_{\text{in}}} \times 100 \quad (4-6) \]

Where \( C_{\text{out, total}} \) is the carbon recovered from the gas phase after evacuating the reaction products.

4.1.3 Balances Level 3. Sulfur and Carbon Balances Based on Solid Residues

Concerning the sulfur and carbon balances based on solid residues left or stripping 2, they were performed after each run completed. The solid particles were left following under argon flow for 2-3 minutes. Solid samples were separated into two fractions using particle sieving: a) the additive and b) the catalyst. Calculations were developed using Eqs. (4-7) and (4-8):

\[ S_{\text{stripping 2}} = \frac{\text{Coke solid} \times m_{\text{solid}} \times MW_S}{S_{\text{in}} \times MW_C \times C/S} \times 100 \quad (4-7) \]

\[ C_{\text{stripping 2}} = \text{coke yield} = \frac{\text{Coke solid} \times m_{\text{solid}}}{C_{\text{in}}} \times 100 \quad (4-8) \]

where \( S_{\text{stripping 2}} \) and \( C_{\text{stripping 2}} \) represent the total sulfur and carbon in coke, \( \text{Coke solid} \) stands for the carbon ratio as grams of C /100 grams of solid (catalyst or additive), \( m_{\text{solid}} \) denotes the mass of catalyst or additive in the reactor, \( C/S \) refers to the carbon/sulfur molar ratio used in the computations. In addition, \( MW_S \) and \( MW_C \) stand for the atomic weight of S and C, respectively. Regarding the C/S ratio, a typical expected value of 5 was considered.

4.2 Base line and Thermal runs

To establish the thermal conversion effects more than 100 runs using the CREC Fluidized Riser Simulator unit without the catalyst or/and the additive being loaded.

Seven different concentrations of thiophene and 2-methylthiophene in TMB solutions were used. These runs were carried out to establish the response of the different detectors used for the planned experiments (FID, FPD, MS), under high and low argon dilution. The
repeated experiments allowed as well, to calibrate the FID, MS and FPD detectors for Th and 2MTh species (refer to Appendix A).

Once calibrations were completed, Balance Level 1 and 2 were performed for thermal cracking runs of Th/TMB and 2MTh/TMB mixtures. One should mention that no significant Th and 2MTh conversions were observed under the various temperatures and reaction times studied. Sulfur and Carbon balances were established, resulting for; a) Balance Level 1: $S_{\text{ads}}$ and $C_{\text{ads}}$, and b) Balance Level 2: $S_{\text{balance}}$ and $C_{\text{balance}}$, and were essentially zero in all cases. In addition, carbon balances were established using: 1) $R_x$: reactor pressure balance only, and 2) $R_x-P_v$: reactor and vacuum box pressure balances (refer to Appendix C). An example of a thermal run is reported in Figure 4-2 with no thermal cracking being observed.

As a result, the thermal cracking runs or “blank runs” helped establish the additive and/or the FCC catalyst effects.

![Figure 4-2. Sulfur and Carbon balances calculated with data from thermal runs at 1.2wt% of 2MTh in TMB at 530 C and 7s. Notes: The left hand bars are for Balance Level 1 calculated with Eq. (4-1) and (4-4). The right hand bars are for Balance Level 2: after quasi total evacuation using Eq. (4-5) and (4-6). Three quantifications were done using MS, FID and FPD for sulfur detection.](image)


4.3 Adsorption Study: Using Thiophene as Sulfur Containing Species

This section reports the various activities developed to quantify the sulfur selective adsorption by using HIPZ-D additive. Thiophenic selective adsorption properties were reported for this additive in (Aponte 2011; Aponte, Djaouadi, and de Lasa 2014). In these experiments, a blend of 10 wt% HIPZ-D additive and 90% of FCC commercial catalyst was used. This was done to demonstrate the high potential of thiophene selective adsorption.

Regarding the selective adsorption of sulfur species, it was confirmed unambiguously using the method reported in section 4.1 with gas phase species from the CREC Reactor Simulator analyzed only. Figure 4-1 reports an example of this type of gas phase product analysis using restricted total pressure change (5-7 psi).

One should emphasize that the described definition of $S_{ads}$ and $S_{balance}$ can be established for every experimental run, with this allowing the quantification of the selective adsorption of sulfur species in the HIPZ-D additive.

4.3.1 Experimental Runs with Thiophene/TMB Mixture using 10% HIPZ-D Additive +90% FCC Catalyst

Thus, one the thermal runs were completed, runs were effected using Th at 1.2 wt% in TMB at 530°C and 7s. One should notice that in this series the HIPZ-D additive and FCC catalyst mixture was loaded in the CREC Riser Simulator Reactor.

Figure 4-3 reports both $S_{ads}$ and $S_{balance}$ using Eq. (4-1) and (4-5). It can be observed that the $S_{balance}$ remains in the 1 ±3 wt % at quasi complete product species evacuation (right hand side-brown bar in Figure 4-3). One should notice that the sulfur balance ($S_{balance}$) is expected to have ±3% error. Regarding the Sulfur Balance Level 2, the MS, helped to establish the missing sulfur species in the balance.
Regarding \( S_{ads} \), it was calculated using the three techniques: MS, FID and FPD. In all the cases, the quantified amount of adsorbed sulfur was in the range of 26-29 wt\%, with new formed sulfur species being in less amounts.

Figure 4-3. Sulfur and Carbon balances calculated with data from catalytic cracking runs using 10wt\% of HIPZ-D Additive and 90\% of FCC catalyst blends. Notes: a) 1.2wt\% of Th in TMB at 530 C and 7s, b) The left hand bars are for Balance Level 1 calculated with Eqs. (4-1) and (4-4), c) The right hand bars are for Balance Level 2: after quasi total evacuation using Eqs. (4-5) and (4-6). Three quantifications were done using MS, FID and FPD for sulfur detection.

Figure 4-3 compares carbon balances performed using the Eqs. (4-4) and (4-6) for Balance Level 1 \( (C_{ads}) \) and Balance Level 2 \( (C_{balance}) \).

Regarding the light and dark blue bars in the left side in Figure 4-3, they represent \( C_{ads} \) (e.g. \( C_{ads} \) 5.6 ± 0.3 wt\%). This shows the limited adsorption of hydrocarbon species. Supporting this observation, is the finding that the reported \( C_{balance} \) in Figure 4-3 (right hand side blue bars) is 3 ± 2 wt\%. This is in contrast, with the more significant sulfur containing species adsorption with \( S_{ads} \) being 26 ±3 wt\% (left hand side brown bar in Figure 4-3).

Other important observations from these runs are the alkylthiophene species fraction formed such as methylthiophenes, di-methylthiophenes, and methyl-ethylthiophenes. All
these species combined represent 16 ± 1 wt% of the total recovered sulfur after quasi total reactor evacuation with no sulfur alkyl species in the reactor gas phase sample. On this basis, it can be hypothesized that the selective adsorption process in the HIPZ-D additive involves alkylated species.

Table 4-1 reports the results of Balance level 3. One can observe the low sulfur left as coke in the additive.

Table 4-1. Sulfur and Carbon balances evaluated at Balance Level 3 using data from catalytic cracking runs using 10wt% of HIPZ-D additive and 90% of FCC commercial catalyst blends and 1.2wt% of Th in TMB at 530 C and 7s.

<table>
<thead>
<tr>
<th></th>
<th>HIPZ-D additive</th>
<th>FCC Catalyst</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>S_{stripping 2}, wt%</td>
<td>0.20</td>
<td>2.43</td>
<td>2.63</td>
</tr>
<tr>
<td>Coke yield, wt%</td>
<td>0.53</td>
<td>0.70</td>
<td>1.23</td>
</tr>
</tbody>
</table>

4.3.2 Experimental Runs with Thiophene/TMB Mixture using HIPZ-D Additive only

Given the above described findings (section 4.3.1), it was thus felt, that additional clarification of the selective adsorption quantification and mechanism was required. With this end, the following was effected in runs using the CRC Riser Simulator: a) A 0.1 g of HIPZ-D additive with no FCC catalyst added was loaded, b) A 0.17 g of combined 1.2 wt% thiophene and 98.8 wt% was injected. One should note that the 0.1g of additive used is equivalent to 10% additive in the additive in 1g of Additive-FCC catalyst blend, proven to be most effective for thiophene selective adsorption.

Figure 4-4 shows that S_{ads} and S_{balance} were respectively 1 ± 2wt% and 0 ± 1wt % (brown bars) when these parameters were calculated before and after evacuation. As well, the C_{ads} and C_{balance} (blue bars) were consistently in the 1-2 wt% deviation range. Considering these results, it can be concluded that thiophene selective adsorption does not take place on the HIPZ-D additive directly. It appears that concurrent alkylation of C3-C5 groups is required (produced by the FCC commercial catalyst) for this to happen.
Figure 4-4. Sulfur and Carbon balances calculated with data from runs using 0.1 g of HIPZ-D Additive and 1.2 wt% of Th in TMB at 530 °C and 7s. Notes: The left hand bars are for Balance Level 1, which is calculated with Eqs. (4-1) and (4-4). The right hand bars are for Balance Level 2, which represents “quasi” total evacuation using Eqs. (4-5) and (4-6).

4.3.3 Experimental Runs with 2-Methylthiophene/TMB using HIPZ-D Additive only

Figure 4-5 reports the quantification of adsorbed sulfur species for these runs. Left hand bars report the results of Balance Level 1 using Eqs. (4-1) and (4-4). And the right hand bars Balance Level 2: after quasi total evacuation using Eqs. (4-5) and (4-6). It is observed that 23 ±5 wt% of sulfur (brown bar) is now adsorbed as quantified with gas phase sulfur species using the method described in the section 4.1.

It is important to mention that a consistent 9-11 wt% of thiophenic species with different alkyl groups is now observed. The more abundant observed sulfur species were the 3-methylthiophene, followed by di-methylthiophenes and by thiophene.
Figure 4-5. Sulfur and Carbon balances calculated with data from the runs utilizing 0.1g of HIPZ-D Additive and 1.2wt% of 2MTh in TMB at 530 ºC and 7s. Notes: The left hand bars are for Balance Level 1 calculated with Eqs. (4-1) and (4-4). The right hand bars are for Balance Level 2: after “quasi” total evacuation using Eqs. (4-5) and (4-6)

One can notice that new thiophenic species were observed using 2-methylthiophene and this on the basis of product samples analyzed. Figure 4-6 provides insights into the role of alkylation for selective sulfur species adsorption. For instance, in the case of thiophene and 2-methylthiophene, the HIPZ-D additive displays selective adsorption when alkylthiophene species is present only.
Figure 4-6. Yield Product Distribution for runs utilizing 0.1g of HIPZ-D Additive at 530 °C, 7s and using a) 1.2 wt% of Th in TMB, b) 1.2wt% of 2MTh in TMB

Figure 4-7 reports a sulfur species conversion network using the HIPZ-D additive. The network reported includes species as detected in the gas phase analysis and species analysis following total evacuation. One can see that together with the 2-methylthiophene (model compound), there are other sulfur species formed, such as 3-methylthiophene and dimethylthiophene. These other sulfur species formed were detected in minute amounts.
4.4 Conclusions

a) A method was established to quantify the selective thiophenic species adsorption using CREC Riser Simulator. Three different calibrate detectors (FID, FPD, and MS) were used to quantify the sulfur adsorption. It was shown that the use of these three detectors helps quantifying selective adsorption.

b) It was proven that thermal cracking of thiophene, 2-methylthiophene and 1,3,5-TMB at 510°C to 540 °C and 3 s to 7 s, is negligible.

c) It was quantified and demonstrated the selective thiophenic species adsorption using a HIPZ-D additive. This was accomplished by sampling the gas phase as
well as the evacuated gas products and adsorbed species. To achieve this, separate experiments were developed by operating the CREC Riser Simulator and the vacuum box, with two pressure difference modes

d) It was shown that selective adsorption on the HIPZ-D additive is favored by the alkylation of sulfur containing species
Chapter 5

5 Synthesis and Characterization of OFF and Zn-OFF zeolites and additives

This chapter aims to report the OFF and Zn-OFF zeolites and additive-pellets preparation method and characterizations. Detailed descriptions of the methods for preparing each component, and the pelletizing procedures followed, are provided in the subsequent sections.

5.1 Introduction

Offretite zeolite synthesis methods have been studied by several authors. For example, Howden (Howden 1986; Howden 1987b) found that the use of a tetramethylammonium (TMA) template is required for offretite synthesis. This is useful to avoid erionite zeolite formation. In addition, other authors proposed other methods for the OFF synthesis using other templates, cations as well as silicate sources (Yang and Evmiridis 1996; Moudafi et al. 1986; Whyte 1971; Wu et al. 1974).

Furthermore, researchers have also focused on the stabilization of the OFF via dealumination, which yields OFF zeolites with an increased stability and pore volume (Fernandez, Vedrine, et al. 1986; Carvalho et al. 1993). Most recently, an optimization of the synthesis of high pure OFF was achieved by Wang et al. (Y. Wang et al. 2010) via magadiite recrystallization. In addition, Itakura et al. (Itakura et al. 2010) claimed to have developed a method to obtain a highly thermally stable OFF by the hydrothermal conversion of faujasite.

Zinc-loaded zeolites are suitable catalysts for different processes. In this respect, Aponte et al. (Aponte 2011; Aponte, Djaouadi, and de Lasa 2014) proposed a novel alternative for gasoline sulfur reduction in FCC units using additive based on Fe and Zn-Offretite zeolites. A thiophenic selective adsorption process was observed using Offretite topology.
The present study proposes the inclusion of Zn in the OFF zeolites. These modified zeolites are designated as Zn(2.0wt%)-OFF or Zn(3.5wt%)-OFF with this designation referring to the different zinc contents used. To the best of our knowledge, there is no previous study on the effect of Zn inclusion in the OFF structure.

Since 2007, this method has been used to prepare Zn-ZSM5 (L. Wang et al. 2007; J. Gao et al. 2009; Ni et al. 2011; Niu et al. 2014). Most recent, Meng et al. (Meng et al. 2015) reported a method to prepared Zn-ZSM-11. One should notice however, that a different ZSM5 and ZSM-11 zeolites were used in the mentioned studies. These authors claim a better zinc dispersion and superior stability, in the modified zeolites.

Regarding the Zn-OFF, the present study reports an improvement of the selective sulfur species adsorption properties with Zn inclusion. To demonstrate this, fluidizable particles named as the Zn-OFF additive with a 25wt% Zn-OFF zeolite, 50 wt% inert fused alumina and 25wt% of Ludox contents were prepared. The Zn-OFF additive was first evaluated using physicochemical characterization.

The application of the Zn-OFF additives is envisioned for FCC sulfur removal. This approach considers that sulfur species could be adsorbed on the additive with low sulfur left as coke. This thus reduces, the SO\textsubscript{x} formation in the catalyst regenerator, mitigating the overall FCC plant sulfur emissions to the environment.

### 5.2 Syntheses of Offretite and Zn-Offretite Based Additives

Three additives were synthesized. Each additive was prepared with three different active materials or zeolites: Offretite, Zn(2.0wt%)-Offretite and Zn(3.5wt%)-Offretite. Zeolites were mixed with a matrix.

#### 5.2.1 Zeolites: Offretite, Zn(2.0wt%)-Offretite and Zn(3.5wt%)-Offretite

Three types of zeolites were prepared in this study. All of the zeolites synthesized displayed the OFF morphology. The Zn(2.0wt%)-OFF and Zn(3.5wt%)-OFF zeolites however, were
synthetized with the Zn included in the zeolite framework. One should note that the OFF preparation procedures of the present study are in line with previous work (Quesada and Vitale-Rojas 2006; Lechert 1992). These methods differ however, from the ones practiced by others (Arous et al. 2005; Arous et al. 2007; Chen and Garwood 1981). These authors considered metal ions deposited via ion-exchange or metals loaded using incipient wetness.

Figure 5-1 reports a summary of the experimental steps followed in the proposed OFF synthesis method. First, to synthesize the offretite morphology, a viscous gel solution designated as Gel 1 was prepared by blending 1.2 g of aluminum hydroxide hydrate, 2.5 g of sodium hydroxide (NaOH, +99%), 1.2 g of potassium hydroxide (KOH, +99%) and 10 g of distillate water for 30 minutes. This mixture formed a gel as reported in Rx.1 of Figure 5-1. The molar ratio for each zeolite prepared is described in Table 5-1.

Table 5-1. Molar ratio of the zeolite components

<table>
<thead>
<tr>
<th>Molar ratio</th>
<th>Offretite</th>
<th>Zn(2.0wt%)-Offretite</th>
<th>Zn(3.5wt%)-Offretite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃/SiO₂</td>
<td>0.0494</td>
<td>0.0494</td>
<td>0.0494</td>
</tr>
<tr>
<td>ZnO/SiO₂</td>
<td>-</td>
<td>0.0429</td>
<td>0.0858</td>
</tr>
<tr>
<td>(K+Na)₂O/SiO₂</td>
<td>0.4421</td>
<td>0.4421</td>
<td>0.4421</td>
</tr>
<tr>
<td>TMA/SiO₂</td>
<td>0.1153</td>
<td>0.1153</td>
<td>0.1153</td>
</tr>
</tbody>
</table>

Following the preparation of Gel 1, a second gel, designated as Gel 2, was prepared with the following components: 60 g of sodium silicate (26.7 wt% SiO₂, 10.8 wt% Na₂O and 62.5 wt% H₂O) and 14 g of TMA (tetra-methyl-ammonium) at a 5 M concentration. This mixture was stirred for 30 minutes.

Once Gel 1 and Gel 2 were prepared, 17 g of Gel 1 and 74 g of Gel 2 were blended with the progressive addition of Gel 2 into Gel 1. The resulting solution was kept under high stirring conditions for a 3 h period. On this basis, the OFF precursor was obtained with the following expected composition (based on the initial component mixture):

**OFF Precursor** (based on the initial constitutive component mixture):

0.08Al₂O₃: SiO₂: 0.51Na₂O: 0.04K₂O: 0.25TMA: 14.8H₂O
Figure 5-1. Schematic Description of the OFF and Zn-OFF Zeolite Syntheses. Broken line: reports Zn addition for Zn-OFF zeolite synthesis only. Right hand side: Rx.1) Formation of [Al(OH)$_4$]$^-$ unit; Rx. 2-3) Formation of Zn(OH)$_2$ and [Zn(OH)$_4$]$^{2-}$ units

One should note that despite of having set a 12 SiO$_2$/Al$_2$O$_3$ ratio for the OFF precursor (Gel 1 + Gel 2) initial components, a practical SiO$_2$/Al$_2$O$_3$ ratio of 5 was obtained, as reported later. These findings are in agreement with Moudafi et al. (Moudafi et al. 1987) showed that in order to achieve a set SiO$_2$/Al$_2$O$_3$ ratio, more than double of the SiO$_2$/Al$_2$O$_3$ initial component ratios are required.

Furthermore, and to achieve the OFF morphology with added zinc, designated in the present study as Zn-OFF, the OFF synthesis method of Figure 5-1 was modified as follows:

a) Zinc nitrate hexahydrate (Zn(NO$_3$)$_2$, reagent grade) in a 10wt% water solution was added drop-by-drop to Gel 1 (broken line in Figure 5-1). This formed as a result, a so-called Modified Gel 1. The resulting Modified Gel 1 was intensively blended for 30 minutes, securing in this manner, the expected interaction with the available OH$^-$ solution species.
b) Following this, the *Modified Gel 1* was transferred to the *Gel 2* slowly. In addition, an extra 20 g of water were added progressively while mixing *Modified Gel 1* and *Gel 2* to avoid precipitation. The above described method was considered for two different Zn(NO$_3$)$_2$ amounts forming two *Zn-OFF Precursors*. The expected formulas established using the initial amounts of zinc, *Gel 1 and Gel 2* are:

i) **Zn(2.0wt%)-OFF Precursor** (based on the initial constitutive component mixture):

\[
0.08\text{Al}_2\text{O}_3: \text{SiO}_2: 0.53\text{Na}_2\text{O}: 0.04\text{K}_2\text{O}: 0.02\text{ZnO}: 0.25\text{TMA}: 20.4\text{H}_2\text{O}
\]

ii) **Zn(3.5wt%)-OFF Precursor** (based on the initial constitutive component mixture):

\[
0.08\text{Al}_2\text{O}_3: \text{SiO}_2: 0.53\text{Na}_2\text{O}: 0.04\text{K}_2\text{O}: 0.04\text{ZnO}: 0.25\text{TMA}: 20.4\text{H}_2\text{O}
\]

One should mention that the proposed method to prepare the Zn-OFF Precursor addresses the following critical issues:

a) The value of having Zn$^{2+}$ both in a tetrahedral and square-planar coordination (Figure 5-2) as primary building units, and these prior to Zn-OFF Precursor formation. To accomplish this, a pH of 10 is required. This is achieved using NaOH and KOH with a NaOH/KOH molar ratio of 3.14. This approach is supported by the findings of Stahl *et al.* (Stahl, Niewa, and Jacobs 1999) and Debiemme-Chouvy *et al.* (Debiemme-Chouvy *et al.* 1995) who suggested that high pH concentrations are required for the formation of Zn tetrahedral and Zn square-planar coordination.

b) The importance of adding the Zn(NO$_3$)$_2$ solution into the *Gel 1* on a drop-by-drop basis. This is needed to avoid the precipitation of other zinc crystalline phases leading to amorphous materials, which prevent the formation of the Zn-OFF precursor.
Following the above described synthesis steps, the *OFF Precursor* with and without Zn was loaded into a 250 ml teflon lined synthesis autoclave. The synthesis autoclave with the *OFF* precursor solution was heated at 160 °C in an oven during 70-90 h. After this, the synthesis autoclave was cooled down to 25 °C. At this point, the formed *OFF* zeolite appeared as a white solid. The zeolite particles were separated by filtration. Following this, they were washed with distillate water until a pH 10 in a filtered liquid was obtained. Once this was achieved, the zeolite particles were dried at 120 °C for 10 h and calcined at 550 °C during 7 h under an air flow. This step allowed one to calcine the TMA, removing it from the *OFF* structure.

A last step in this process of the *OFF* preparation was an ion exchange for sodium removal using an ammonium nitrate solution. This step required zeolite washing using ammonium nitrate as proposed by Hagey (Hagey 1997). The resulting zeolite was dried at 120 °C and calcined in air at 550 °C during 7 h. This calcination left the *OFF* in a protonated form.
Once all these steps were completed, the quantification of Al$_2$O$_3$, Na$_2$O, K$_2$O, SiO$_2$ components was effected using XRF. On the other hand, Zn content was established using ICP-AES. On this basis, the following zeolite formulas were established:

\[
\text{OFF}: \quad \text{Na}_{0.1}\text{K}_{0.6}\text{Al}_{3.6}\text{Si}_{9.2}\text{O}_{25.6}
\]

\[
\text{Zn(2.0wt\%)-OFF}: \quad \text{Na}_{0.3}\text{K}_{0.6}\text{Zn}_{0.5}\text{Al}_{3.4}\text{Si}_{9.9}\text{O}_{27.4}
\]

\[
\text{Zn(3.5wt\%)-OFF}: \quad \text{Na}_{0.6}\text{K}_{0.6}\text{Zn}_{0.9}\text{Al}_{3.3}\text{Si}_{10.5}\text{O}_{29.0}
\]

The yield of OFF zeolites produced was calculated based on the OFF and Zn-OFF collected. It was observed that a total of 62-87 % of aluminum and 53-59 % of silicon initial components were incorporated into the OFF structure. In this respect, the modest efficiency reductions were assigned to particles losses during filtration, washing and drying. Moudafi et al. (Moudafi et al. 1986) reported similar yield values for the TMA-Offretite synthesis with the incorporation of 50% of silicon. Furthermore, and for both the Zn(2.0wt\%)-OFF and Zn(3.5wt\%)-OFF synthesized in the present study, it was noticed that zinc was incorporated into the zeolites structure with a 58-60% yield.

### 5.2.2 Additives: OFF, Zn(2.0wt\%)-OFF and Zn(3.5wt\%)-OFF

Given that the sorbent for thiophenic species in the gasoline range requires fluidizable particles to be implemented in an industrial process, the so-called OFF Additive (pellets) was prepared as follows: (a) 25 wt\% of zeolite (Offretite, Zn(2.0wt\%)-Offretite or Zn(3.5wt\%)-Offretite), (b) 50 wt\% of fused alumina (Aluminum oxide, fused 99%) provided by Sigma Aldrich as a filler, and (c) 25 wt\% of colloidal silica (Ludox AS-40 colloidal silica, 40 wt\% suspension in water) from Aldrich as a binder. The highly viscous resulting slurry was mixed in a mortar forming a homogeneous paste. Then, it was dried at 110 ℃ for 4 hours. Following this, the dried solid cake was calcined at 370 ℃ for 3 hours. Once having completed these steps, the resulting solid was ground and sieved keeping the particles in the 53 to 100 μm size range for further studies in the CREC Riser Simulator. One should mention that the method followed to manufacture the pellets was similar to the one proposed by Al-Bogami (Al-bogami 2013) for forming ZSM5 zeolite pellets.
5.3 Physicochemical Characterization

Table 5-2 summarizes the chemical compositions, NH$_3$-TPD, pyridine FTIR, BET, micro and macropore area, and pore volume for:

a) OFF, Zn(2.0wt%)-OFF, and Zn(3.5wt%)-OFF zeolites

b) OFF, Zn(2.0wt%)-OFF, and Zn(3.5wt%)-OFF additives

c) Ludox- Fused Alumina and the matrix used for pelletization

The results of Table 5-2 are discussed in the upcoming sections.
Table 5-2. Physicochemical Properties of the Zeolites, Additives and Matrix

<table>
<thead>
<tr>
<th></th>
<th>OFF Zeolite</th>
<th>OFF Additive</th>
<th>Zn(2.0wt%)-OFF Zeolite</th>
<th>Zn(2.0wt%)-OFF Additive</th>
<th>Zn(3.0wt%)-OFF Zeolite</th>
<th>Zn(3.0wt%)-OFF Additive</th>
<th>Matrix</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Physicochemical Properties</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lewis/Brönsted Ratio</td>
<td>0.64</td>
<td>0.68</td>
<td>1.54</td>
<td>1.40</td>
<td>1.59</td>
<td>1.79</td>
<td>0.00</td>
</tr>
<tr>
<td>NH₃ TPD, mmol NH₃/g STP at 15°C/min</td>
<td>1.53</td>
<td>0.36</td>
<td>2.07</td>
<td>0.47</td>
<td>2.00</td>
<td>0.49</td>
<td>0.00</td>
</tr>
<tr>
<td><strong>Chemical Composition</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al₂O₃, wt%</td>
<td>20.6</td>
<td>67.6</td>
<td>19.3</td>
<td>69.3</td>
<td>18.9</td>
<td>68.6</td>
<td>81.3</td>
</tr>
<tr>
<td>SiO₂, wt%</td>
<td>58.9</td>
<td>26.7</td>
<td>63.5</td>
<td>25.7</td>
<td>67.5</td>
<td>25.7</td>
<td>16.5</td>
</tr>
<tr>
<td>Na₂O, wt%</td>
<td>0.59</td>
<td>0.28</td>
<td>1.29</td>
<td>0.42</td>
<td>3.31</td>
<td>1.01</td>
<td>0.20</td>
</tr>
<tr>
<td>Fe₂O₃, wt%</td>
<td>0.06</td>
<td>0.04</td>
<td>0.07</td>
<td>0.04</td>
<td>0.06</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>K₂O, wt%</td>
<td>2.02</td>
<td>0.54</td>
<td>2.08</td>
<td>0.51</td>
<td>2.19</td>
<td>0.56</td>
<td>&lt; 0.01</td>
</tr>
<tr>
<td>Zn, wt%</td>
<td>0.00*</td>
<td>0.00*</td>
<td>1.97</td>
<td>0.55</td>
<td>3.50</td>
<td>1.04</td>
<td>0.00*</td>
</tr>
<tr>
<td>Si/Al (mol/mol)</td>
<td>2.42</td>
<td>0.33</td>
<td>2.79</td>
<td>0.31</td>
<td>3.03</td>
<td>0.32</td>
<td>0.17</td>
</tr>
<tr>
<td>Al/(Si+Al) (mol/mol)</td>
<td>0.29</td>
<td>0.75</td>
<td>0.26</td>
<td>0.76</td>
<td>0.25</td>
<td>0.76</td>
<td>0.85</td>
</tr>
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<td><strong>Physical properties</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BET Surface Area, m²/g</td>
<td>430</td>
<td>144</td>
<td>460</td>
<td>183</td>
<td>438</td>
<td>161</td>
<td>19</td>
</tr>
<tr>
<td>t-Plot Micropore Area, m²/g</td>
<td>376</td>
<td>99</td>
<td>408</td>
<td>137</td>
<td>390</td>
<td>115</td>
<td>1</td>
</tr>
<tr>
<td>t-Plot External Surface Area, m²/g</td>
<td>54</td>
<td>45</td>
<td>52</td>
<td>32</td>
<td>48</td>
<td>33</td>
<td>-</td>
</tr>
<tr>
<td>Total Volume in Pores, cm³/g</td>
<td>0.195</td>
<td>0.113</td>
<td>0.194</td>
<td>0.122</td>
<td>0.185</td>
<td>0.114</td>
<td>0.040</td>
</tr>
</tbody>
</table>

*less than 0.000001 wt%
5.3.1 Pelletization effect over Zeolites: Additives versus Zeolites

It can be noticed in the last column of Table 5-2 that NH$_3$-TPD and pyridine-FTIR of the matrix additive report no measurable acidity. This demonstrates that the additive matrix used in the OFF and Zn-OFF additives preparations is inert and does not contribute to its overall sorption performance. This can be later confirmed when comparing the NH$_3$-TPD for the OFF zeolites with the one for the OFF additives (Figure 5-3a and 4b). One should mention that the Ludox-Fused Alumina Matrix involved in the OFF Additive preparation creates an expected reduction effect on the NH$_3$-TPD acidity.

Figure 5-3. NH$_3$-TPD Spectra for the a) OFF Zeolites with and without Zn, and b) OFF Additives with and without Zn (units of concentration in term of zeolite content)

Table 5-3 reports NH$_3$-TPD results for the three OFF zeolites and OFF additives. Furthermore, Table 5-3 shows both weak and strong sites for all these materials. One can notice that the NH$_3$-TPD for the OFF zeolites and that for the Zn-OFF additives display:

a) A close total acidity, b) A displacement of the maximum NH$_3$-TPD temperature with Zn content, c) An observed third high temperature peak for both Zn-OFF studied

Figure 5-4 reports the characteristic bands for pyridine coordinated on the Lewis sites at 1450 cm$^{-1}$ and for the protonated pyridine on Brönsted sites at 1545 cm$^{-1}$. These bands show the same tendency for both zeolite and additives.

One can thus, conclude that the matrix is inert and does not contribute to its overall acidity, only an expected dilution effect.
Table 5-3. TPD-NH₃ Results for the Zeolites and Additives using a β=15°C/min temperature ramp

<table>
<thead>
<tr>
<th></th>
<th>OFF</th>
<th>Zn(2.0wt%)-OFF</th>
<th>Zn(3.5wt%)-OFF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeolite</td>
<td></td>
<td>Zeolite</td>
<td>Zeolite</td>
</tr>
<tr>
<td>Temp., °C</td>
<td>mmol NH₃/g STP</td>
<td>Temp., °C</td>
<td>mmol NH₃/g STP</td>
</tr>
<tr>
<td>Weak</td>
<td>227</td>
<td>0.53</td>
<td>223</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Strong</td>
<td>379</td>
<td>1.00</td>
<td>365</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 5-4. FTIR Spectra for a) Active Materials (zeolites) and b) Additives and Matrix
5.3.2 Acidity Characterization: NH$_3$-TPD and Pyridine-FTIR

Figure 5-5a reports NH$_3$-TPD profile examples for OFF, Zn(2.0wt%)-OFF and Zn(3.5wt%)-OFF zeolites. The TPD profiles were obtained at different temperature ramps $\beta=10, 15, 20, 25$ and 30 °C/min. One can notice in Figure 5-5a-c, the existence of three distinct temperature peaks in each figure. For instance, Figure 5-5a displays three peaks for the OFF, which are located at 430-532K (215-264°C), 641-730K (435-485°C) and at 857-927K (600-650°C) at different $\beta$s. These three peaks represent different types of acidity strengths: i.e. one weak, one of middle strength and one strong.

One can observe that the first peak appears in the Low Temperature range (LT) while the other two peaks are in the High Temperature range (HT). In this respect, Ni et al. (Ni et al. 2011) reported that calcined Zn-ZSM5 at quick ramping rate, led to higher Lewis acid sites and a shift of NH$_3$-TPD peaks towards higher temperatures.

The three NH$_3$-TPD identified peaks were associated as Site I (weak acid site), Site II (moderate strength acid site) and Site III (strong acid site). On this basis, one can speculate that acid site characterizations as per the NH$_3$-TPD, can provide insights into the adsorption properties of the Zn-OFF zeolites. Similar findings by others were obtained from the literature, with the OFF using NH$_3$-TPD (Penchev et al. 1983b; Mirodatos and Barhomeuf 1979) and 1-Butene-TPD (Cichocki 1980). In this respect, in these studies, it is claimed that both adsorption and catalytic offretite properties are influenced by the original form of the OFF and its modified forms such as H-OFF, K-OFF, Na-OFF, Cs-OFF and Cu-OFF (Penchev et al. 1983b; Merz and Fetting 1996; Mirodatos and Barhomeuf 1979; Mirodatos et al. 1978).

Regarding the NH$_3$-TPD peaks used to characterize the acid sites in the OFF zeolites, one can notice that Figure 5-5a-c reports a progressive increase in the LT-Peak (Site I) as well as the MT and HT-Peaks (Site II and III). This is the case when the OFF is modified with Zn. Thus, it can be concluded that the addition of zinc increases the strengths of the acid sites.
Figure 5-5. NH₃-TPD profiles at various βs for one run of: a) the OFF zeolite, b) the Zn(2.0wt%)-OFF zeolite and c) the Zn(3.5wt%)-OFF zeolite.
On the other hand, Figure 5-5b and 5-5c report a significant increase in the desorbed ammonia volume from both Site I and Site III. In this respect, one can also observe that Site III becomes more important in the case of the Zn(3.5wt%)-OFF. Furthermore, it can also be noticed that the acidity of Site III can be better quantified when using a temperature ramp above 15 °C/min (β>15 °C/min). Thus, it can be argued that these heating ramps lead to sharper NH₃-TPD peaks with reduced overlapping. This is the result of the NH₃-TPD which takes advantage of desorption activation energies as follows: $E_{d,\text{Site I}} \cong E_{d,\text{Site II}} < E_{d,\text{Site III}}$. The magnitude and relative order of these activation energies are quantified later in Chapter 7.

As shown in Figure 5-5, more than one Zn-OFF site were recorded using NH₃-TPD. Multiple types of adsorption sites are frequently accompanied with different desorption energies that should be assessed separately (Bhatia, Beltrami, and Do 1990). In particular, three sites were identified in the OFF, using deconvolution with an Inverse Gamma distribution. Other distribution functions such as Gauss, Pearson IV and Beta Area were also considered. However, the inherent symmetry of these functions makes their adjustment difficult. Thus, the Inverse Gamma function was preferred given that it provided the lowest summation of the residuals. An example of the deconvolution performed is given in Figure 5-6.
Figure 5-6. Deconvolution of the OFF Sites (Sites I, II and III) for the Zn (3.5wt%)-OFF Zeolite with NH₃-TPD using a β=25°C/min ramp. Notes: a) Inverse Gamma Distribution individual areas are assessed with a $R^2=0.998$. Summation of the 3 peaks areas are calculated with a 0.0623 residual.

Table 5-4 reports the results of NH₃-TPD deconvolution (refer to Figure 5-6). One can notice that there is a significant rise in the total acidity in the Zn-OFF. In fact, the Zn-modified OFF shows an 80% acid density increase in Site I when compared to its parent OFF zeolite. Another important observation is also the increase of the acid Site II and III densities, when there is zinc in the OFF.

Table 5-4. NH₃-TPD after deconvolution of the peaks using a β=30°C/min temperature ramp (values are the average of three repetitions)
Table 5-4 shows as well, the temperatures at which NH₃-TPD peaks display maximum values (T<sub>p</sub>). One can observe that the T<sub>p</sub> for the Sites I and III increases gradually, with zinc content. On this basis, it can have concluded that the Zn in the OFF increases adsorption site density, as well as adsorption bonding strength. These results are further confirmed in Figure 5-7, where the total desorbed ammonia for the 3 identified sites augments as a function of the Zn/Al ratio in the OFF.

![Figure 5-7. Change in Acid Site Density in the OFF as a Function of the Zn/Al Ratio](image)

Figure 5-7 reports the pyridine-FTIR spectra of all the zeolites used in this study. Figure 5-8 reports the pyridine-FTIR spectra of all the zeolites used in this study. Figure 5-8a displays the spectrum of zeolites between 1400-1800 cm<sup>-1</sup>. Brönsted acid sites band was observed at 1545 cm<sup>-1</sup>. On the other hand, IR bands characteristic of pyridine interacting with Lewis acid sites were detected at 1440, 1451 and 1615 cm<sup>-1</sup>. Hydrogen bonded pyridine was also seen at 1631 cm<sup>-1</sup>. In addition, a 1490 cm<sup>-1</sup> band was recorded and assigned to the combined contribution of Brönsted and Lewis acid sites.

Furthermore, there was an increase in the intensity of the peaks at 1615 cm<sup>-1</sup> and 1451 cm<sup>-1</sup> with Zn addition as well as in those of the double band at 1440-1451 cm<sup>-1</sup>. This showed that the addition of Zn led to the formation of new Lewis acid sites. These observations are in agreement with the findings using other materials such as zinc silicates and Zn-β zeolite, where Zn addition modifies acidity (Orazov and Davis 2016; Saravanamurugan et al. 2006). Furthermore, Beyer et al. (Beyer, Pál-Borbély, and Keindl 1999) reported that the shoulder band at 1440-1451 cm<sup>-1</sup> observed with the zinc addition is an indication of a modified crystallographic lattice.
Figure 5-8. Pyridine-FTIR spectra of the OFF and Zn-OFF zeolites measured: a) 1400-1800 cm\(^{-1}\), b) 3590-3790 cm\(^{-1}\) and c) 430-1030 cm\(^{-1}\)
Figure 5-8b reports the 3590-3790 cm\(^{-1}\) FTIR spectra. This band allows determining the effects of zinc on the acid sites, particularly those on the Brönsted OH groups. On this basis, three significant bands were identified in the 3610, 3690 and 3745 cm\(^{-1}\) OH stretching regions. Each band can be assigned to different OH vibrations. However, none of these bands showed a significant change, except for the 3745 cm\(^{-1}\) peak which provided information about non-acidic OH bands (Saravanamurugan et al. 2006; Weitkamp 2000; Kazansky 1991). This enhanced the non-acidic OH bands that can be assigned to the zinc located either on the external surface of the crystals or in the amorphous inclusions in the OFF structure (Weitkamp 2000). Furthermore, Figure 5-8c showed a modest change in the 450-480 cm\(^{-1}\) FTIR bands, which may be attributed to the bending modes of T–O–T bridges (Y. Wang et al. 2010). It can be speculated as a result, that zinc addition may modify these bridges, creating different strengths or acid site interactions (Aponte and de Lasa 2016).

Brönsted and Lewis acid site concentrations were determined using peaks at 1545 cm\(^{-1}\) and 1448 cm\(^{-1}\), respectively. Table 5-5 reports the FTIR area peaks and their relative Lewis/Brönsted acidities. One can observe that acidities are not proportional to the aluminum content. However, a raise of Lewis/Brönsted site ratios is observed with the increase of Al+Zn fractions

<table>
<thead>
<tr>
<th>Lewis/Brönsted ratio</th>
<th>OFF Zeolite</th>
<th>Zn(2.0wt%)-OFF Zeolite</th>
<th>Zn(3.5wt%)-OFF Zeolite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brönsted</td>
<td>0.50</td>
<td>0.67</td>
<td>0.54</td>
</tr>
<tr>
<td>Lewis</td>
<td>0.32</td>
<td>1.03</td>
<td>0.86</td>
</tr>
<tr>
<td>Total</td>
<td>0.82</td>
<td>1.70</td>
<td>1.40</td>
</tr>
<tr>
<td>Al, mol/unit cell</td>
<td>3.60</td>
<td>3.40</td>
<td>3.30</td>
</tr>
<tr>
<td>Zn, mol/unit cell</td>
<td>0.00</td>
<td>0.50</td>
<td>0.90</td>
</tr>
<tr>
<td>Al+Zn, mol/unit cell</td>
<td>3.60</td>
<td>3.90</td>
<td>4.20</td>
</tr>
</tbody>
</table>

Note: Bands’ range for Lewis acid sites: 1430-1467 cm\(^{-1}\) and for Brönsted acid sites: 1533-1560 cm\(^{-1}\)
In summary, zinc addition leads to: a) A change in the acid site distribution as shown with TPD, b) An enhancement of Lewis acidity as observed with Pyridine-FTIR. These changes can be attributed to: a) the Zn incorporated into the OFF lattice that can cause a change in the strength of the bridging hydroxyl groups (Si-O-Zn) (H.G. Karge and Weitkamp 2014), b) the formation of new stronger Lewis acid sites and new Brönsted sites, c) Possible defects created by Zn (Orazov and Davis 2016), e) The ZnO clusters that are able to interact with the oxygen framework atoms and increase their charges, enhancing their acid-base characters (H.G. Karge and Weitkamp 2014), d) the zinc atoms placed in the neighborhood of Al atoms (e.g. Al-O-Zn) that may influence the charge distribution and basicity of the oxygen atoms (H.G. Karge and Weitkamp 2014). In this respect, Figure 5-9 reports examples of possible acid site structures formed in the Zn-OFF.

Figure 5-9. Possible Brönsted and Lewis acid sites formed in the Zn-OFF zeolites. (a), (c), (e) and (g) adapted from Meng et al. and Orazov et al. (Meng et al. 2015; Orazov and Davis 2016)

Another important characterization of the OFF is to establish basicity changes given by electronegativity considerations. To accomplish this, one can consider a mean zeolite electronegativity parameter (S_{zeolite}), as proposed by Sanderson (Sanderson 1983). This S_{zeolite} parameter, which increases with decreasing basicity (Barthomeuf 1996), allows one to establish a zeolite basicity strength.
Table 5-6 reports calculated values for the three OFFs of the present study. One can observe that the lowest electronegativity or the lowest S_{zeolite} is displayed by the OFF with the highest Zn content. Thus, zinc in the framework may also lead to an increased density of negative basic sites and an increased basicity (Barthomeuf 1996).

<table>
<thead>
<tr>
<th>Name</th>
<th>S_{zeolite}</th>
<th>Oxygen Charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>OFF</td>
<td>Na_{0.1}K_{0.6}Al_{3.6}Si_{19.2}O_{25.6}</td>
<td>3.997</td>
</tr>
<tr>
<td>Zn(2.0wt%)-OFF</td>
<td>Na_{0.3}K_{0.6}Zn_{0.5}Al_{3.4}Si_{19.9}O_{27.7}</td>
<td>3.956</td>
</tr>
<tr>
<td>Zn(3.5wt%)-OFF</td>
<td>Na_{0.6}K_{0.6}Zn_{0.9}Al_{3.3}Si_{10.5}O_{26.6}</td>
<td>3.906</td>
</tr>
</tbody>
</table>

Barthomeuf (Barthomeuf 1996) described that the basic strength can be evaluated using CO2-TPD. It was reported that lowest desorption temperatures are evidences of higher basicity materials. Results of the CO2-TPD analysis for the OFF and Zn-OFF zeolites are given in Table 5-7. Two peaks were identified in each of the OFFs. Minute differences in the maximum desorption temperatures were observed.

Table 5-7 also shows that the amount of CO2 desorbed increases with the zinc content in the OFF. It is believed that small ZnO clusters in Zn(3.5wt%)-OFF can cause that increase. In this respect, Kim et al. (Kim et al. 1994) and Lasperas et al. (Laspéras et al. 1995) reported a direct connection between Cs loaded in X zeolite and CO2 desorbed amounts. It is expected however, that given the acid sites of the OFF and Zn-OFF are the only ones involved on the methylthiophene adsorption, they do not require additional consideration in the context of this PhD dissertation.

Table 5-7. CO2-TPD results for the zeolites at β=20˚C/min

<table>
<thead>
<tr>
<th>T_p, K</th>
<th>OFF Zeolite</th>
<th>Zn(2.0wt%)-OFF Zeolite</th>
<th>Zn(3.5wt%)-OFF Zeolite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site I</td>
<td>376</td>
<td>375</td>
<td>375</td>
</tr>
<tr>
<td>Site II</td>
<td>953</td>
<td>953</td>
<td>950</td>
</tr>
<tr>
<td>CO2 amount, mmol/g STP</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Site I</td>
<td>0.05</td>
<td>0.32</td>
<td>0.58</td>
</tr>
<tr>
<td>Site II</td>
<td>1.44</td>
<td>1.24</td>
<td>1.49</td>
</tr>
<tr>
<td>Total</td>
<td>1.48</td>
<td>1.56</td>
<td>2.07</td>
</tr>
</tbody>
</table>
5.3.3 N₂ Isotherm

Table 5-2 reports N₂ absorption in the synthesized OFF zeolites. Measured BET surface areas for the OFF were 430 m²/g, 460 m²/g and 438 m²/g for the OFF, the Zn(2.0wt%)-OFF and the Zn(3.5wt%)-OFF, respectively. One can notice in Figure 5-10 that the OFF and the Zn-OFF zeolites display an Isotherm Type I without hysteresis in accordance with the IUPAC classification (highly microporous).

This isotherm shows first a limiting N₂ uptake, which is governed by the accessible micropore volume (Sing et al. 1985; Sing et al. 1982). The slightly enhanced uptake of N₂ at P/P₀ values greater than 0.9 is due to the presence of a small quantity of macropores (< 0.1m²/g of area contribution). The OFF isotherm (black line) also exhibits a small degree of hysteresis, indicating the presence of some mesopores and the possibility of capillary condensation. The total accessible micropore volumes in the zeolites are 0.18-0.20 cc/g (refer to Table 5-2).

![Figure 5-10. N₂ Absorption Isotherms at 77 K for OFF and Zn-OFF Zeolites](image)

Figure 5-11 reports the pore size distribution calculated using BJH method for the Zn(2.0wt%)-OFF, Zn(3.5wt%)-OFF and OFF zeolite. A cylindrical parallel model was considered in the calculations. The calculation of the Pore Size Distribution using BJH Method is reported in Appendix D. One can notice a similar pore size distribution for all the OFF materials: 8 ring and 12 ring pore width dimensions of 4.3-4.4Å and 4.6-5.4 Å. This is in agreement with the observation of others (Baerlocher, Meier, and Olson 2001; Aponte, Djaouadi, and de Lasa 2014).
Figure 5-11. Porosity Distribution calculated by BJH method for a) the OFF zeolite, b) the Zn(2.0wt%)-OFF zeolite and c) the Zn(3.5wt%)-OFF zeolite. Pore distribution is based on N$_2$ adsorption at 77K.
5.3.4 Zn in OFF Framework

Regarding the Zn added to the OFF structures (2.0 and 3.5 wt% of Zn), TPR and TPO analyses did not record any measurable hydrogen or oxygen consumption. Thus, it can be hypothesized that the Zn-OFF does not contain significant ZnO and/or Zn extra framework crystallites and most of the available ZnO and/or Zn are included in the OFF framework.

One can mention that the literature reported mildly the relative acidity Lewis/Brönsted acidity ratio when zinc is in the extra framework zeolites (L. Wang et al. 2007). These authors observed however, a significant increase in the relative Lewis/Brönsted acidity when Zn was incorporated into the ZSM5 structure. These observations are in good agreement with the findings of the present study, where a speculated incorporation of zinc is accompanied with a significant change in the relative Lewis/Brönsted acidity (refer to Section 5.3.2).

Figure 5-12 report the XRD for the prepared OFF zeolites before and after pelletization. One can notice the characteristic X-ray diffraction patterns for the OFF zeolites as reported in the literature (Fernandez, Vedrine, et al. 1986; Carvalho et al. 1993; Y. Wang et al. 2010; Itakura et al. 2010; Gorshunova et al. 2015; Aponte, Djaouadi, and de Lasa 2014). One can also notice that the synthesized OFF are free from the possible erionite or phillipsite contamination.
Furthermore, one can also see that the addition of Zn (e.g. Zn(2.0wt%)-OFF and Zn(3.5wt%)-OFF zeolites) shows a XRD pattern very close to that of the pure offretite. The most significant and common peaks for the OFF, the Zn(2.0wt%)-OFF and the Zn(3.5wt%)-OFF zeolites are located as expected at 7.7°, 23.8°, 24.9° and 31.5° in the 2θ scale.

In particular, the peak at 23.8° is consistently the highest, with this being similar to that found in the results of Gorshunova et al. (Gorshunova et al. 2015), Wang et al. (Y. Wang et al. 2010) and Quesada et al. (Quesada and Vitale-Rojas 2006). One can notice that no new peaks for ZnO (2θ axis at 31.7°, 34.4°, 36.1°, 56.6°) were observed. This was

Figure 5-12. X-Ray Diffraction Patterns for the Zeolites (a-c), Additives (f-h), Matrix (e) and Fused Alumina (d).
attributed to two possible causes: a) a low zinc content up to 3.50 wt % in the Zn-OFF, b) the possible absence of sizable extra framework crystallites.

Regarding the OFF, the Zn(2.0wt%)-OFF and the Zn(3.5wt%)-OFF additives (see Figure 5-12f-g), one can notice that the observable XRD peaks come from the Ludox-Fused Alumina Matrix mainly (Figure 5-12d and e). The relatively poor discrimination of the OFF peaks in these diffractograms was assigned to the OFF zeolite dilution when preparing the OFF Additive: a 25w% OFF zeolite in the OFF additive.

Figure 5-13 reports the UV-visible diffuse reflectance spectra for the various OFF zeolites of the present study. Synthesized OFF shows peaks with shoulders at 230nm and 260nm. One can observe major differences between the Zn included in the OFF and pure ZnO. The ZnO displays a large adsorption band at 360nm corresponding to the $O^2- \rightarrow Zn^{2+}$ ligand (L. Wang et al. 2007; Bordiga et al. 2004). Therefore, the UV-visible results support a small OFF extra-framework ZnO amount (L. Wang et al. 2007).

![Figure 5-13. Diffuse Reflectance UV-Vis Spectra for the OFF, the Zn(2.0wt%)-OFF, the Zn(3.5wt%)-OFF Zeolites and the ZnO.](image)

Figure 5-14 shows the morphology of the OFF zeolites with and without Zn. All the zeolites show a similar type of crystallites with a 2-5μm in length. It appears that the crystallites observed are aggregate rods of hexagonal-shaped crystals.
One can also notice that formed crystallites contain parallel formations with core like bundles of small hexagonal rods. It has been reported (Moudafi et al. 1987; Occelli et al. 1987; Bengoa et al. 1997) that if: a) Na is included in the zeolite synthesis and b) TMA is used as a synthesis template, the resulting crystallite morphology is very close to the one of the present study. Furthermore, it is also confirmed in Figure 5-14b and 9c that the above rod bundle type crystallite morphology does not change with zinc content. This suggests in our view, that zinc is an included species in the OFF structure.

Figure 5-14. SEM View of the a) OFF, b) Zn(2.0wt%)-OFF and c) Zn(3.5wt%)-OFF. Note: Reference dimension is 6μm

Figure 5-15 describes Raman spectra for the three OFF zeolites of the present study. One can notice that from all recorded bands in the OFF, they remain unmodified with zinc addition. One can also observe that the highest bands corresponding to the T-O-T (T=Al, Si or Zn) oxygen angles from bending vibrations (C. Li and Wu 2003; Y. Yu et al. 2001; Knops-Gerrits et al. 1997). These bands are very close to the expected bands for the OFF (black line) at 317, 430 and 490 cm\(^{-1}\) (Angell 1973; Lafuente et al. 2015). These bands are assigned to the bending modes of 8-, 6- and 4-membered rings of the OFF zeolite.
Figure 5-15. Raman Spectra for the OFF, the Zn(2.0wt%)-OFF, the Zn(3.5wt%)-OFF zeolites

Figure 5-15 also shows that adding zinc in the OFF (e.g. 2.0wt% of zinc) increases the intensity of Raman strongest bands. In this respect, Yu et al. (Y. Yu et al. 2001) reported that the stronger Raman signals, suggest higher structural order in zeolites. It can thus, be inferred that 2wt% of zinc improves somehow the structural OFF order. Regarding the Raman spectrum for 3.5wt% of zinc in the OFF, there is an increase of broad bands. One can speculate, that the broad bands may be caused by a small quantities of nanoparticle of Zn-O extra-framework (Vempari, Mitra, and Dawson 2012; Schumm 2008).

5.4 Conclusions

a) Zn-OFF additives with two levels of zinc were synthesized using Zn-OFF zeolites. The OFF and Zn-OFF zeolites were proved to be the unique acidity contributor in the additives.

b) Zn-OFF additives were prepared using a matrix, to have the OFF zeolites as fluidizable particles.

c) Zn was added to the OFF zeolites during the gel synthesis process. It is thought that the prepared Zn-OFF zeolites likely contain most of the zinc species included in the OFF framework.
d) The Zn in the OFF zeolites increased the total acidity as well as the acid site strength, with more Lewis acidity being promoted.

e) Pyridine-FTIR results showed an increase of Lewis / Brönsted site ratios with the Al+Zn fraction. The FTIR data suggested that the zinc content may be modified through the OFF’s T-O-T bridges producing different and new acid site interactions.

f) The introduction of NH$_3$-TPD showed that acidity in the OFF and Zn-OFFs involves at least three types of acid sites. The three acid types are; one weak site and two strong sites. The measured acid amounts of Site I, II and III increased with the Zn/Al content in the OFF.
Chapter 6

Selective Thiophenic Species Adsorption. Additive Performance under FCC Conditions

This chapter reports the effect of adding Zn in the OFF on the sulfur removal adsorption properties. This section also describes the best operational conditions to promote the sulfur selective adsorption in gasoline. The candidate Zn-OFF catalyst with the adequate properties is then employed to investigate the best operational conditions and the thiophenic selective adsorption mechanism. This was done to understand and quantify the thiophenic selective adsorption of Zn-OFF materials.

6.1 Introduction

Desulfurization via selective adsorption is considered a promising approach in petroleum refining (Patil et al. 2014). In this respect, new sorbents for sulfur removal have been proposed. For example, activated carbon was considered for the adsorptive deep desulfurization of gasoline by Patil et al. in 2014 (Patil et al. 2014). Using a similar approach, other authors used activated carbons impregnated with Ni, Co, Cu, and Ag (Guo et al. 2012; Ania and Bandosz 2006).

Other adsorbents with a high potential for sulfur removal are described in the technical literature such as Ni/ZnO particles and Ag-polystyrene nanofibrous membranes (Zhang et al. 2012; L. Li et al. 2010). Cu, Pd and Zr supported on mesoporous silica (MCM-41 and SBA-15) have been found to be promising for jet fuel desulfurization (Y. Wang, Yang, and Heinzl 2008; Qi et al. 2015). In addition, zeolites have shown also promise. For instance, HZSM5 has been considered for gasoline desulfurization under mild temperatures (350-430 °C) (Jaimes, Badillo, and Lasa 2011). Furthermore, an offretite zeolite has recently been reported for use in thiophenic species selective adsorption under FCC operating conditions (Aponte 2011; Aponte, Djaouadi, and de Lasa 2014; Aponte and de Lasa 2016). In this respect, impregnated Ni-Y, Cu-Y, Fe-Y, La-Y and Zn-Y appear to be suitable for sulfur removal from diesel, and LaNaY, Cu-Beta and Ag-Beta from gasoline, and finally CuY, AgY, NaY and CuX from H2S (Shi et al. 2013; Bhandari et al. 2006; Gong et al. 2009; P. Kumar et al. 2011).
However, the availability of sorbents that could selectively retain sulfur with little interaction with other hydrocarbons still remains a challenge. In this regard, our research team proposes sulfur removal under FCC conditions using Zn embedded in an offretite framework. This Zn confers a higher Lewis acid site density than a conventional offretite, as shown by Aponte and de Lasa (Aponte and de Lasa 2016). It is anticipated that given that thiophenic sulfur compounds in fuels have a Lewis base character, they can be adsorbed on Lewis acid sites (Qi et al. 2015; Xue et al. 2005).

Specifically, the offretite can allow sulfur species removal via adsorption in the FCC riser cracker. Adsorbed sulfur species could be desorbed in the FCC stripper unit and recovered as a separate gas product stream (high in thiophenic species, refer to Figure 2-5). Thus, the sulfur containing compounds could be safely released from the FCC catalyst and the additive before reaching the FCC regenerator. This approach may significantly reduce the SO\(_x\) formation, mitigating the overall FCC plant sulfur emissions to the environment (Aponte and de Lasa 2016).

This chapter aims showing the role of zinc in the sulfur removal as well as best operating conditions for the Zn-OFF additive under FCC conditions. To achieve this reactivity, studies were developed in the CREC Fluidized Simulator covering a wide range of thiophenic species (thiophene, 2-methylthiophene and 2,5-dimethylthiophene in 1,3,5-trimethylbenzene), temperatures, partial pressures, reaction times, zinc-loaded in the zeolite, and additive/FCC catalyst ratio.

### 6.2 Thermal Runs

Thermal cracking runs were developed using the CREC Fluidized Riser Simulator unit with no catalyst or additive being loaded in the unit. Various model compounds were used: a) thiophene (Th) - 1,3,5 trimethylbenzene (TMB), b) 2-methylthiophene (2MTh) - 1,3,5-trimethylbenzene, and c) 2,5-dimethylthiophene (25DMTh)- 1,3,5-trimethylbenzene mixtures. The Th, 2MTh and 25DMTh conversions were analyzed at various temperatures and reaction times. TMB conversion was in the 1-3 wt% with the highest value observed at 550 °C and 7 s. Main products for the TMB thermal conversion were toluene, o- and m-xylene, tetramethylbenzene and isomers of TMB.
Figure 6-1 reports an example of results from a thermal run. This shows that there is no thiophenic conversion with both sulfur and carbon balances remaining in all cases in a deviation range less than a 2 wt%.

Figure 6-1. Sulfur and TMB Conversions and Sulfur and Carbon Balances Calculated with Data from Thermal Runs using 1.2 wt% of 2MTh, Th and 25DMTh in TMB at 530 ºC and 7 s.

6.3 Role of Zn in the selective adsorption: Zn Content Effect under Thiophenic Species Adsorption

In order to assess the selective adsorption of thiophenic species with different zinc loaded content in the OFF, runs with 0.1 g of OFF, Zn(2.0wt%)-OFF and Zn(3.5wt%)-OFF additives (additive/HC = 0.6) were performed at 530 ºC and 7 s. Three key model compounds were selected for the present study: a) thiophene (Th), a) 2-methylthiophene (2MTh) and c) 2,5-di-methylthiophene (25DMTh). This involved blending 1.2 wt% of sulfur containing compounds with TMB. In addition, and to evaluate thiophenic species adsorption.

Figure 6-2 to 6-4 report the sulfur balances, $S_{ads}$, $S_{balance}$, and $S_{stripping 2}$ calculated with Eqs. (4-1), (4-5) and (4-7), respectively, contrasted with different zinc loaded in the offretite. It is important to mention that in Figure 6-2 to 6-4 the 0% of zinc content is represented by OFF additive, the 2.0wt% and 3.5wt% of zinc-loaded in the offretite are demonstrated by Zn(2.0wt%)-OFF and Zn (3.5wt%)-OFF, respectively.
Figure 6-2. Sulfur Adsorbed ($S_{ads}$) calculated with Eq. (4-1) and Data from Runs in the CREC Riser Simulator using 0.1g of OFF, Zn(2.0wt%)-OFF and Zn(3.5wt%)-OFF additives and 1.2wt% of Th, 2MTh and 25DMTh in TMB at 530 °C and 7s.

Figure 6-2 presents the $S_{ads}$ parameters. This parameter establishes the Zn-OFF additives capability for sulfur species capture. One can notice that the $S_{ads}$ increases when zinc content in the OFF augments. For instance, a rise to 35.0 and 37.4 wt% levels is observed using 2MTh. This enhanced adsorption capacity due to zinc can be assigned to the Zn-OFF displaying: a) higher total acidity, b) higher density of Lewis acid sites, c) stronger site adsorption strength (refer to Section 5.3.2).

Figure 6-3 reports $S_{balance}$ which represents the sulfur deficiency in product species for the Balance Level 2 (stripping 1). This consistently missing sulfur (at least 3 repeats per experiment) can only be attributed to the trapped alkylthiophenes remaining in the OFF additive (0% of zinc).

One can however, foresee that there are sulfur species that cannot be removed from the OFF additive under the 1.5-2.0 psi conditions of the CREC Riser Simulator vacuum box during the 10-15s of evacuation. In fact, a significant fraction of these sulfur species close to 8.7 wt%, requires a second hydrocarbon stripping stage to be removed. This is shown in the TOC analysis of the OFF additive with 1.1% sulfur content in coke assuming an expected C/S ratio of 5 (refer to Figure 6-4). One should note that the OFF additive sample analyzed with TOC was collected from the CREC Riser Simulator basket, after a second additional stripping of at least 2-5 min with argon at 530°C.
Figure 6-3. Sulfur Balance ($S_{\text{balance}}$) calculated with Eq. (4-5) and Data from Runs in the CREC Riser Simulator using 0.1g of OFF, Zn(2.0wt%)-OFF and Zn(3.5wt%)-OFF additives and 1.2wt% of Th, 2MTh and 25DMTh in TMB at 530 °C and 7s

Figure 6-4. Sulfur as coke ($S_{\text{stripping 2}}$) calculated with Data from Runs in the CREC Riser Simulator using 0.1g of OFF, Zn(2.0wt%)-OFF and Zn(3.5wt%)-OFF additives and 1.2wt% of Th, 2MTh and 25DMTh in TMB at 530 °C and 7s

Regarding the Zn(2.0wt%)-OFF additive, which stands for 2.0 wt% of Zn in the OFF, the $S_{\text{ads}}$ reaches a 35 wt% sulfur capture capacity, while the $S_{\text{balance}}$ shows a product deficiency in sulfur of 27.9 wt%. One should notice as well that the sulfur in coke for a C/S of 5, increases to 7.9% (refer to Figure 6-4). Thus and as a result, the non-stripped sulfur species amount under the initial 1.5-2.0 psi vacuum conditions in the CREC Riser
Simulator is 20 wt%. As in the case of the OFF additive, this 20 wt% can be assigned to trapped alkylthiophenes and can be largely reduced under the second stripping.

Similar trends when using 3.5wt% of zinc loaded in the offretite (Zn(3.5wt%)-OFF additive) were observed, with the S_{ads} being 37.4 wt%. However, the Zn(3.5wt%)-OFF additive yields a S_{balance} deficient by 22.8 wt% only, which suggests a better removal of sulfur adsorbed species under the 1.5-2.0 vacuum conditions of the CREC Riser Simulator. In addition, one can notice that if there is a second stripping of hydrocarbons as during the TOC analysis, the sulfur remaining in coke is 1.3% assuming a C/S of 5 (refer to Figure 6-4).

It is thus, anticipated that the Zn(3.5wt%)-OFF additive subject to the most severe stripping conditions as in an FCC plant will lead to the following: a) high sulfur capture, b) low sulfur in coke.

Concerning the reported results, one can hypothesize that surpassing the 2.0 wt% Zn in the Zn-OFF promotes more (Zn-O-Zn)^2+. These bridges lead to, as shown in Figure 5-2, larger acid site (aluminum ions) separation. This modified zeolite structure with increased distance between acid sites promotes sulfur species adsorption rather than sulfur species conversion. This is the case given that alkylation and bimolecular precursor reactions leading to coke are less likely to occur in the Zn(3.5wt%)-OFF additive. In this respect, Penzien et al. (Penzien et al. 2004), Shubin et al. (Shubin et al. 2003); Barbosa et al. (Barbosa and Santen 2007); Kazansky et al. (Kazansky, Serykh, and Pidko 2004) reported the formation of adjacent aluminum sites, when Zn^{2+} was included as (Zn-O-Zn)^2+ in the zeolite structure. Thus, one can hypothesize that an increased zinc content in the OFF leads to a higher density of aluminum acid sites placed further apart.

Regarding the OFF, the Zn(2.0wt%)-OFF and the Zn(3.5wt%)-OFF sorption performances, one should also consider the sulfur species recovered from both the gas phase following evacuation under 1.5-2.0 psi vacuum in the CREC Riser Simulator. Figure 6-5 reports in this respect, all the new species recovered. One can notice that the increase of zinc content reduces the thiophenic conversion.
Figure 6-5. New total sulfur species formed Runs in the CREC Riser Simulator using 0.1g of Additive and 1.2wt% of Th, 2MTh and 25DMTh in TMB at 530 °C and 7s

Figure 6-6 shows consistently and in all cases, that the OFF additive with and without zinc, yields products with 2MTh and its isomer 3-methylthiophene as the main components. These two chemical species combined represent almost 90 wt% of the sulfur products, with the other product species being thiophene, ethanethiol, dimethylthiophene and trimethylthiophene.

Thus, the selective adsorption of the desired species takes place with very limited chemical changes. A similar observation can be made when reviewing the products of the Zn(2.0wt%)-OFF and the Zn(3.5wt%)-OFF additives. The 2MTh and 3MTh continue to dominate the product species with these species being 88-97 wt% of the products. Thus, it can be speculated that adding Zn to the OFF zeolite structure promotes thiophenic selective adsorption, facilitating isomerization and alkylation reactions, as a result of the Zn-OFF modified acidity.
Figure 6-6. Example of Distribution of Product Species Containing Sulfur after Runs in the CREC Riser Simulator using 0.1g of Additive and 1.2wt% of 2MTh in TMB at 530 °C and 7s.

Furthermore, when compare the $S_{ads}$ and $S_{balance}$ using 2MTh with Th for the OFF and the Zn-OFF additives, it is observed small values in all cases. This is an indication of the low selective adsorption of nonalkylated sulfur species.

Thus, it appears that alkyl groups such as methyl, incorporated into thiophenic molecules play a central role in the promoting of sulfur selective adsorption when using both the OFF and Zn-OFF zeolites. These methyl groups have an inductive effect (electron donating group, base strengthening) in the heteroatomic ring of the 2MTh. Released electrons are transmitted through the heteroatomic ring, towards the S atoms increasing their basicity (Smith 2010). These strong bases (electron donors) are more prone to interact with the Lewis acids of the OFF and Zn-OFF zeolites.

Figure 6-2 also provides data for sulfur adsorption using 25DMTh. One can notice that in spite of the anticipated 25DMTh selective adsorption, the 25DMTh with a 3.8 x 6.6 Å molecule size is significantly restricted in its transport. This is consistent with the smaller 5.0 x 6.3 Å pores of the OFF, as shown in Figure 6-7.
Regarding the limited 25DMTh adsorption, this shows the little role played by the larger 9.4 - 10.5 Å OFF pores in the 25DMTh selective adsorption. This points as well, towards very low density of acid sites in the 9.4 to 10.5 Å OFF larger pores. One should mention as well that; these results agree with the limited effect of the large pores in the conversion of TMB as described in Section 6.4.1.

Figure 6-4 also displays a relatively smaller coke formation when 3.5wt% of zinc content in the offretite is used. This confirms the value of Zn bridges, which facilitate unimolecular reactions instead of bimolecular reactions. The bimolecular reactions are precursor reaction steps for coke formation.

In summary, one can notice that the selective adsorption of alkylated thiophenes on the Zn-OFF additives, as one can expect in an FCC unit, can lead to the important removal of sulfur species. This happens with very limited coke formation. Thus, 3.5wt% of zinc content in the offretite is the most suitable additive for thiophenic sulfur removal via selective adsorption under FCC conditions. Zn(3.5wt%)-OFF additive provide: a) the highest sulfur adsorption of the three thiophenic species studied, b) the lowest thiophenic conversion, c) the lowest coke production.
6.4 Sulfur Selective Adsorption of Zn(3.5wt%)-OFF Additive

In the above section was demonstrated that the candidate additive for thiophenic species selective adsorption is the one with higher zinc content in the offretite, Zn(3.5wt%)-OFF additive.

This section aims to evaluate the influence of operational variables in the Zn(3.5wt%)-OFF additive performance.

6.4.1 TMB Conversion and Coke Production

Runs with pure TMB were effected to define the quantity of coke produced by both the sulfur species and the TMB. This was also valuable to elucidate the relative role played by the 9.4 to 10.5 Å larger pores and the 5.0 to 6.3 Å smaller pores of the OFF additive.

Table 6-1 reports the TMB conversion and coke yields when using either pure TMB or a 2MTh and TMB mixture (2MTh/TMB). It can be noticed that when the Zn(3.5wt%)-OFF additive particles (Table 6-1, condition 3 and 7) was the only one loaded in the reactor, the TMB conversion remained in 1.3-1.5 wt%. Given that the observed TMB thermal conversion was 1.3 wt% only (refer to Section 6.2, and Table 6-1 condition 4 and 8), it can be considered that altogether the Zn(3.5wt%)-OFF additive does not, contribute to the catalytic conversion of TMB. It should be mentioned that this finding provides relevant information showing that:

a) The 9.4 to 10.5 Å OFF larger pores do not contribute with acid sites to TMB conversion

b) The 7 Å molecular size TMB is unable to be transported into the 5.0- 6.3 Å narrow OFF zeolite pores.
### Table 6-1. TMB Conversion and Coke Production using Zn-OFF Additive and FCC Catalyst Blends at 530 °C and 7 s.

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Condition</th>
<th>TMB</th>
<th>TMB</th>
<th>TMB</th>
<th>TMB</th>
<th>2MTh/TMB</th>
<th>2MTh/TMB</th>
<th>2MTh/TMB</th>
<th>2MTh/TMB</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>6</td>
<td>7</td>
<td>8</td>
</tr>
<tr>
<td>Catalyst Mixture:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn(3.5wt%)-OFF additive, wt%</td>
<td></td>
<td>0</td>
<td>10</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>10</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>FCC Catalyst, wt%</td>
<td></td>
<td>100</td>
<td>90</td>
<td>0</td>
<td>0</td>
<td>100</td>
<td>90</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>TMB Conversion, wt%</td>
<td></td>
<td>19.2 ± 2.9</td>
<td>18.8 ± 0.5</td>
<td>1.5 ± 0.8</td>
<td>1.3 ± 1.0</td>
<td>18 ± 2</td>
<td>16.4 ± 2.0</td>
<td>1.3 ± 1.2</td>
<td>1.6 ± 1.2</td>
</tr>
<tr>
<td>Coke in the Additive, wt%</td>
<td></td>
<td>-</td>
<td>0.22 ± 0.01</td>
<td>0.04</td>
<td>-</td>
<td>-</td>
<td>0.19</td>
<td>0.07</td>
<td>-</td>
</tr>
<tr>
<td>Coke in the FCC Cat., wt%</td>
<td></td>
<td>0.31 ± 0.06</td>
<td>0.41 ± 0.04</td>
<td>-</td>
<td>-</td>
<td>0.82 ± 0.01</td>
<td>0.43</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Additive Coke Yield, wt%</td>
<td></td>
<td>-</td>
<td>0.174 ± 0.002</td>
<td>0.028 ± 0.002</td>
<td>-</td>
<td>-</td>
<td>0.12 ± 0.04</td>
<td>0.044 ± 0.001</td>
<td>-</td>
</tr>
<tr>
<td>FCC Cat. Coke Yield, wt%</td>
<td></td>
<td>1.82 ± 0.05</td>
<td>3.40 ± 0.04</td>
<td>-</td>
<td>-</td>
<td>4.69 ± 0.02</td>
<td>2.3 ± 0.63</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Note: 0.9 g of FCC Catalyst was used for conditions 1, 2, 5, and 6. And, 0.1 g of Zn(3.5wt%)-OFF additive for conditions 2, 3, 6 and 7.
On the other hand, Table 6-1 reports the TMB conversion and the coke when using FCC catalyst and TMB alone (condition 1). In this scenario, one can notice a 19.2 wt% TMB conversion and 1.82 wt% coke yield. Furthermore, Table 6-1 (condition 5) also shows a TMB conversion and coke appearing when employing 2MTh and TMB blends. It can be noticed that in the latter case, coke increases 2.7 times while TMB remains at the same level. This shows that thiophenic species compete for the available FCC catalyst acid sites. Thus, sulfur species yield an increased coke production, with this being in line with the reported influence of sulfur species in commercial FCC units (Aponte 2011; Corma et al. 2001).

Furthermore, Table 6-1 also shows that a blend of 10 wt% Zn(3.5wt%)-OFF additive and a 90 wt% FCC catalyst (condition 5 and 6) leads to a significant reduction of coke yield from 4.7 wt% to 2.3wt%. This shows the effectiveness of the Zn(3.5wt%)-OFF additive in a FCC process. It is assumed, as will be shown further in this chapter that the Zn-OFF additive can selectively adsorb thiophenic species moderating coke formation in the FCC process. This may have a significant impact in reducing SOx during catalyst regeneration. It is anticipated that this will be the case if one is able to readily desorb sulfur species in the FCC stripper, mitigating as a result, the overall FCC plant sulfur emissions to the environment.

### 6.4.2 Thiophenic Species Adsorption

To understand in deep the Zn(3.5wt%)-OFF additive, the selective adsorption study were established using three thiophenic species: Th, 2MTh, and 25DMTh. Figure 6-8 reports three sulfur selective adsorption parameters: a) $S_{ads}$ accounts for sulfur adsorbed species at the reactor operating conditions, b) $S_{stripping\ 1}$ accounts for the sulfur absorbed remaining after the 1.6 psi vacuum box pressure species removal (Stripping 1), c) $S_{stripping\ 2}$ accounts for sulfur species remaining following extensive stripping (Stripping 2).
Figure 6-8. Sulfur Balance Level 1 ($S_{ads}$), Sulfur Balance Level 2 ($S_{stripping 1}$), and Sulfur Left in Coke -Balance Level 3 ($S_{stripping 2}$) Calculated with Eqs. (4-1), (4-5) and (4-7). Conditions: 0.1 g of Zn(3.5wt%)-OFF Additive (additive/HC = 0.6), 1.2 wt% of sulfur species (Th, 2MTh or 25DMTh) in TMB at 530 °C and 7 s.

Figure 6-8 (yellow bars) shows an enhanced sulfur selective adsorption when using alkylated thiophenic species. For instance, the $S_{ads}$ for Th and for 2MTh increases from 7 to 37 wt%. This selective adsorption can be linked to the stronger basic character of the alkylated Th compounds. As explained in Section 6.3, methyl groups with their electron donating capacity and their enhanced basic character favor selective adsorption. It is assumed that the electron released from the alkyl group is donated to the sulfur containing aromatic ring. This thus, increases electron density and augments basicity, as well.

Figure 6-8 (green bars) reports the $S_{stripping 1}$ following the first step of stripping as accomplished in the CREC Riser Simulator with the vacuum box at 1.6 psi. It is observed that the $S_{stripping 1}$ for 2MTh and 25DMTh is in this case, 22 wt% and 16 wt%, respectively. This means that 2MTh sulfur species are partially evacuated, with the 25DMTh remaining essentially unremoved. It is assumed that the Th and 2MTh selective adsorption is enhanced in the smaller OFF pores via alkylation.

Therefore, and as a result of alkylation, the adsorbed Th becomes MTh and the MTh is transformed into DMTh. This is quite apparent given the observed composition of the
evacuated products, as reported in the Figure 6-9. In fact, in runs using 2MTh and Th, other alkylated DMTh isomers (25DMTh, 34DMTh and 24DMTh) and trimethylthiophene were observed. Accordingly, it can be hypothesized that the desorption of these alkylated sulfur containing species from the OFF structure involves significantly higher desorption energies than the ones required for adsorption.

Figure 6-9. Distribution of Product Species Containing Sulfur Runs in the CREC Riser Simulator using: a) 0.1 g of Zn(3.5wt%)-OFF Additive (additive/HC = 0.6), b) 1.2 wt% of sulfur species (Th, 2MTh or 25DMTh) in TMB, c) 530 °C temperature and d) 7s contact time.

One should mention, that selective adsorption application is closely linked to the ability of sulfur species to be removed (desorbed) in the stripper of a FCC commercial unit. To demonstrate the viability of selective adsorption in this respect, $S_{stripping\ 2}$ balances were also performed using Eq. (4-7), when the Zn(3.5wt%)-OFF additive was subjected to extensive sulfur removal. Figure 6-8 (black bars) reports this case and shows that in all cases, for Th, 2MTh and 25MTh, only 2 wt% of the original elemental sulfur remained in the Zn(3.5wt%)-OFF additive, with the sulfur removal being essentially complete.

Figure 6-10 and Table 6-2 report the carbon elemental balances for the three carbon balances studied. One can notice that carbon balances remain in the 2 wt% range consistently, with this being the case for $C_{ads}$, $C_{stripping\ 1}$ and $C_{stripping\ 2}$. This level of error
is considered consistent with typical level of experimental error in carbon balance closure in the CREC Riser Simulator.

Figure 6-10. Carbon Balance Level 1 ($C_{ads}$), Carbon Balance Level 2 ($C_{stripping\ 1}$), and Coke Yields - Carbon Balance Level 3 ($C_{stripping\ 2}$) Calculated with Eqs. (4-4), (4-6) and (4-8). Conditions: 0.1 g of Zn(3.5wt%)-OFF additive (additive/HC = 0.6), 1.2 wt% of sulfur species (Th, 2MTh or 25DMTh) in TMB at 530 °C and 7 s.

Therefore, one can conclude that there is no significant selective adsorption of carbon containing species prior to and following the moderate $Stripping\ 1$ and more extensive $Stripping\ 2$, as defined in Section 6.3.

Table 6-2. Elemental Carbon and Sulfur Balances Comparison.

<table>
<thead>
<tr>
<th>Balances</th>
<th>TMB</th>
<th>2MTh/TMB</th>
<th>Th/TMB</th>
<th>25DMTh/TMB</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{ads}$</td>
<td>2.44</td>
<td>0.91</td>
<td>0.15</td>
<td>0.72</td>
</tr>
<tr>
<td>$C_{stripping\ 1}$</td>
<td>0.30</td>
<td>0.74</td>
<td>0.33</td>
<td>1.95</td>
</tr>
<tr>
<td>$C_{stripping\ 2}$</td>
<td>0.03</td>
<td>0.04</td>
<td>0.06</td>
<td>0.05</td>
</tr>
<tr>
<td>$S_{ads}$</td>
<td>-</td>
<td>37.4</td>
<td>7.3</td>
<td>12.5</td>
</tr>
<tr>
<td>$S_{stripping\ 1}$</td>
<td>-</td>
<td>22.8</td>
<td>3.2</td>
<td>12.6</td>
</tr>
<tr>
<td>$S_{stripping\ 2}$</td>
<td>-</td>
<td>1.3</td>
<td>1.7</td>
<td>0.7</td>
</tr>
</tbody>
</table>

Furthermore, Table 6-2 reports a summary of sulfur and carbon elemental balances. It can be noticed that the $S_{ads}$ for 2MTh is 37.4wt%. One can also observe that $S_{ads} > S_{stripping\ 1} > S_{stripping\ 2}$, with this being a consistent result for all sulfur containing species as shown
in rows 4, 5 and 6 of Table 6-2. One can notice however, that these sulfur balance differences are especially significant for 2MTh/TMB mixtures as discussed earlier. This highlights the value of selective adsorption for the 2MTh/TMB sulfur species using the Zn(3.5wt%)-OFF additive.

6.4.3 Effect of Temperature and of Contact Time on the Sulfur Adsorption Process

6.4.3.1 Selective Adsorption under Optimum Conditions

On the basis of these encouraging results, the Zn(3.5wt%)-OFF additive was evaluated at 510, 530 and 550 °C and three contact times (3, 5 and 7 s). This was required to establish the effect of operating variables and to define an optimum condition for selective adsorption.

Figure 6-11 reports the $S_{ads}$ and its changes with temperature and contact times. This figure shows the optimum operating parameters for maximum $S_{ads}$ values.

![Figure 6-11](image)

Figure 6-11. Sulfur Balance Level 1 ($S_{ads}$), Calculated with Eq. (4-1) as a Function of the Contact Time and Temperature using 1.2 wt% of 2MTh in TMB and 0.1 g of Zn(3.5wt%)-OFF (additive/HC = 0.6).

Figure 6-11 displays a $S_{ads}$ maximum of 42 wt% at 530 °C and 5 s. This maximum value is consistent with a $S_{ads}$ parameter affected by two competing phenomena: a) Selective
adsorption being favoured at lower temperatures and b) Isomerisation and disproportionation promoted at higher temperatures.

To analyse the possible influence of these three reactions the reaction thermodynamics as described with Rxs. (1), (2), (3) in Figure 6-12 can be considered:

![Diagram of reactions]

Figure 6-12. Isomerisation and disproportionation reactions

It can be noticed that reactions described in Figure 6-12, Rxs (1), (2) and (3c) are slightly exothermic, with equilibrium constants in the 0.28-1.35 range (Frenkel et al. 1994). Thus, all these three reactions are thermodynamically allowed, with the temperature likely favouring higher isomerisation and disproportionation at the higher thermal levels. This is confirmed by the reported disproportionation of aromatic species (Tsai, Liu, and Wang 1999), enhanced at higher temperatures (I. Wang, Tsai, and Huang 1990). Boita et al. (Boita et al. 2006) reported disproportionation and isomerisation as main thiophenic species reactions over acidic zeolites. As well, Belliere et al. (Bellière et al. 2004) showed that adsorbed MThs are involved on isomerisation-alkylation reactions over zeolites.

On the other hand, adsorption may be reduced by temperature. In fact, the extent of adsorption can be evaluated using the -37.2 kJ/mole 2MTh heat of condensation (U.S. Secretary of Commerce 2016). Rakhmatkariev et al. (Rakhmatkariev and Isirikjan 1991) reported that polar molecules such as water are adsorbed on micropore zeolites with energies close to the heat of vapor condensation. On this basis, and using 510 °C as a
reference it can be found that the $K/K_{0i(510 \, ^\circ C)}$ ratio decreases by 28% in the 510-550 °C range.

With respect to contact times, one can also argue the need of optimization of this operational parameter. For instance, $S_{ads}$ is reduced at 7 seconds, as reported in Figure 6-11. At these conditions, new sulfur species were observed with a significant extra sulfur in coke (refer to Figure 6-14, axis-a). Furthermore, 3 seconds also provides a lower $S_{ads}$ than the one at 5 seconds contact time. On this basis, one can speculate that 5 seconds is the needed contact time that allows for the adsorption process to be essentially completed.

Consequently, it is shown that the observed $S_{ads}$ optimum of Figure 6-11, is the result of competition of selective adsorption and isomerisation/disproportionation reactions, with 530 °C and 5 s yielding the best adsorption values.

### 6.4.3.2 Sulfur Species Observed under Best Conditions

Figure 6-13 reports the sulfur distribution in various sulfur containing product species after *Stripping 1* using 5 seconds as a contact time.

![Figure 6-13. Distribution of Product Species Containing Sulfur using 0.1 g of Zn(3.5wt%)-OFF Additive (additive/HC = 0.6), and 1.2 wt% of 2MTh in TMB at 510 °C, 530 °C, 550 °C and 5 s](image-url)
One can notice in Figure 6-13 that Th, 3MTh, 25DMTh and 34DMTh sulfur species were observed in most of the cases. These species were observed at very low levels, and individually never supersede the 1.5 wt% species mixture content. Thus, while these species have little effect on sulfur balances, they are valuable to provide insights on the combined adsorption-reaction paths.

Figure 6-14 (axis-b) reports the coke yields calculated using TOC (Total Organic Carbon) analysis. TOC, as reported in Figure 6-15, allows calculating the TOC CO$_2$ formed from coke. This is accomplished, following the integration of the CO$_2$ output curve. On this basis, a total carbon in coke is calculated using a calibration curve. In this manner, one can appraise the coke yield and its changes in CREC Fluidized Reactor with both temperatures and contact times.

Figure 6-14. Coke Yields ($C_{stripping\,2}$) calculated with Eq. (4-8) and Sulfur in Coke ($S_{stripping\,2}$) Calculated with Eq. (4-7), as a Function of Contact Time and Temperature using 1.2 wt% of 2MTh in TMB at 530 ºC and 0.1 g of Zn(3.5wt%)-OFF (additive/HC = 0.6).

Furthermore, Figure 6-14 (axis-b) reports sulfur in coke following Stripping 2. One can observe the consistently low levels of sulfur in coke after Stripping 2. The only exception is the data obtained at 7s and 550 ºC. This data also reinforces, the soundness of selecting an optimum value for the selective adsorption at 5 s and 530 ºC.

Comparing Figure 6-15a and Figure 6-15b, one can also observe the different types of coke formed. Figure 6-15a reports that in the 510-550 ºC range and 5 s contact time, the coke combusted at 900 ºC is quite reactive. The oxygen consumption peaks display two
maxima at 1.3 and 2.3 min, with oxygen consumption completed in 3.5 min. This coke is designated as “fast coke”. On the other hand, Figure 6-15b shows a less reactive coke at 550 °C and 7s with a maximum oxygen consumption at 3.8 min. These results further support the value of limiting contact times and temperatures to 5 s and 530 °C. In other words, the 5s and 530 °C conditions yield an easily combustible coke and consequently an easily regenerable Zn(3.5wt%)-OFF additive.

Figure 6-15. TOC Signal for the Coke Analysis in the Additive at Different Contact Times and Temperatures. Conditions: 0.1 g of Zn(3.5wt%)-OFF and 1.2 wt% 2MTh in TMB and 7s. a) 510-550 °C and 5 s and b) 510-550 °C and 7 s.

Considering the various results of the present study, the following operational strategy is proposed for using the Zn(3.5wt%)-OFF additive:

a) 5 s and 530 °C, for maximum selective adsorption
b) 3-5 s and 510-550 °C for negligible sulfur in coke left after Stripping 2.
c) 3-5 s and 510-550 °C for the fast combustion coke type formed.

Figure 6-16 describes the expected adsorption and reaction events taking place, under the proposed 5 s and 530 °C conditions in the small Zn(3.5wt%)-OFF pores:

1. Step 1) The Th and 2MTh molecules are transported into the smaller OFF channels. A high adsorption interaction takes place with the strong acid sites of the Zn(3.5wt%)-OFF additive.

2. Step 2) The 25DMTh species are, in their majority excluded from the small OFF pores due to diffusional constraints.

3. Step 3) The Th or 2MTh species are alkylated and/or isomerised in the small OFF pores following adsorption.
4. Step 4) The Th or alkylated Th adsorbed species can be removed via stripping and in particular via the extensive *Stripping 2*.

The 25DMTh formed via disproportionation or alkylation in the small *OFF* pores can be desorbed partially from the *OFF* additive.

It is believed that the adsorption processes described above may be enhanced by the zinc in the *OFF* framework. Aponte and de Lasa reported (Aponte and de Lasa 2016) that the addition of zinc increases Lewis acidity with a mild reduction of Bronsted acidity. Thus, the dominant Lewis acid influence in the *OFF*, reduces sulfur species cracking, with the sulfur species adsorption being enhanced.
Figure 6-16. Adsorption and Reaction Network Taking Place While Using the Zn(3.5wt%)-OFF Additive.
6.5 Zn(3.5wt%)-OFF Additive and FCC Catalyst Mixture

Given the above selective adsorption findings, it was thus felt, that application to an actual FCC process was required using: a) 5 wt% of Zn(3.5wt%)-OFF and 95 wt% of FCC catalyst, b) 10 wt% of Zn(3.5wt%)-OFF and 90 wt% of FCC catalyst, c) 15 wt% of Zn(3.5wt%)-OFF and 85 wt% of FCC commercial catalyst and d) 100 wt% (1.0g) of FCC catalyst with no Zn-OFF added.

Figure 6-17 reports the carbon balances for various Zn(3.5wt%)-OFF additive and FCC catalyst blends following runs in the CREC Fluidized Reactor Simulator.

![Graph showing carbon balances](image)

Figure 6-17 Carbon Balance Level 1 ($C_{ads}$) and Carbon Balance Level 2 ($C_{stripping 1}$). Parameters are calculated with Eqs. (4-4) and (4-6) for different the Zn(3.5wt%)-OFF Additive + FCC Catalyst Blends. Tests performed using a 1.2 wt% 2MTh in TMB at 530 °C and 5 s.

Figure 6-17 shows that the $C_{ads}$ are in the 2.5-5.3 wt% range. These amounts are reduced by less than 2wt%, following Stripping 1 ($C_{stripping 1}$). As a result, and in agreement with
the findings of Section 6.4.1, there is a limited adsorption of carbon species free of sulfur following *Stripping 1*.

Figure 6-18 reports $S_{ads}$, $S_{stripping \, 1}$, and $S_{stripping \, 2}$ for 100 wt% of FCC catalyst (0% of Zn(3.5wt%)-OFF) loaded in the CREC Fluidized Simulator.

![Graph](image-url)

Figure 6-18. Sulfur Balance Level 1 ($S_{ads}$), Sulfur Balance Level 2 ($S_{stripping \, 1}$), Sulfur Balance Level 3 ($S_{stripping \, 2}$) Calculated with Eqs. (4-1), (4-5) and (4-7) as a Function of the Percentage of Zn(3.5wt%)-OFF Additive + FCC Catalyst Blends using 1.2 wt% 2MTh in TMB at 530 °C and 5 s.

Under these conditions, a 35 wt% $S_{ads}$ is observed. However, one can also notice that 21 wt% sulfur ($S_{stripping \, 1}$) is not removed. Furthermore, following the second stripping, the entire 21 wt% sulfur remains as coke as shown with $S_{stripping \, 2}$. If one tries to consider these results in the context of carbon and sulfur balances, one can notice that adopting a C/S of 5 for the coke lay down in the Zn(3.5wt%)-OFF additive, this leads to a sulfur amount remaining on the FCC catalyst exceeding the sulfur injected. This points to a coke formed on the catalyst, with a lower sulfur content, with a possible C/S molar ratio of 20-30.
Figure 6-18 also shows sulfur balances when the Zn(3.5wt%)-OFF additive is mixed with the FCC catalyst. One can notice that sulfur adsorption ($S_{ads}$) is augmented when the Zn(3.5wt%)-OFF additive is augmented in the additive-FCC catalyst blends. In this respect, a maximum $S_{ads}$ value of 52.5 wt% is observed for a 15 wt% Zn(3.5wt%)-OFF additive and 85 wt% FCC catalyst blend.

This increase in $S_{ads}$ may occur given the FCC catalyst cracks TMB transforming it into smaller molecules. Under these conditions, there is no diffusional constraint in the Zn(3.5wt%)-OFF additive. These formed methyl radicals can alkylate the 2MTh (refer to Figure 6-16 step 3). As a result, there is a potential enhancement of the selective adsorption via the interactions of cracking and alkylation when using a 5 wt% to 10 wt% of Zn(3.5wt%)-OFF additive providing 48.5 wt% to 51.6 wt% of $S_{ads}$. These favorable results are combined with the 2.24 wt% and 2.42 wt% of $S_{stripping \ 2}$.

Figure 6-19a reports the 2MTh and TMB conversions as function of the Zn(3.5wt%)-OFF additive - FCC catalyst blends, with the 100% FCC catalyst yielding the highest 2MTh conversion, and the TMB conversion remaining essentially unchanged.
Figure 6-19. a) TMB and 2MTh Conversion and b) Coke Yields as functions of the percentage of the Zn-OFF Additive in the Zn(3.5wt%)-OFF Additive + FCC Catalyst Blends using 1.2 wt% 2MTh in TMB at 530 °C and 5 s.

Figure 6-19b reports coke yields as follows: a) Total coke yield, b) Coke yield in the Zn(3.5wt%)-OFF additive, c) Coke yield in the FCC catalyst. One can notice a significant reduction of the total coke yield from 6.8 wt% for the 100 wt% FCC Catalyst to 1.5-2.2 wt% for Zn(3.5wt%)-OFF additive-FCC catalyst blends. Thus, the Zn(3.5wt%)-OFF additive when mixed with an FCC catalyst inhibits coke formation. Coke formed in the FCC catalyst under these conditions, was found to be in the same range as when using pure TMB as a feedstock: 0.21-0.32 wt% of coke for 530°C and 5 s. These findings also confirm as stated earlier in Section 6.4.1, the significant role of sulfur containing species and the needed development of additives for the selective adsorption of sulfur compounds as described in the present study.
Regarding the $S_{stripping\ 1}$, another interesting finding, as shown in Figure 4-4, is that this parameter remains between 5.2 - 7.6 wt% for the Zn(3.5wt%)-OFF additive + FCC catalyst blends. This is a valuable indicator that most of the adsorbed sulfur (86-87 %) is removed in the first stripping stage. Then, following the extensive stripping (Stripping 2) a 91-95 % of the total adsorbed sulfur is desorbed, remaining only 5-9% as coke. Given this, one can forecast that the Zn(3.5wt%)-OFF additive can reduce the sulfur in coke in 79-89 %, when comparing $S_{stripping\ 2}$ of the Zn(3.5wt%)-OFF additive + FCC catalyst blends with $S_{stripping\ 2}$ using 100% FCC Catalyst.

Thus, this section of the manuscript shows that the Zn(3.5wt%)-OFF is a suitable additive for the selective adsorption of sulfur containing species in the gasoline range at 5 s and 530 °C. The use of this additive also displays the following advantages:

a) The coke formed is reduced considerably, with this being a major feature for FCC commercial units

b) The coke formed after extensive stripping contains negligible sulfur content

c) The light coke formed can be easily combusted in the FCC regenerator.

In summary, the results of the present study highlight the value of using a Zn(3.5wt%)-OFF additive for sulfur species removal in FCC processes. On this basis, one can recommend implementation of the additive in an FCC process, with 5wt% of Zn(3.5wt%)-OFF, yielding 48.5 wt% of 2MTh removal with only a 2.24wt% sulfur left after $S_{stripping\ 2}$. 
6.6 Conclusions

The following are the main conclusions of the present study:

a) It was demonstrated that increasing Zn content embedded in OFF zeolite promotes sulfur adsorption rather than sulfur conversion.

b) It is proven that a new sulfur removal Zn(3.5wt%)-OFF additive with high Lewis acid sites is suitable for sulfur containing species removal in the gasoline range, under FCC conditions.

c) It is shown that the small pores with strong acids sites of this Zn(3.5wt%)-OFF additive promote the adsorption of sulfur species.

d) It is proven that the Zn(3.5wt%)-OFF shows a most favorable operation at 530 °C and 5 s. Under these conditions, a 42% sulfur adsorption is achieved with 1.3 wt% sulfur in coke.

e) It is demonstrated that blends of the 5 wt% Zn(3.5wt%)-OFF additive and a 95 wt% FCC commercial catalyst enhance sulfur selective adsorption reaching 48.5 wt% sulfur adsorption with a limited coke yield of 2.2 wt%.
Chapter 7

7 NH$_3$-TPD desorption models

This chapter reports the effect of adding zinc to the acid properties of the OFF. NH$_3$ desorption kinetic parameters are reported in this section. Two numerical methodologies, linear and nonlinear regression, are implemented for parameter evaluation.

7.1 Introduction

Zeolites of the offretite family have been identified as having good prospects for a number of chemical processes such as: a) the transformation of toluene and the isomerization of m-xylene (Mavrodinova et al. 1985; Sastre et al. 1990), b) the catalytic selective reduction of NOx using Cu (II) ion exchange (Arous et al. 2007), c) methanol conversion using an OFF protonic form (Dejaifve et al. 1981) d) n-hexane conversion to C$_3$ hydrocarbons and o-xylene conversion to p-xylene (Bourdillon et al. 1986), and e) CO$_2$ adsorption using K-OFF (Gorshunova et al. 2015).

As mentioned in Chapter 4 and 6, a new application for OFF zeolites was demonstrated (Aponte, Djaouadi, and de Lasa 2014; Aponte 2011) in FCC units. Zn-OFF can be used as an additive for sulfur reduction in gasoline. This selective adsorption takes advantage of the OFF topology consisting of 8 smaller member ring pores and OFF acid sites (Aponte, Djaouadi, and de Lasa 2014; Aponte 2011; Aponte and de Lasa 2016; Aponte, Che-Galicia, and de Lasa 2016).

The effect of zinc in the framework (loaded by direct synthesis) of other zeolites, such as ZSM-5, ZSM-11 and Beta has already been reported (Orazov and Davis 2016; Meng et al. 2015; J. Gao et al. 2009). To our knowledge however, there is no published study that evaluates the Zn influence on OFF acidic properties.

To accomplish this, NH$_3$-TPD, a commonly used method for measuring the surface acidity of zeolites (Damjanovic and Auroux 2009; Gorte 1996; Niwa and Katada 1997; Hellmut G. Karge 1991), is employed to study the following offretites: a) an OFF zeolite free of
zinc, b) an OFF with a 2.0wt% Zn loading designated as Zn(2.0wt%)-OFF and c) an OFF with 3.5wt% Zn, loading designated as Zn(3.5wt%)-OFF zeolites. NH$_3$-TPD is also employed to determine ammonia desorption kinetic parameters in these three OFF materials.

It is found, as advised by our research group (Al-Dughaither and de Lasa 2014; Al-Ghamdi et al. 2013; Tonetto, Atias, and de Lasa 2004) and as described later in this manuscript, that nonlinear numerical analysis is required, in order to assess desorption parameters. This rigorous method allows establishing realistic values for ammonia desorption parameters. This is the case for the three observed acid sites of the OFF.

### 7.2 Experimental Conditions for NH$_3$-TPD tests

As mentioned in Chapter 3 (Section 3.3.3), NH$_3$ -TPD was carried out using an AutoChem II 2920 Analyzer from Micromeritics. Ammonia was adsorbed for 1 h at 100 °C using a NH$_3$/He gas mixture (19.04 molar ratio of He/ NH$_3$). Samples were prepared by heating them under helium gas flow for 2 h at 500 °C. Then, the temperature was increased linearly using five different temperature ramps (β): 10, 15, 20, 25 and 30 °C/ min until 680 °C was reached.

It is important to mention that the experiments were performed 3-5 times using the OFF analyzed to ensure reproducibly. The following parameters remained unchanged during each repeat run (Bhatia, Beltramini, and Do 1990; Hunger et al. 1990):

a) The measured flow rate, Q, had a constant value of 50.25 ± 0.07 cm$^3$ STP/min
b) A NH$_3$-He certified gas mixture had 4.99% ammonia and 95.01% helium
c) The mass of the zeolites, m$_{cat}$, was 0.12g ± 0.02g
d) The particle size of the zeolites was 2-5µm (Aponte and de Lasa 2016)
e) The system pressure was at 1 atm.
7.3 Modeling Ammonia TPD Desorption

To evaluate the desorption kinetic parameters, two cases were considered in this study:

- **Method 1**: A first order kinetics without readsoption of ammonia, using linear regression: conventional method
- **Method 2**: A first order kinetics without readsoption of ammonia and employing nonlinear regression: non-conventional method (Al-Dughaither and de Lasa 2014)

To develop the desorption kinetic model, some considerations were taken into account:

a) There is adsorption equilibrium between the adsorbed ammonia on the zeolite and the ammonia in the gas phase. As a result, the following equation can be considered to describe desorption-adsorption processes:

\[(\text{NH}_3)^* \rightleftharpoons \text{NH}_3 + \theta_v \quad (7-1)\]

where \((\text{NH}_3)^*\) or \(\Theta\) represents the adsorbed ammonia and \(\theta_v\) stands for the vacant sites in the OFF. Therefore, the balance of acid sites can be represented as follows:

\[\theta + \theta_v = 1 \quad (7-2)\]

\[\theta_v = \frac{v_d}{v_m} \quad (7-3)\]

where \(v_d\) denotes the desorption volume and \(v_m\) stands for the monolayer volume, both per unit of mass of the solid phase.

b) The temperature in the OFF particle bed increases lineally with time, as follows:

\[T = T_0 + \beta t \quad (7-4)\]

where \(T\) denotes temperature at any time \(t\), \(T_0\) stands for the initial temperature of ammonia desorption (i.e \(T_0=100^\circ\text{C}\) at \(t = 0\) s), \(t\) represents the time and \(\beta\) indicates the heating rate coefficient.

c) There are no diffusional effects affecting the ammonia desorption. According to the literature (Demmin and Gorte 1984; Sharma et al. 1993), the following dimensionless criterion must be satisfied in order to be able to neglect the concentration gradients inside the OFF particles:
\[
\frac{Q\cdot R}{4\pi R^2 \cdot N \cdot D_P} < 0.05 \quad (7-5)
\]

where \(Q\) is the carrier gas flow rate, \(R\) stands for the catalyst particle radius, \(N\) represents the number of particles used in the TPD analysis, and \(D_P\) denotes the particle diffusion coefficient. To evaluate these parameters, the following data were considered:

c.1) The diffusion coefficient for ammonia in the OFF was approximated with the one reported by Sprynskyy (Sprynskyy et al. 2005) for mordenite. This \(D_P\) was reported to be in the \(0.7-3.6 \times 10^{-8}\) cm\(^2\)/s range. This coefficient accounts for the diffusional effects in the mordenite zeolites with two types of channels: 6.7x7.0 Å and 2.9x5.7Å. Given the resemblance of the mordenite and the OFF pore network, this \(D_P\) value was considered as a good approximation.

c.2) The 2-5 µm catalyst particle radius was established using the average particle size as measured with SEM (Aponte and de Lasa 2016).

c.3) \(Q\) and \(N\) parameters were calculated from the conditions utilized in the TPD analyses (Section 7.2).

Using this approach, the dimensionless parameters as in Eq. (7-5) were calculated to be in the range of \(6 \times 10^{-11} - 3 \times 10^{-10}\) for the three zeolites studied. These values were significantly lower than the recommended 0.05.

d) The desorption kinetics was first rate. Thus, this rate can be expressed by:

\[
-v_m \frac{d\theta}{dt} = k_d \theta \quad (7-6)
\]

where \(t\) is the time and \(k_d\) stands for the rate constant of desorption.

One can assume that adsorption kinetic parameters, \(k_d\) and its changes with temperature can be expressed via the Arrhenius’ equation as follows:

\[
k_d = k_{do} \cdot \exp \left( -\frac{E_d}{RT} \right) \quad (7-7)
\]
where \( k_{do} \) stands for the intrinsic desorption constant in \( \text{min}^{-1} \), \( E_d \) is the desorption energy, and \( R \) denotes the universal gas constant. Given all the above, the procedure proposed by Cvetanovic et al., Konvalinka et al. and Niwi et al. (Cvetanović and Amenomiya 1972; Konvalinka, Scholten, and Rasser 1977; Niwa and Katada 1997; Niwa et al. 1995), was implemented as follows:

Combining Eq. (7-4), Eq. (7-6) and Eq. (7-7), one obtains the following:

\[
-\frac{d\theta}{dT} = \frac{k_{do}}{\beta} \theta \cdot \exp\left(-\frac{E_d}{RT}\right)
\]  

(7-8)

With \( k_{do} = k_{do}'/v_m \)

Furthermore, expressing Eq. (7-8) in terms of \( v_d \), this results in the following equation,

\[
\frac{dv_d}{dT} = k_{do} \frac{1}{\beta} \left(1 - \frac{v_d}{v_m}\right) \cdot \exp\left(-\frac{E_d}{RT}\right)
\]  

(7-9)

**Method 1.** One should notice that the \( d\theta/dT \) rate, displays a maximum at \( d^2\theta/dT^2=0 \), where \( T=T_p \) and \( \theta=\theta_p \). The resultant \( (d\theta/dT)_{MAX} \) from the derivation combines with Eq. (7-8) evaluated at the maximum, as proposed by White (White 1990), a equation in the maximum can be written as follows:

\[
\left(\frac{d\theta}{dT}\right)_{MAX} = \frac{E_d\theta_p}{RT_p^2} = \frac{k_{do}}{\beta} \theta_p \cdot \exp\left(-\frac{E_d}{RT_p}\right)
\]  

(7-10)

where \( T_p \) denotes the temperature at the maximum.

By expressing the resulting Eq. (7-10) in the natural logarithmic form, this results in the following equation:

\[
2ln(T_p) - ln(\beta) = \frac{E_d}{R} \left(\frac{1}{T_p}\right) + ln\left(\frac{E_d}{k_{do}R}\right)
\]  

(7-11)

Thus, one can consider the linearized form of Eq. (7-11), by assessing the slope in a \( (2ln[T_p]-ln[\beta]) \) versus \( 1/T_p \) plot. This gives \( E_d/R \) and as a result, \( E_d \) which is the desorption energy. The intercept also allows one to establish the \( k_{do} \).
**Method 2:** This approach entailed solving the nonlinear Eq. (7-9) numerically and directly (Al-Dughaither and de Lasa 2014; Al-Ghamdi et al. 2013; Tonetto, Atias, and de Lasa 2004). In this case, Eq. (7-9) was solved using a modified version, involving the average $T_M$ (centering temperature) to reduce cross-correlation between parameters:

$$\frac{dv_d}{dT} = k_{do''} \left(1 - \frac{v_d}{v_m}\right) \cdot \exp\left(-\frac{E_d}{R} \left(\frac{1}{T} - \frac{1}{T_M}\right)\right) \quad (7-12)$$

With $k_{do} = k_{do''} \cdot \exp(E_d/RT_M)$.

To accomplish this, Eq. (7-12) was solved numerically using the ODE45 (4th order Runge-Kutta) method as implemented in MATLAB®. This was done in conjunction with the numerical regression of $k_{do''}$ and $E_d$ in order to achieve the least square of residuals.

The NH$_3$-TPD temperature ramp data used for the model parameter calculations were $\beta = 15, 20, 25, 30$ °C/min for Site I and II, and $\beta=20, 25, 30$°C/min for Site III, with each site analyzed separately.

Prior to the application of Methods 1 and 2, NH$_3$-TPD data for Site I, Site II and Site III, were obtained via “deconvolution” as explained in Section 5.3.2 (refer to Figure 5-6). This allowed one to establish the temperature desorption ranges relevant for each site as follows: a) From $T_0$ to $T_1$ for Site I, b) From $T_2$ to $T_3$ for Site II, and c) From $T_4$ to $T_{end}$ for Site III.

Furthermore, a rigorous statistical analysis was performed using both Method 1 and Method 2. For instance, for the two kinetic parameters ($E_d$ and $k_{do}$) determined using nonlinear regression, the following variables were considered: a) a 95% confidential interval, b) a correlation coefficient ($R^2$), c) a mean square error (MSE), and d) cross-correlation coefficients between kinetic parameters.
7.4 Desorption Rate Modeling Results: Linear and Nonlinear Regression

7.4.1 Linear Regression

Given the above described Method 1, the desorption kinetic parameters were established by first using linear regression. All the ramping temperature rates, \( \beta = 10, 15, 20, 25, 30 \) °C/min, with at least three repeats for each case were considered.

As previously stated in Section 5.3.2 the deconvolution for each NH\(_3\)-TPD profile was established. Once each deconvolution was performed, and the \( T_p \) and \( \Theta_p \) were obtained for each site, Eq. (7-11) was used for the evaluation of Site I, II and III, separately. Following this, the slope of the \( (2\ln[T_p]-\ln[\beta]) \) versus \( 1/T_p \) was calculated, with this yielding the \( E_d/R \) and the subsequently the \( E_d \) desorption activation energy. Furthermore, the \( \ln \left( \frac{E_d}{k_{do}R} \right) \) intercept made possible the \( k_{do} \) intrinsic desorption rate constant calculation.

Figure 7-1 shows the linear regression performed for each ones of the OFFs studied. In addition, Table 7-1 reports both \( E_d \) and \( k_{do} \) for each of the sites as calculated by the linear regression.
Figure 7-1. Linear Regression Using Eq. (7-11) for a) OFF, b) Zn(2.0 wt%)-OFF zeolite and c) Zn(3.5 wt%)-OFF zeolite. Horizontal bars represent the standard deviations for 3-5 repeats.
Table 7-1. Desorption Activation Energies ($E_d$, kJ/mol) and Intrinsic Desorption Rate Constants ($k_{do}$, ml/g STP·min) Determined by Linear Regression Eq. (7-11)

<table>
<thead>
<tr>
<th></th>
<th>OFF Zeolite</th>
<th>Zn(2.0wt%)-OFF Zeolite</th>
<th>Zn(3.5wt%)-OFF Zeolite</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_d$ (kJ/mol)</td>
<td>$k_{do}$ (ml/g STP·min)</td>
<td>$E_d$ (kJ/mol)</td>
</tr>
<tr>
<td>Site I</td>
<td>41</td>
<td>1.4x10^4</td>
<td>42.3</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>3x10^3</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>0.991</td>
<td>0.991</td>
<td>0.977</td>
</tr>
<tr>
<td>Site II</td>
<td>31</td>
<td>1.8x10^3</td>
<td>36.2</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>2x10^2</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>0.984</td>
<td>0.984</td>
<td>0.988</td>
</tr>
<tr>
<td>Site III</td>
<td>99</td>
<td>3.4x10^2</td>
<td>93</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>3x10^2</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>0.967</td>
<td>0.967</td>
<td>0.966</td>
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</table>
Figure 7-1 also shows the standard deviations for repeats using horizontal error bars. One can notice, that the error bars for Site II (middle peak) are consistently larger. It is speculated that Site II which is in between, Site I and Site III, may accumulate errors that can be traced to Site I (first peak) and the Site III (last peak).

Table 7-1 reports the $E_d$ and $k_{do}$ parameters obtained by linear regression. One can observe that $E_d$ values in the table are in agreement with the typical $E_d$ in zeolites reported in the literature (Hunger et al. 1990; Niwa and Katada 1997; Al-Dughaither and de Lasa 2014; Xi et al. 2003). One can also notice that the spans for the $E_d$ for Sites I and II are in the 10% range. One can also observe that the 95% CI for the Site III, augments considerably to 20%. This increase in the 95% CI was attributed to the smaller $v_d$ values for Site III versus the ones for Sites I and II. Furthermore, Table 7-1 reports modest changes of $E_d$ with the zinc addition.

Moreover, Table 7-1 also reports the $k_{do}$ calculated by linear regression. One can notice that the $k_{do}$ calculated are out of the range while compared to the ones reported for other zeolites (Al-Dughaither and de Lasa 2014; Al-Ghamdi et al. 2013). These $k_{do}$ were obtained with large 95% CI spans as well. In some cases, they even yielded unrealistic negative $k_{do}$ values.

One can thus conclude, that the fitting of Eq. (7-11) may be adequate to determine the heat desorption parameter for some materials but with some specific zeolites may fail, as shown here and as reported by Tonetto et al. (Tonetto, Atias, and de Lasa 2004). However, the $k_{do}$ obtained via linear regression may yield inaccurate intrinsic desorption constant values. Thus, as is shown later, $k_{do}$ and $E_d$ have to be calculated by using non-linear regression (Al-Ghamdi et al. 2013; Al-Dughaither and de Lasa 2014; Tonetto, Atias, and de Lasa 2004).

### 7.4.2 Non-Linear regression

Non-linear regression of Eq. (7-12) parameters was developed by using different temperature ramps. This allowed the calculation of desorption parameters applicable to an sample range of desorption rates (Al-Dughaither and de Lasa 2014). In this respect, for
Sites I and II, βs of 15, 20, 25, and 30 °C/min were used while for Site III βs of 20, 25, and 30 °C/min were employed.

Figs. 7-2 to 7-4 report data fittings using Eq. (7-12) for Sites I, II and III and an OFF with: a) no zinc, b) 2.0 wt% of Zn and c) 3.5wt% of Zn.

One can observe in Figs. 7-2 to 7-4, a good model agreement of experimental data for desorbed ammonia: a) the weak acid sites (Site I), b) moderate acidity strength sites (Site II), c) strong acid sites (Site III). Table 7-2 reports the calculated activation energy of desorption ($E_d$) and the intrinsic desorption rate constant ($k_{d0}$) for the three acid sites and three OFF zeolites.
Figure 7-2. Non-linear Regression for Site I Using Eq. (7-12) for: a) OFF, b) Zn(2.0 wt%)-OFF Zeolite and c) Zn(3.5 wt%)-OFF Zeolite.
Figure 7-3. Non-linear Regression for Site II Using Eq. (7-12) for: a) OFF, b) Zn(2.0 wt%)-OFF Zeolite and c) Zn(3.5 wt%)-OFF Zeolite.
Figure 7-4. Non-linear Regression for Site III Using Eq. (7-12) for: a) OFF, b) Zn(2.0 wt%)-OFF Zeolite and c) Zn(3.5 wt%)-OFF Zeolite.
Table 7-2. Activation Energies \((E_d, \text{kJ/mol})\) and Intrinsic Desorption Rate Constants \((k_{do}, \text{ml/g STP.min})\) Determined by Nonlinear Regression.

<table>
<thead>
<tr>
<th></th>
<th>OFF Zeolite values</th>
<th>95% CI</th>
<th>(R^2)</th>
<th>Zn(2.0wt%-OFF Zeolite values</th>
<th>95% CI</th>
<th>(R^2)</th>
<th>Zn(3.5wt%-OFF Zeolite values</th>
<th>95% CI</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E_d) (kJ/mol)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Site I</td>
<td>36</td>
<td>5</td>
<td>0.994</td>
<td>46</td>
<td>2</td>
<td>0.999</td>
<td>47</td>
<td>1</td>
<td>0.999</td>
</tr>
<tr>
<td>Site II</td>
<td>32</td>
<td>3</td>
<td>0.998</td>
<td>33</td>
<td>4</td>
<td>0.996</td>
<td>45</td>
<td>5</td>
<td>0.996</td>
</tr>
<tr>
<td>Site III</td>
<td>95</td>
<td>9</td>
<td>0.999</td>
<td>94</td>
<td>3</td>
<td>1.000</td>
<td>100</td>
<td>3</td>
<td>0.999</td>
</tr>
<tr>
<td>(k_{do}) (cc/g STP-min)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Site I</td>
<td>2.57</td>
<td>0.16</td>
<td>0.994</td>
<td>3.45</td>
<td>0.08</td>
<td>0.999</td>
<td>3.77</td>
<td>0.08</td>
<td>0.999</td>
</tr>
<tr>
<td>Site II</td>
<td>4.41</td>
<td>0.18</td>
<td>0.998</td>
<td>4.17</td>
<td>0.20</td>
<td>0.996</td>
<td>4.77</td>
<td>0.25</td>
<td>0.996</td>
</tr>
<tr>
<td>Site III</td>
<td>0.66</td>
<td>0.03</td>
<td>0.999</td>
<td>1.72</td>
<td>0.03</td>
<td>1.000</td>
<td>2.95</td>
<td>0.06</td>
<td>0.999</td>
</tr>
<tr>
<td>(k_{do}) (cc/g STP-min)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Site I</td>
<td>2.8x10^4</td>
<td>1x10^3</td>
<td>0.994</td>
<td>2.18x10^5</td>
<td>5x10^3</td>
<td>0.999</td>
<td>2.88x10^5</td>
<td>6x10^3</td>
<td>0.999</td>
</tr>
<tr>
<td>Site II</td>
<td>7.3x10^2</td>
<td>3x10^1</td>
<td>0.998</td>
<td>8.1x10^2</td>
<td>4x10^1</td>
<td>0.996</td>
<td>6.8x10^3</td>
<td>4x10^2</td>
<td>0.996</td>
</tr>
<tr>
<td>Site III</td>
<td>1.09x10^5</td>
<td>6x10^3</td>
<td>0.999</td>
<td>2.69x10^5</td>
<td>5x10^3</td>
<td>1.000</td>
<td>9.8x10^5</td>
<td>2x10^4</td>
<td>0.999</td>
</tr>
</tbody>
</table>

Note: \(k_{do}\) is calculated as \(k_{do} = k_{do}'' \exp(E_d/RT_M)\)
Table 7-2 shows that $E_d$ for Sites I and II are in the same range, while $E_d$ for Site III is much larger. These variations can be attributed to the different ammonia coordination on each type of acid site. The existence of dissimilar bindings on the OFF acid sites, was suggested by others (Penchev et al. 1983b). Furthermore, when zinc was embedded in the OFF, the $E_d$ was modified as well, showing that the $E_d$ for 3.5wt% Zn > $E_d$ for 2.0wt% Zn > $E_d$ for OFF. This suggests that ammonia binding energies are strengthened with zinc addition.

Moreover, Table 7-2 reports the intrinsic desorption rate constants ($k_{do}$). This suggests that while interacting with the Sites I, II and III, ammonia displays a frequency of interaction with the OFF sites which is quite different. Furthermore, Table 7-2 shows that the addition of zinc appears to also have an influence on $k_{do}$, increasing mildly with higher zinc contents.

Finally, Table 7-2 also provides statistical indicators for the calculated parameters. In this respect, the following were found in all cases: a) small spans for the 95% confidence interval, b) an MSE lower than 0.1 and c) an $R^2$ close to one. Consistent with this, Figure 7-5 displays a close agreement in the parity plot, between the numerically calculated desorbed volume using the parameters of Table 7-2 and the experimentally measured values.
Figure 7-5. Experimental and Predicted Ammonia Desorption Volume: a) OFF, b) Zn(2.0 wt%)-OFF Zeolite, and c) Zn(3.5 wt%)-OFF Zeolite.

Regarding the numerical fitting of the parameters of the proposed ammonia desorption model Eq. (7-12), one should notice that the degrees of freedom (DOF=Number data Points-Number of parameters) were higher than 100, in all runs.

Furthermore, concerning the cross-correlation of the estimated parameters, Table 7-3 reports the values obtained.

Table 7-3. Cross-Correlation Coefficient Matrix for the Desorption Kinetic Constants

<table>
<thead>
<tr>
<th></th>
<th>OFF Zeolite</th>
<th>Zn(2.0wt%)-OFF Zeolite</th>
<th>Zn(3.5wt%)-OFF Zeolite</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k_{do}$</td>
<td>$E_d$</td>
<td>$k_{do}$</td>
</tr>
<tr>
<td>Site I</td>
<td>1</td>
<td>-0.027</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>$E_d$</td>
<td>1</td>
<td>$E_d$</td>
</tr>
<tr>
<td>Site II</td>
<td>1</td>
<td>0.867</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>$k_{do}$</td>
<td>$E_d$</td>
<td>$k_{do}$</td>
</tr>
<tr>
<td>Site III</td>
<td>1</td>
<td>0.926</td>
<td>1</td>
</tr>
</tbody>
</table>
It is observed that for Site I, the cross-correlation coefficients displayed a smaller than one required value. This showed that the numerical technique used with temperature centering ($T_p$) led to $E_d$ and $k_{do}$ values with little interdependence. On the other hand, in the case of Sites II and III, the calculated cross-correlation coefficients raised to levels closer to one. This was particularly true for Site III. These less desirable cross-correlation coefficients were assigned to the inherent difficulty of fitting parameters, using small TPD ammonia desorbed volumes, as it was the case for Site III.

In brief, three different acid sites with different acid strengths were identified using NH$_3$-TPD profiles. These three sites were described using a desorption rate model, with $E_d$ and $k_{do}$ parameters being evaluated. It was observed that kinetic desorption parameters in the OFF were influenced by the zinc addition.

### 7.5 Conclusions

a) NH$_3$-TPD was employed to further characterize the OFF and the OFF with added zinc. Ammonia desorption shows that zinc addition, preserves the three OFF acid sites.

b) Three acid sites were identified and evaluated the NH$_3$ desorption kinetic parameters: a) abundant number of weak acid sites (Site I), b) fair number of moderate acid strength sites (Site II), and c) scarce number of strong acid sites (Site III). This sites leads desorption activation energies in the following order: $E_d,\text{Site I} \cong E_d,\text{Site II} < E_d,\text{Site III}$.

c) An ammonia desorption model was considered in order to describe NH$_3$-TPD. Desorption parameters were evaluated using both a linear and nonlinear regression of the desorption model parameters. The nonlinear regression led to a more trustable set of $E_d$ and $k_{do}$ parameters complying with the required regression data analysis statistical indicators.
d) For the Zn-OFF zeolites, it was observed that zinc addition led to significant changes in the energy of desorption and the frequency factor. The $E_d$ augments with zinc loaded in the OFF in the following: $E_d$ for OFF $< E_d$ for Zn(2.0wt%)-OFF $< E_d$ for Zn(3.5wt%)-OFF
8 Conclusions and Recommendations

This PhD dissertation addresses the reduction of thiophenic sulfur species in the gasoline range via selective adsorption, using a new Zn-OFF based additive. It was envisioned, at the beginning of this PhD research, that zinc in the OFF zeolite could be an important species to use for achieving a selective adsorption process.

It was, in fact, demonstrated in this PhD, that these targeted Zn-OFF zeolites could be synthesized using novel preparation methods. The physicochemical and structural properties of the Zn-OFF were established using a number of advanced zeolite surface characterization methods. In addition, new experimental procedures were validated using CREC Riser Simulator in order to quantify the adsorption of sulfur species in the Zn-OFF additives.

Furthermore, the Zn-OFF selective adsorption and reactivity under conditions close to the ones of FCC industrial units were established in the CREC Riser Simulator. With this end, three sulfur containing model compounds were used as follows: thiophene, 2-methylthiophene and 2,5-dimethylthiophene. The gasoline hydrocarbon fraction was emulated using trimethylbenzene.

8.1 Conclusions

The following summarize the most relevant contributions of the present PhD research:

1. It is shown that the CREC Riser Simulator coupled with GC-MS/FID/FPD offers a valuable tool to quantify the selective thiophenic species adsorption. A method to quantify the selective thiophenic species adsorption was successfully demonstrated using this unit. A gas phase sample was taken from the reactor through the vacuum box. This permitted the direct sampling of the gas phase of reaction product to be analyzed in the GC-MS/FID/FPD. The method allowed one to determine the
quantity of sulfur species and carbon adsorbed on both the FCC additive and commercial catalyst in the CREC Riser Simulator.

2. Zn-OFF zeolites were successfully obtained by adding zinc in the OFF zeolite during the direct synthesis. The prepared Zn-OFF zeolites likely contained most of the zinc species, included in the OFF framework. Zn species promoted different desirable Lewis acidities.

3. Zn-OFF additives with two levels of zinc were successfully obtained. The OFF and Zn-OFF zeolites were proven to provide valuable acidity to the additives. Zn-OFF additives were dispersed in an inert matrix. This was done to obtain OFF fluidizable particles.

4. The Zn in the OFF zeolites increased the total acidity as well as the acid site strength, with more Lewis acidity being promoted. It was found using pyridine adsorption that the amount of Zn loading in the OFF increased Lewis / Brönsted site ratios. It is speculated that the zinc content may modify OFF’s T-O-T bridges producing different and new acid site interactions. The NH$_3$-TPD showed that acidity in the OFF and Zn-OFFs involved at least three types of sites: weak acid site, moderate acid sites and strong acid sites. It was also proven that the abundance of Sites I, II and III increased with the Zn/Al content in the OFF. This sites displayed desorption activation energies with the following relative magnitudes: $E_{d,\text{Site I}} \approx E_{d,\text{Site II}} < E_{d,\text{Site III}}$.

5. The adsorption experimental runs in the CREC Riser Simulator were valuable to demonstrate that Zn embedded in OFF zeolites, promotes sulfur adsorption rather than sulfur conversion. This was a desirable result since the formation of coke is a bimolecular reaction, with coke increasing the undesirable SO$_x$ emissions in the FCC catalyst regenerator.

6. Additional runs using alkyl aromatics such as 1,3,5-trimethylbenzene and 2,5-dimethylthiophene, allowed to demonstrate that the smaller OFF pores contain strong acids sites. These smaller OFF pores are considered to provide the sites where sulfur species are selectively adsorbed.
7. It is proven that a new sulfur removal Zn(3.5wt%)-OFF additive with high Lewis acid sites is suitable for sulfur containing species reduction under FCC conditions. It was found that the Zn(3.5wt%)-OFF shows a most favorable operation at 530 °C and 5 s. Under these conditions, a 42% sulfur adsorption is achieved with 1.3 wt% sulfur in coke.

8. It was demonstrated that blends of the 5 wt% Zn(3.5wt%)-OFF additive and a 95 wt% FCC commercial catalyst enhance sulfur selective adsorption reaching 48.5 wt% sulfur adsorption. This was achieved with a limited coke yield of 2.2 wt% or an equivalent 70% of coke reduction. This reduced coke may become a significant Zn-OFF additive feature for mitigating SO\textsubscript{x} emissions in the FCC regenerator.

9. An ammonia desorption model was considered in order to describe the desorption kinetic parameters. For the Zn-OFF zeolites, it was revealed that zinc addition led to significant changes in the energy of desorption and the frequency factor. In this respect, it is shown $E_d$ changes with zinc in OFF as follows: $E_d$ for OFF < $E_d$ for Zn(2.0wt%)-OFF < $E_d$ for Zn(3.5wt%)-OFF.
8.2 Recommendations

On the basis of the above, the following recommendations can be advanced for future research:

1. To study more extensively the selective adsorption of thiophenic species using the Zn-OFF additive or/and other additives of the same family. In this respect, future studies should evaluate more thoroughly, the best Zn loadings for the Zn-OFF additive, while blending them with the FCC commercial catalyst.

2. To analyse thoroughly the design and operational changes in FCC stripper units as required by sulfur species desorption. One should in this respect consider, the effect of different stripper designs and conditions (combustion gases or steam) to be used in these modified FCC strippers. In addition, this study should involve the evaluations of mechanical properties (attrition index) for the Zn-OFF additive.

3. To develop sulfur reduction additives using zeolites accommodating bigger sulfur containing molecules such as 2,5-dimethylthiophene and benzothiophene. These new additives will help to remove more effectively, the sulfur species with boiling points close to those of methylbenzothiophene and benzothiophene (high range of gasoline boiling point and diesel).

4. To study sulfur reduction of gasoline species using VGO feedstocks. In this manner, it will be possible to evaluate the effect of other coexisting molecules over the Zn-OFF additives and their competition for acid sites during sulfur species selective reduction. This may involve reaction testing under various reactions times, temperatures, stripping conditions, and additive - catalyst blends.

5. To consider the application of a Zn-OFF in a post-treatment gasoline desulfurization process. This post-treatment process could involve the Zn-OFF additive and a commercial FCC catalyst. This process might include lower temperatures, reaction times smaller than 7 s, different additive-catalyst blends and adequate conditions for sulfur species stripping.
References


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Appendices

Appendix A: Thiophenic Species Calibration Curves

Multiple thiophenic species calibration curves that correlates thiophenic concentration with FPD, MS and FID detector chromatogram areas and concentrations were determined. They were carried out using the two thiophenic species: 1) thiophene (Th) / 1,3,5-tri-methyl-benzene (TMB), 2) 2-methyl thiophene (2MTh)/TMB mixtures and the GC-MS/FID/FPD system. In Figure A.1 is reported an example the three signals obtained in each experiment injection.

![Figure A.1](image)

Figure A.1. Example of GC-MS/FID/FPD signals from catalytic cracking runs using 10wt% of HIPZ-D additive and 90% of FCC commercial catalyst blends and 1.2wt% of thiophene in TMB at 530 C and 7s at Balance Level 1 (Gas Sampling)
One can mention that all the integration parameters are obtained for each signal. Then, it is possible to correlate the measured area (FPD signal) or concentrations (FID and MS signals) with the sulfur species concentration.

It has to be mentioned that two calibration curve for each detector were established in the two operation modes tested in the CREC Riser Simulator (Balance Level 1 and Balance Level 2), refer to Sections 3.5 and 4.1.

In the following section, it is reported an example of the calibrations completed using Th/TMB as a reference of the procedure used.

**A.1. Flame Photometric Detector (FPD)**

FPD uses the chemiluminescent reactions in a hydrogen/air flame as a source of analytical information that is relatively specific for substances containing sulfur. The emitting species for sulfur compounds is excited S$_2$. Then, FPD only can make a relation between areas of the peak and sulfur mass. It is why was needed and MS coupled to the GC, to identified the sulfur species relate with a peak. To do any calibration curve the whole components in the system has to be considered (TMB, thiophene and Ar).

First of all, a leak tested was done the reactor and the vacuum box was heated at 250 °C, while an argon flow circulating. The reactor temperature was 530 °C, well above the boiling point of TMB (166 °C) and Th (84°C), assuring that the entire sample injected was evaporated. When the reactor reached the set temperature, the flow of argon was stopped and the pressure in the reactor was allowed to equilibrate to atmospheric pressure. Then the reactor was sealed by closing the 4PV. After that, the vacuum box was settle in two conditions:

1) A low pressure of approximately 1.5-3.0 psia to evaluate experiments at Balance Level 1 (typical CREC Riser Runs), refer to Sections 3.5 and 4.1

2) A moderate pressure of approximately 28-30 psi to evaluate experiments at Balance Level 2 (Gas phase sampling), refer to Sections 3.5 and 4.1
After that, samples of different initial thiophene concentrations (0, 0.123, 0.244, 0.852, 1.224, 2.444, and 3.657 wt % with the balance being TMB) were prepared. About 200 µL (0.171-0.178g) of each sample was injected to the CREC Riser Simulator using a calibrated gas tight Hamilton syringe. And after few seconds, the 4PV was opened allowing the pressures of the reactor and the vacuum box to equilibrate. The 6PV valve, initially in load position to fill up the sample loop, was turned to inject position to send the sample to the GC/FID/FPD system.

The two mode were carried out to study the influence of the Argon in the System when it is operated in low and high dilution of argon.

The GC method used for to establish the calibration curve was the same one used for the analysis which is described in the experimental part (Chapter 3) of this thesis. Every injection run was repeated at least three times to secure reproducibility of the results.

Then, a total of 50 experiments were carried out. And, three calibrations were adopted to relate the FPD area with the concentration of thiophenic species:

1) Balance Level 1 (Gas phase sampling, Vacuum box at 28-30 psia), using the thiophene concentration in the feedstock injected

2) Balance Level 2 (Typical CREC Riser run, Vacuum box at 1.5-2.5 psia), using Th concentration in the feedstock injected

3) Balance Level 1 and 2 using the Th concentration in the system (reactor + vacuum box) including the Ar. For the last one, a whole mass balance in the system was done. It is important to highlight that the Ar has a big influence in the peak area over the FPD, because it is diluting the sample. The influence of Ar in the concentration of thiophene were also taking in account. An detailed example of the calculation of the concentration of thiophene in the system is reported in the thesis of dissertation of Aponte (Aponte 2011).

Equations A.1 and A.3 based on the fact that FPD detector response to sulfur species is of a second order (Wilson and Klee 1997). The calibration curve obtained from thiophene at thiophene concentration in the feedstock and in the Vacuum box versus FPD
chromatogram area data. Examples of these calibrations are reported in Figure A.1. The proposed second order polynomials adequately represent the data with its determination coefficient $R^2$ of 0.992-0.995

\[ C_{th,0\text{BL}_1} = 8.419 \cdot 10^{-02}(A_{FPD})^2 + 7.764 \cdot 10^{-2}(A_{FPD}) - 1.118 \cdot 10^{-2} \quad (A.1) \]

\[ C_{th,0\text{BL}_2} = 8.419 \cdot 10^{-02}(A_{FPD})^2 + 7.764 \cdot 10^{-2}(A_{FPD}) - 1.118 \cdot 10^{-2} \quad (A.1) \]

\[ C_{th,VB} = 4.312 \cdot 10^{-02}(A_{FPD})^2 - 1.195 \cdot 10^{1}(A_{FPD}) - 8.051 \cdot 10^{1} \quad (A.3) \]

Where

$C_{th,0\text{BL}_1}$ = Initial concentration of Thiophene injected in the reactor considering Gas Sampling (Balance Level 1), wt%

$C_{th,0\text{BL}_2}$ = Initial concentration of Thiophene injected in the reactor considering quasi total evacuation (Balance Level 2), wt%

$C_{th,VB}$ = Final concentration the thiophene in the system \(^{(\text{reactor + vacuum box})}\), entering to FPD, wt%

$A_{FPD} = \text{FPD Area} \times 10^{10}$

Figure A.2. Examples of FPD calibration curves for 2MTh. a) Th concentration in the feedstock at Balance Level 1 conditions, and b) Th concentration in the Vacuum box (2MTh+Ar+TMBs) using the data of both conditions: Balance Level 1 and 2.
A.2. Flame Ionized Detector (FID)

It was observed that FID always showed reasonable and stable peaks for thiophenic compounds in all the runs effected. In addition, when low concentration of thiophenic species (200ppm) were observed in MS and FID signals, the FPD could not detected. Then, the FID signal was used for quantification as well as verification as is reported in Chapter 4 of this PhD dissertation. In this respect, it is well known that FID has a response factor (RSF) of 1 for hydrocarbon compounds only. Dietz et al. (Dietz 1967) proposed that FID can be used to quantify sulfur containing compounds if the RSF for them is known. For example, Al-Bogami (Al-bogami 2013) reported the used of this method to quantify Benzothiophene, with a RSF of 0.81.

Then, using the calibration experiments (refer to Figure A.1), a “modified RSF” that correct the thiophene concentration injected regarding the FID concentration measure in the chromatograms was evaluated. Seven different initial thiophene concentrations (0, 0.123, 0.244, 0.852, 1.224, 2.444, and 3.657 wt % with the balance being TMB) were used. Figure A.2 and Eq. A.4 report the modified RSF value used for the transformation. One can mention is that the FID measured were not affected for the argon concentration (refer to Figure A.1). Thus, it was used for most the experiment calculation reported in this PhD thesis.

\[
C_{th} = 0.6196 \left( C_{th_{FID}} \right) \quad \text{(A.4)}
\]

Where

\[ C_{th_{FID}} = \text{The Thiophene concentration measured by FID, wt\%} \]
Figure A.2. FID calibration curve for thiophene. Note: 50 experiments are reported in this figure.

A.3. Mass Spectrometer signal (MS)

In this case, a correlation was established as a reference of the missing sulfur species read in the MS spectrum. This was considered to take advantage of the three chromatogram signals obtained in each injection to the GC-MS/FID/FPD, refer to Figure A.1. The main goal of this setting was to assess the missing sulfur compounds and double check the results obtained by FID and FPD detectors. Refer to Chapter 4, in the adsorption section.

Then, using the calibration experiments, two equations were found to associate the thiophene concentration injected with the MS concentration measure in the chromatograms was evaluated. The two equations describe the two operation modes: a) Balance Level 1 (high argon dilution) and b) Balance Level 2 (Low argon dilution). One can mention is that the Ar has a big influence in the peak area over MS, because it is diluting the sample. Then, the two modes considered the influence of Ar in the concentration of thiophene.

Figure A.3 and Eqs. A.5 and A.6 report the equation for the MS concentration transformation.

\[
C_{thBL1} = 2.2245 \left( C_{thMS-BL1} \right) \quad (A.5)
\]

\[
C_{thBL2} = 1.1968 \left( C_{thMS-BL2} \right) \quad (A.6)
\]
Where

\[ C_{th, BL1} = \text{Concentration of Thiophene injected in the reactor, considering Gas Sampling (Balance Level 1), wt\%} \]

\[ C_{th, BL2} = \text{Concentration of Thiophene injected in the reactor, considering quasi-total evacuation (Balance Level 2), wt\%} \]

\[ C_{th, MS-BL1} = \text{Concentration of Thiophene measured by MS, considering Gas Sampling (Balance Level 1), wt\%} \]

\[ C_{th, MS-BL2} = \text{Concentration of Thiophene measured by MS, considering quasi-total evacuation (Balance Level 2), wt\%} \]

Figure A.3. MS calibration curve for thiophene. a) Balance Level 1: Gas phase sampling, and b) Balances Level 2: Reactor Evacuation
Appendix B: Product Distribution GC-MS/FID/FPD reports

This Appendix aims to report an example of a typical product distribution collected from the experiments.

As was mentioned in Chapter 3 and 4, the identification and quantification of products were done in 6890N gas chromatograph (GC) connected to an Agilent 5973N mass selective detector (MSD), with flame photometric detector (FPD) and flame ionization detector (FID) allowed the quantification of the products. Figure B.1 reports an example of the signals obtained.

Figure B.1. Example of GC-MS/FID/FPD signals using 1.2 wt% of Th in TMB at 530 °C and 7s at Balance Level 1 (Gas Sampling)

The most significant sulfur species observed in the three signals are reported in Table B.1. In addition, Table B.2 reports a typical catalytic product distribution obtained from a GC/FID/FPD data after the integration of each peak. Table B.2 corresponds to the peak integration results of the signals display in Figure B.1.
Table B.1 Sulfur species detected by FID and FPD and identified by MS

<table>
<thead>
<tr>
<th>MS TIME</th>
<th>FID TIME</th>
<th>FPD TIME</th>
<th>NAME</th>
<th>MW</th>
<th>STRUCTURE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.45</td>
<td>2.14</td>
<td>2.19</td>
<td>C$_3$H$_6$S</td>
<td>62</td>
<td><img src="image" alt="structure" /></td>
</tr>
<tr>
<td>2.84</td>
<td>4.04</td>
<td>4.08</td>
<td>Thiophene (C$_4$H$_8$S)</td>
<td>84.14</td>
<td><img src="image" alt="structure" /></td>
</tr>
<tr>
<td>5.66</td>
<td>6.09</td>
<td>6.13</td>
<td>Thiophene -2-methyl (C$_5$H$_8$S)</td>
<td>98.17</td>
<td><img src="image" alt="structure" /></td>
</tr>
<tr>
<td>5.72</td>
<td>6.17</td>
<td>6.22</td>
<td>Thiophene -23-methyl (C$_5$H$_8$S)</td>
<td>98.17</td>
<td><img src="image" alt="structure" /></td>
</tr>
<tr>
<td>8.13</td>
<td>9.13</td>
<td>9.2</td>
<td>Thiophene -3,4-dimethyl (C$_6$H$_8$S)</td>
<td>112.17</td>
<td><img src="image" alt="structure" /></td>
</tr>
<tr>
<td>8.34</td>
<td>9.36</td>
<td>9.2</td>
<td>Thiophene -2,5-dimethyl (C$_6$H$_8$S)</td>
<td>112.17</td>
<td><img src="image" alt="structure" /></td>
</tr>
<tr>
<td>8.77</td>
<td>9.69</td>
<td>9.45</td>
<td>Thiophene -2,4-dimethyl (C$_6$H$_8$S)</td>
<td>112.17</td>
<td><img src="image" alt="structure" /></td>
</tr>
<tr>
<td>11.3</td>
<td>11.33</td>
<td>11.35</td>
<td>Thiophene -2,3,4 trimethyl (C$_7$H$_10$S)</td>
<td>126.17</td>
<td><img src="image" alt="structure" /></td>
</tr>
<tr>
<td>11.85</td>
<td>11.82</td>
<td>11.43</td>
<td>Thiophene -2-(1-methyl ethyl) (C$_7$H$_10$S)</td>
<td>126.17</td>
<td><img src="image" alt="structure" /></td>
</tr>
<tr>
<td>17.75</td>
<td>17.58</td>
<td>17.62</td>
<td>Thiophene -3,3 ethalinediyl)bis-(C$<em>{10}$H$</em>{10}$S$_2$)</td>
<td>194</td>
<td><img src="image" alt="structure" /></td>
</tr>
<tr>
<td>17.89</td>
<td>17.68</td>
<td>17.71</td>
<td>Thiophene -2,2 ethalinediyl)bis-(C$<em>{10}$H$</em>{10}$S$_2$)</td>
<td>194</td>
<td><img src="image" alt="structure" /></td>
</tr>
</tbody>
</table>
Table B.2. Hydrocarbon and sulfur products from catalytic conversion of Th/TMB, using 90 wt% FCC catalyst and 10 wt% additive, 1.2 wt% thiophene, 530 °C, reaction time 7 s, and C/O=5.9±0.2 (direct results from the GC).

<table>
<thead>
<tr>
<th>FID Signal Hydrocarbons products</th>
<th>FID Signal</th>
<th>MS Signal</th>
<th>FPD Area</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>FID Area</td>
<td>MS Area</td>
<td>FID Area</td>
</tr>
<tr>
<td>Argon</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Propane</td>
<td>1.29E+07</td>
<td>4.29E+08</td>
<td>8.23%</td>
</tr>
<tr>
<td>Isobutane</td>
<td>8.01E+06</td>
<td>3.49E+06</td>
<td>0.15%</td>
</tr>
<tr>
<td>Ethanethiol</td>
<td>5.47E+06</td>
<td>6.67E+06</td>
<td>0.13%</td>
</tr>
<tr>
<td>Butane-2,3-DiMethyl</td>
<td>2.67E+06</td>
<td>8.16E+06</td>
<td>0.16%</td>
</tr>
<tr>
<td>Hexane</td>
<td>2.09E+06</td>
<td>4.37E+06</td>
<td>0.08%</td>
</tr>
<tr>
<td>Pentane-1-Methyl</td>
<td>4.88E+05</td>
<td>1.47E+06</td>
<td>0.03%</td>
</tr>
<tr>
<td>Benzene</td>
<td>3.93E+06</td>
<td>1.47E+06</td>
<td>0.03%</td>
</tr>
<tr>
<td>Thiophene</td>
<td>3.02E+07</td>
<td>1.01E+07</td>
<td>0.05%</td>
</tr>
<tr>
<td>Toluene</td>
<td>7.26E+07</td>
<td>8.24E+07</td>
<td>1.58%</td>
</tr>
<tr>
<td>Thiophene-2-Methyl</td>
<td>5.53E+05</td>
<td>1.53E+07</td>
<td>1.50E+08</td>
</tr>
<tr>
<td>Thiophene-3-Methyl</td>
<td>5.48E+05</td>
<td>3.66E+06</td>
<td>1.99E+08</td>
</tr>
<tr>
<td>1,3-Dimethyl Benzene</td>
<td>2.90E+08</td>
<td>2.40E+06</td>
<td>0.05%</td>
</tr>
<tr>
<td>Thiophene-3,4-dimethyl</td>
<td>4.13E+05</td>
<td>8.79E+08</td>
<td>16.87%</td>
</tr>
<tr>
<td>Thiophene-2,5-dimethyl</td>
<td>3.38E+05</td>
<td>2.17E+06</td>
<td>0.04%</td>
</tr>
<tr>
<td>p-Xylene</td>
<td>9.90E+07</td>
<td>2.17E+06</td>
<td>0.04%</td>
</tr>
<tr>
<td>Thiophene-2,4-dimethyl</td>
<td>3.38E+05</td>
<td>2.20E+06</td>
<td>0.04%</td>
</tr>
<tr>
<td>Benzene-1-ethyl-2-methyl</td>
<td>5.10E+06</td>
<td>2.02E+06</td>
<td>0.04%</td>
</tr>
<tr>
<td>1,3,5-Trimethylbenzene</td>
<td>3.97E+09</td>
<td>1.56E+09</td>
<td>29.88%</td>
</tr>
<tr>
<td>Thiophene-2,3,4-Trimethyl</td>
<td>1.37E+06</td>
<td>2.02E+06</td>
<td>0.04%</td>
</tr>
<tr>
<td>Benzene-1-ethyl-3-methyl</td>
<td>4.72E+08</td>
<td>2.81E+08</td>
<td>5.39%</td>
</tr>
<tr>
<td>1,2,3-Trimethylbenzene</td>
<td>7.42E+07</td>
<td>1.06E+07</td>
<td>0.20%</td>
</tr>
<tr>
<td>1,2,4-Trimethylbenzene</td>
<td>2.07E+06</td>
<td>1.03E+07</td>
<td>0.20%</td>
</tr>
<tr>
<td>Thiophene-2-(1-methyl)-ethyl</td>
<td>2.03E+06</td>
<td>3.94E+08</td>
<td>0.00E+00</td>
</tr>
<tr>
<td>1,2,4,5-Tetramethylbenzene</td>
<td>1.40E+08</td>
<td>5.69E+08</td>
<td>7.56%</td>
</tr>
<tr>
<td>1,2,3,4-Tetramethylbenzene</td>
<td>4.15E+07</td>
<td>1.75E+08</td>
<td>10.93%</td>
</tr>
<tr>
<td>1,2,3,5-Tetramethylbenzene</td>
<td>2.30E+07</td>
<td>1.04E+07</td>
<td>3.36%</td>
</tr>
<tr>
<td>Pentamethyl Benzene</td>
<td>1.52E+06</td>
<td>5.78E+06</td>
<td>2.12%</td>
</tr>
<tr>
<td>Naphthalene-x-methyl</td>
<td>1.04E+06</td>
<td>3.30E+06</td>
<td>0.11%</td>
</tr>
<tr>
<td>Naphthalene-x,y-dimethyl</td>
<td>2.05E+06</td>
<td>1.08E+07</td>
<td>0.21%</td>
</tr>
<tr>
<td>Naphthalene-x,y-trimethyl</td>
<td>3.02E+06</td>
<td>8.77E+06</td>
<td>0.17%</td>
</tr>
<tr>
<td>2,4,6-Tri-t-butylbenzene</td>
<td>3.83E+06</td>
<td>1.94E+07</td>
<td>0.37%</td>
</tr>
<tr>
<td>Ethane 1,1-di-3,4-Xylyl</td>
<td>2.49E+06</td>
<td>1.51E+07</td>
<td>0.29%</td>
</tr>
<tr>
<td>Benzene 1,1-ethylenabis-4-ethyl</td>
<td>6.63E+06</td>
<td>4.08E+07</td>
<td>0.78%</td>
</tr>
</tbody>
</table>

It can be observed in Table B.2, that the response factor (RF) for each hydrocarbon was considered equal to 1 (Dietz 1967), and because of that, the area percent of the peak
calculated for each compound in the FID gave directly the weight percent of the species in the sample being analyzed. However, to establish the Sulfur and Carbon elemental balances (Appendix C) the modified RF reported in Appendix A is implemented. Then, a corrected product distribution is used to assess all the balances.

Regarding the sulfur species distribution obtained in the FPD, the hydrocarbon distribution in a sulfur basis is then calculated, as it is shown in the next appendix.
Appendix C: Sulfur and Carbon Elemental Balance

Example

This appendix reports the carbon and sulfur elemental balance for the experimental data. For all the Balances covered in Chapter 4, which includes Balance Level 1, Balance Level 2 and Level 3.

C.1. Balance Level 1

Chapter 4, section 4.1.1, reports the carbon balance for the gas phase sampling (Balance Level 1) as:

\[
CB_{level\,1} = C_{ads} = \frac{C_{in} - C_{out, gas\, phase}}{C_{in}} \times 100 \quad (C.1)
\]

Where

\[CB_{level\,1} = \text{Carbon balance evaluated in the gas phase (Level 1), wt\%}\]
\[C_{in} = \text{Total carbon mass of reactants injected, g}\]
\[C_{out, gas\, phase} = \text{Total carbon mass in the gas phase sample, g}\]

The amount of carbon injected \((C_{in})\) was calculated as elemental carbon content in the injected mass of the syringe. The fed mass to the reactor was assessed by the weight difference between before \((m_{feed, bi})\) and after \((m_{feed, ai})\) performing the injection. The following equation describes in detail the calculation when a mixture of 2MTh and TMB is injected:

\[
C_{in} = (m_{feed, bi} - m_{feed, ai}) \left( \frac{X_{TMB_{in}} \times \#C_{TMB}}{MW_{TMB}} + \frac{X_{2MTh_{in}} \times \#C_{2MTh}}{MW_{2MTh}} \right) \times AW_C \quad (C.2)
\]

Where

\[X_{TMB_{in}} = \text{Concentration of TMB in the injected solution, wt\%}\]
\[X_{2MTh_{in}} = \text{Concentration of 2MTh in the injected solution, wt\%}\]
\[\#C_i = \text{Number of carbon in the specie } i\]
\[MW_i = \text{Molecular weight for the component } i, g/mol\]
$AW_c = \text{Carbon atomic weight, } g/\text{gmol}$

The total carbon mass in the products was determined by adding the individual carbon contribution of each molecule. It was determined with the following formula:

$$C_{out,\text{gas phase}} = \sum_{i=1}^{n} [n_{p,r}Y_i(\#C_i)AW_c] \quad (C.3)$$

Where

$Y_i = \text{Molar concentration of the specie } i \text{ after the reaction, mole\%}$

$n_{p,r} = \text{Total moles of product using the reactor, mole}$

The mass of products was determined calculating the total product moles in the system with ideal gas law. The following expressions were obtained:

$$n_{p,r} = \frac{(P_{r,f} - P_{r,i})V_r}{RT_r} \quad (C.4)$$

$$n_{p,vb} = \frac{(P_{vb,f} - P_{vb,i})V_{vb}}{RT_{vb}} + \frac{(P_{r,fe} - P_{r,i})V_r}{RT_r} \quad (C.5)$$

Where

$n_{p,vb} = \text{total moles of product using the whole system (reactor + vacuum box), mole}$

$P_{r,fe} = \text{final equilibrium reactor pressure when the 4PV is open, psia}$

$V_{vb} = \text{vacuum box volume, cm}^3$

$T_{vb} = \text{vacuum box temperature, K}$

$P_{vb,f} = \text{final vacuum box pressure, psia}$

$P_{vb,i} = \text{initial vacuum box pressure, psia}$

$V_r = \text{reactor volume, cm}^3$

$R = \text{ideal gas constant, } 1205.91 \text{ cm}^3\text{ psia/gmol K}$

$T_r = \text{reactor temperature, K}$

$P_{r,f} = \text{final reactor pressure, psia}$

$P_{r,i} = \text{initial reactor pressure, psia}$
Previous research in this CREC Riser Simulator Reactor (Aponte 2011), reported the reactor volume as 60.08 ± 0.77 cm$^3$ and the vacuum box volume as 1174.6 ± 2.8 cm$^3$, both evaluated at 99% confidence intervals.

Regarding the Sulfur balance in the gas sampling (Balance Level 1), Chapter 4 (Section 4.1.1) defines the elemental Sulfur balances as follows:

$$SB_{level\,1} = S_{ads} = \frac{s_{in} - s_{out,\,gas\,phase}}{s_{in}} \times 100$$

(C.6)

Where

$SB_{level\,1}$ = Sulfur balance evaluated in the gas phase (Level 1), wt%

$s_{in}$ = Total Sulfur mass of reactants injected, g

$s_{out,\,gas\,phase}$ = Total Sulfur mass in the gas phase sample, g

The amount of Sulfur injected ($s_{in}$) was calculated as elemental sulfur content in the injected mass of the syringe (refer to equation C.2).

$$s_{in} = (m_{feed,\,bl} - m_{feed,\,al}) \left( \frac{X_{2Mth,\,in} \times \#S_{i} \times MW_{2Mth}}{MW_{2Mth}} \right) \times AW_{S}$$

(C.7)

Where

$\#S_{i}$ = Number of sulfurs in the specie $i$

$AW_{S}$ = Sulfur atomic weight, g/gmol

The total sulfur mass in the gas sample was determined by adding the individual sulfur contribution of each molecule. It was determined with the following formula:

$$s_{out,\,gas\,phase} = \sum_{i=1}^{n} \left[ n_{p,i} Y_{S,i} (\#S_{i}) \times AW_{S} \right]$$

(C.8)

Where

$Y_{S,i}$ = Molar Concentration of the sulfur specie $i$ after the reaction, mole%

In Table C.1 is reported a sulfur and Carbon elemental balances example of the gas phase sample (Balance Level 1). The balances are calculated for a selected catalytic runs of 2-
methylthiophene/TMB mixtures reacted at 530 °C at 5 s using Zn(3.5wt%)-OFF additive. In addition, Table C.2 is presented in order to exemplify the values mole fraction conversion used for the results on Table C.1.

Regarding to the sulfur species distribution, the thiophene concentration in the gas phase product (Table C.1 and C.2) is calculated using the calibration curve that correlates the FID respond factor, the FPD area, and MS area of this sulfur compound and its weight percent (refer to Appendix A). Moreover, the concentration of the sulfur species different to thiophene is then obtained using the calculated thiophene factor with the molecular weight ratio between the sulfur species.

It is important to highlight that this PhD research reports the results obtained by FID because they display the most conservative values. One can notice that $S_{ads}$ measured by FPD always was around 25-35wt% higher than the $S_{ads}$ measured by FID.
Table C.1. Sulfur and Carbon Balances for Run GP1ZN9 using 1.2 wt% 2MTh in TMB at 530 °C, reaction time 5 s, 0.1g of Zn(3.5wt%)-OFF additive

<table>
<thead>
<tr>
<th>Run Name</th>
<th>GP1ZN9A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reaction Time, s</td>
<td>5s</td>
</tr>
<tr>
<td>$m_{feed,bi}$, g</td>
<td>19.614</td>
</tr>
<tr>
<td>$m_{feed,ai}$, g</td>
<td>19.442</td>
</tr>
<tr>
<td>$m_i$, g</td>
<td>0.1716</td>
</tr>
<tr>
<td>$MW_p$, g/gmol</td>
<td>120.42</td>
</tr>
<tr>
<td>$T_r$, °C</td>
<td>530</td>
</tr>
<tr>
<td>$T_{vb}$, °C</td>
<td>250</td>
</tr>
<tr>
<td>$P_{r,t}$, psi</td>
<td>25.47</td>
</tr>
<tr>
<td>$P_{r,f}$, psi</td>
<td>47.77</td>
</tr>
<tr>
<td>$P_{r,fe}$, psi</td>
<td>40.03</td>
</tr>
<tr>
<td>$P_{vb,t}$, psi</td>
<td><strong>39.39</strong></td>
</tr>
<tr>
<td>$P_{vb,f}$, psi</td>
<td>39.65</td>
</tr>
<tr>
<td>$n_{p,r}$, g</td>
<td>0.00138</td>
</tr>
<tr>
<td>$n_{p,vb}$, g</td>
<td>0.00139</td>
</tr>
<tr>
<td>$m_{p,r}$, g</td>
<td>0.16660</td>
</tr>
<tr>
<td>$m_{p,vb}$, g</td>
<td>0.16773</td>
</tr>
</tbody>
</table>

### Carbon Balances

- $C_{in}$, g: 0.15050
- $C_{out,gas\ phase}$ using Eq. C.4, %wt: 0.14934
- $C_{out,gas\ phase}$ using Eq. C.5, %wt: 0.15035
- $CB_{level\ 1}$ using Eq. C.4, %wt: 0.77
- $CB_{level\ 1}$ using Eq. C.5, %wt: 0.50

### Sulfur Balances

- $S_{in}$, mg: 0.6724
- $S_{out,gas\ phase}$ using FID results and $n_p$ from Eq. C.4, mg: 0.3777
- $S_{out,gas\ phase}$ using FID results and $n_p$ from Eq. C.5, mg: 0.3802
- $S_{out,gas\ phase}$ using FPD results and $n_p$ from Eq. C.4, mg: 0.2051
- $S_{out,gas\ phase}$ using FPD results and $n_p$ from Eq. C.5, mg: 0.2052
- $S_{out,gas\ phase}$ using MSD results and $n_p$ from Eq. C.4, mg: 0.2120
- $S_{out,gas\ phase}$ using MSD results and $n_p$ from Eq. C.5, mg: 0.2134
- $S_{ads}$, using FID $n_p$ from Eq. C.4, wt%: 43.83
- $S_{ads}$, using FID $n_p$ from Eq. C.5, wt%: 43.45
- $S_{ads}$, using FPD $n_p$ from Eq. C.4, wt%: 69.50
- $S_{ads}$, using FPD $n_p$ from Eq. C.5, wt%: 69.49
- $S_{ads}$, using MSD $n_p$ from Eq. C.4, wt%: 68.47
- $S_{ads}$, using MSD $n_p$ from Eq. C.5, wt%: 68.26
Table C.2. Product distribution after applying sulfur modified respond factor for Run GP1ZN9 using 1.297 wt% 2MTh in TMB at 530 °C, reaction time 5 s, 0.1 g of Zn(3.5wt%)-OFF additive

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Fraction by FID corrected, wt%</th>
<th>MW, g/gmol</th>
<th>Mole Fraction, mol%</th>
<th>#C_i mol C/specie i</th>
<th>C_m of each specie i, (calculated Eq. C.4)</th>
<th>C_m of each specie i, (calculated Eq. C.5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2S</td>
<td>0.000</td>
<td>34.05</td>
<td>0.0000</td>
<td>0</td>
<td>0.00000</td>
<td>0.00000</td>
</tr>
<tr>
<td>Ethane</td>
<td>0.000</td>
<td>28.12</td>
<td>0.0000</td>
<td>2</td>
<td>0.00000</td>
<td>0.00000</td>
</tr>
<tr>
<td>Propene</td>
<td>0.000</td>
<td>42.08</td>
<td>0.0000</td>
<td>3</td>
<td>0.00000</td>
<td>0.00000</td>
</tr>
<tr>
<td>Propane</td>
<td>0.000</td>
<td>44.10</td>
<td>0.0000</td>
<td>3</td>
<td>0.00000</td>
<td>0.00000</td>
</tr>
<tr>
<td>Ethanethiol</td>
<td><strong>0.000</strong></td>
<td><strong>62.13</strong></td>
<td><strong>0.0000</strong></td>
<td><strong>2</strong></td>
<td><strong>0.00000</strong></td>
<td><strong>0.00000</strong></td>
</tr>
<tr>
<td>Isobutane</td>
<td>0.008</td>
<td>58.12</td>
<td>0.0166</td>
<td>4</td>
<td>0.00001</td>
<td>0.00001</td>
</tr>
<tr>
<td>1-propene-3-Methyl</td>
<td>0.003</td>
<td>58.12</td>
<td>0.0062</td>
<td>4</td>
<td>0.00000</td>
<td>0.00000</td>
</tr>
<tr>
<td>1-propene-2-Methyl</td>
<td>0.000</td>
<td>58.12</td>
<td>0.0000</td>
<td>4</td>
<td>0.00000</td>
<td>0.00000</td>
</tr>
<tr>
<td>Butane</td>
<td>0.000</td>
<td>58.12</td>
<td>0.0000</td>
<td>4</td>
<td>0.00000</td>
<td>0.00000</td>
</tr>
<tr>
<td>Butane-2-Methyl</td>
<td>0.000</td>
<td>72.15</td>
<td>0.0000</td>
<td>5</td>
<td>0.00000</td>
<td>0.00000</td>
</tr>
<tr>
<td>2-Butene-2-Methyl</td>
<td>0.000</td>
<td>70.15</td>
<td>0.0000</td>
<td>5</td>
<td>0.00000</td>
<td>0.00000</td>
</tr>
<tr>
<td>Pentane</td>
<td>0.000</td>
<td>72.15</td>
<td>0.0000</td>
<td>5</td>
<td>0.00000</td>
<td>0.00000</td>
</tr>
<tr>
<td>Pentane-2-Methyl</td>
<td>0.000</td>
<td>86.18</td>
<td>0.0000</td>
<td>6</td>
<td>0.00000</td>
<td>0.00000</td>
</tr>
<tr>
<td>Butane-2,3-DiMethyl</td>
<td>0.000</td>
<td>86.18</td>
<td>0.0000</td>
<td>6</td>
<td>0.00000</td>
<td>0.00000</td>
</tr>
<tr>
<td>Hexane</td>
<td>0.000</td>
<td>86.18</td>
<td>0.0000</td>
<td>6</td>
<td>0.00000</td>
<td>0.00000</td>
</tr>
<tr>
<td>Pentane-1-Methyl</td>
<td>0.000</td>
<td>78.05</td>
<td>0.0000</td>
<td>6</td>
<td>0.00000</td>
<td>0.00000</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.002</td>
<td>78.05</td>
<td>0.0031</td>
<td>6</td>
<td>0.00000</td>
<td>0.00000</td>
</tr>
<tr>
<td>Thiophene</td>
<td><strong>0.001</strong></td>
<td><strong>84.14</strong></td>
<td><strong>0.0009</strong></td>
<td><strong>4</strong></td>
<td><strong>0.00000</strong></td>
<td><strong>0.00000</strong></td>
</tr>
<tr>
<td>Toluene</td>
<td>0.003</td>
<td>92.14</td>
<td>0.0039</td>
<td>7</td>
<td>0.00000</td>
<td>0.00000</td>
</tr>
<tr>
<td>Thiophene-2-Methyl</td>
<td><strong>0.694</strong></td>
<td><strong>98.17</strong></td>
<td><strong>0.8505</strong></td>
<td><strong>5</strong></td>
<td><strong>0.00071</strong></td>
<td><strong>0.00071</strong></td>
</tr>
<tr>
<td>Thiophene-3-Methyl</td>
<td><strong>0.001</strong></td>
<td><strong>98.17</strong></td>
<td><strong>0.0017</strong></td>
<td><strong>5</strong></td>
<td><strong>0.00000</strong></td>
<td><strong>0.00000</strong></td>
</tr>
<tr>
<td>1,3-Dimethyl Benzene</td>
<td>0.059</td>
<td>106.18</td>
<td>0.0671</td>
<td>8</td>
<td>0.00009</td>
<td>0.00009</td>
</tr>
<tr>
<td>Thiophene-3,4-dimethyl</td>
<td><strong>0.000</strong></td>
<td><strong>112.17</strong></td>
<td><strong>0.0000</strong></td>
<td><strong>6</strong></td>
<td><strong>0.00000</strong></td>
<td><strong>0.00000</strong></td>
</tr>
<tr>
<td>Thiophene-2,5-dimethyl</td>
<td><strong>0.000</strong></td>
<td><strong>112.17</strong></td>
<td><strong>0.0000</strong></td>
<td><strong>6</strong></td>
<td><strong>0.00000</strong></td>
<td><strong>0.00000</strong></td>
</tr>
<tr>
<td>p-Xylene</td>
<td>0.005</td>
<td>106.18</td>
<td>0.0057</td>
<td>8</td>
<td>0.00001</td>
<td>0.00001</td>
</tr>
<tr>
<td>Thiophene-2,4-dimethyl</td>
<td><strong>0.002</strong></td>
<td><strong>106.18</strong></td>
<td><strong>0.0025</strong></td>
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</tr>
<tr>
<td>Benzene-propyl</td>
<td>0.005</td>
<td>120.19</td>
<td>0.0050</td>
<td>9</td>
<td>0.00001</td>
<td>0.00001</td>
</tr>
<tr>
<td>Benzene-1-ethyl-2-methyl</td>
<td>0.195</td>
<td>120.19</td>
<td>0.1959</td>
<td>8</td>
<td>0.00026</td>
<td>0.00027</td>
</tr>
<tr>
<td>1,3,5-Trimethylbenzene</td>
<td>98.394</td>
<td>120.19</td>
<td>98.6072</td>
<td>9</td>
<td>0.14714</td>
<td>0.15019</td>
</tr>
<tr>
<td>Thiophene-2,3,4-Trimethyl</td>
<td><strong>0.000</strong></td>
<td><strong>126.17</strong></td>
<td><strong>0.0000</strong></td>
<td><strong>7</strong></td>
<td><strong>0.00000</strong></td>
<td><strong>0.00000</strong></td>
</tr>
<tr>
<td>Benzene-1-ethyl-3-methyl</td>
<td>0.037</td>
<td>120.19</td>
<td>0.0372</td>
<td>8</td>
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<td>0.00005</td>
</tr>
<tr>
<td>1,2,3-Trimethylbenzene</td>
<td>0.363</td>
<td>120.19</td>
<td>0.3637</td>
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<tr>
<td>1,2,4-Trimethylbenzene</td>
<td>0.007</td>
<td>120.19</td>
<td>0.0070</td>
<td>9</td>
<td>0.00001</td>
<td>0.00001</td>
</tr>
<tr>
<td>Thiophene-2-(1-methyl)-ethyl</td>
<td><strong>0.000</strong></td>
<td><strong>126.17</strong></td>
<td><strong>0.0000</strong></td>
<td><strong>7</strong></td>
<td><strong>0.00000</strong></td>
<td><strong>0.00000</strong></td>
</tr>
<tr>
<td>1,2,4,5-Tetramethylbenzene</td>
<td>0.000</td>
<td>134.22</td>
<td>0.0000</td>
<td>10</td>
<td>0.00000</td>
<td>0.00000</td>
</tr>
<tr>
<td>1,2,3,4-Tetramethylbenzene</td>
<td>0.000</td>
<td>134.22</td>
<td>0.0000</td>
<td>10</td>
<td>0.00000</td>
<td>0.00000</td>
</tr>
<tr>
<td>1,2,3,5-Tetramethylbenzene</td>
<td>0.000</td>
<td>134.22</td>
<td>0.0000</td>
<td>10</td>
<td>0.00000</td>
<td>0.00000</td>
</tr>
<tr>
<td>Pentamethyl Benzene</td>
<td>0.000</td>
<td>148.24</td>
<td>0.0000</td>
<td>11</td>
<td>0.00000</td>
<td>0.00000</td>
</tr>
<tr>
<td>Naphthalene-x-methyl</td>
<td>0.000</td>
<td>156.00</td>
<td>0.0000</td>
<td>11</td>
<td>0.00000</td>
<td>0.00000</td>
</tr>
<tr>
<td>Naphthalene-x,y-dimethyl</td>
<td>0.000</td>
<td>156.00</td>
<td>0.0000</td>
<td>12</td>
<td>0.00000</td>
<td>0.00000</td>
</tr>
<tr>
<td>Naphthalene-x,y-trimethyl</td>
<td>0.000</td>
<td>170.00</td>
<td>0.0000</td>
<td>13</td>
<td>0.00000</td>
<td>0.00000</td>
</tr>
<tr>
<td>2,4,6-Tri-t-butylbenzene</td>
<td>0.000</td>
<td>278.00</td>
<td>0.0000</td>
<td>15</td>
<td>0.00000</td>
<td>0.00000</td>
</tr>
<tr>
<td>Ethane 1,1-di-3,4-Xylyl</td>
<td>0.618</td>
<td>238.37</td>
<td>0.3121</td>
<td>15</td>
<td>0.00078</td>
<td>0.00079</td>
</tr>
<tr>
<td>Benzene 1,1-ethylidenabis-4-ethyl</td>
<td>0.000</td>
<td>238.37</td>
<td>0.0000</td>
<td>15</td>
<td>0.00000</td>
<td>0.00000</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td><strong>0.14922</strong></td>
<td><strong>0.15230</strong></td>
</tr>
</tbody>
</table>
C.2. Balance Level 2

Chapter 4, section 4.1.2, reports the carbon balance for the Balance Level 2 as:

\[ CB_{\text{level} 2} = C_{\text{stripping} 1} = C_{\text{balance}} = \frac{c_{\text{in}} - c_{\text{out,total}}}{c_{\text{in}}} \times 100 \] (C.9)

Where

\[ CB_{\text{level} 2} = \text{Carbon balance evaluated after quasi – total evacuation (Level 2), wt\%} \]
\[ C_{\text{out,total}} = \text{Total carbon mass after quasi – total evacuation, g} \]

The amount of carbon injected \( (C_{\text{in}}) \) was calculated as reported by Eq. C.2. The total carbon mass in the products was determined by adding the individual carbon contribution of each molecule plus the carbon as coke. It was determined with the following formula:

\[ C_{\text{out,total}} = \sum_{i=1}^{n} [n_{p,r} Y_i (\# C_i) AW_C] + m_{T,c} \] (C.10)

The total mass of coke \( (m_{T,c}) \) in the inventory of catalyst is defined as the coke produce in the additive and in the FCC catalyst:

\[ m_{T,c} = m_{\text{add,c}} + m_{\text{bc,c}} \] (C.11)

Where

\( m_{\text{add,c}} = \text{mass of coke in the additive, g} \)
\( m_{\text{bc,c}} = \text{mass of coke in the FCC catalyst, g} \)

Then, the total mass of product can be calculated working only with the reactor (Eq. C.4) or using the whole system reactor+ vacuum box, (Eq. C.5).

\[ m_{p,r} = n_{p,r} MW_p \] (C.12)
\[ m_{p,\text{vb}} = n_{p,\text{vb}} MW_p \] (C.13)

The average molecular weight of the product mixture was calculated using the molecular weight of the individual species and the weight fractions as follows:
\[ MW_p = \frac{1}{\sum wi} \]  \hspace{1cm} (C.14)

With \( wi \) and \( MW_i \) representing the weight fraction and molecular weight (g/gmol) of each product species respectively. The weight fraction of each hydrocarbon species was calculated by normalizing the FID chromatogram peak areas and using response factors, and the weight fraction of each sulphur species was calculated using the FPD chromatogram peak areas and calibration curves.

Regarding the Sulfur balance after quasi-total evacuation (Balance Level 2), Chapter 4 (Section 4.1.2) defines the elemental Sulfur balances as follows:

\[
SB_{level2} = S_{stripping1} = S_{balance} = \frac{S_{in} - S_{out,total}}{S_{in}} \times 100  \hspace{1cm} (C.15)
\]

Where

\( SB_{level2} = Sulfur \ balance \ evaluated \ after \ quasi-total \ evacuation \ (Level \ 2), \ wt\% \)
\( S_{out,total} = \ Total \ Sulfur \ mass \ after \ quasi-total \ evacuation \ (Level \ 2), \ g \)

The amount of Sulfur injected (\( S_{in} \)) was calculated as elemental sulfur content in the injected mass of the syringe (refer to equation C.7). The total sulfur mass after quasi-total evacuation was determined by adding the individual sulfur contribution of each molecule and sulfur as coke. It was determined with the following formula:

\[
S_{out,total} = \sum_{i=1}^{n} [n_{p,r}Y_{S,i}(\#S_i)AW_S]  \hspace{1cm} (C.16)
\]

In Table C.3 is reported a sulfur and Carbon elemental balances example of the quasi total evacuation (Balance Level 2). The balances are calculated for a selected catalytic runs of 2-methylthiophene/TMB mixtures reacted at 530 °C at 5 s using Zn(3.5wt%)-OFF additive. In addition, Table C.4 is presented in order to exemplify the values mole fraction conversion used for the results on Table C.3.
As it was mentioned above (Section C.1) the sulfur species distribution, the 2-methylthiophene concentration in the gas product was calculated using the calibration curves reported in Appendix A.

The coke deposited on the additive and the FCC catalyst measured in a total organic carbon analyzer (TOC-V) with a solid sample module (SSM-5000) from Mandel, for the catalytic run reported in Table C.3 prior to coke measurements additive and FCC catalyst were separated using sieves given their different particle distribution. On the other hand, the sulfur in the coked catalysts and coked additive were determined with an Elemental analyzer for comparison by a CNS LECO equipment model 985.
Table C.3. Sulfur and Carbon Balances for Run PP1ZN9A using 1.2 wt% 2MTh in TMB at 530 °C, reaction time 5 s, 0.1g of Zn(3.5wt%)-OFF additive (Total evacuation)

<table>
<thead>
<tr>
<th>Run Name</th>
<th>PP1ZN9A</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Reaction Time, s</td>
<td>5s</td>
</tr>
<tr>
<td>$m_{feed,bi}$, g</td>
<td>19.222</td>
</tr>
<tr>
<td>$m_{feed,ai}$, g</td>
<td>19.053</td>
</tr>
<tr>
<td>$m_{i}$, g</td>
<td>0.1686</td>
</tr>
<tr>
<td>$MW_{p}$, g/gmol</td>
<td>120.21</td>
</tr>
<tr>
<td>$T_r$, °C</td>
<td>530</td>
</tr>
<tr>
<td>$T_{vb}$, °C</td>
<td>250</td>
</tr>
<tr>
<td>$P_{r,i}$, psi</td>
<td>25.08</td>
</tr>
<tr>
<td>$P_{r,f}$, psi</td>
<td>47.42</td>
</tr>
<tr>
<td>$P_{r,fe}$, psi</td>
<td>3.28</td>
</tr>
<tr>
<td>$P_{vb,i}$, psi</td>
<td>1.48</td>
</tr>
<tr>
<td>$P_{vb,f}$, psi</td>
<td>2.94</td>
</tr>
<tr>
<td>$n_{p,r}$, g</td>
<td>0.00139</td>
</tr>
<tr>
<td>$n_{p,vb}$, g</td>
<td>0.00135</td>
</tr>
<tr>
<td>$m_{p,r}$, g</td>
<td>0.16661</td>
</tr>
<tr>
<td>$m_{p,vb}$, g</td>
<td>0.16249</td>
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</table>

<table>
<thead>
<tr>
<th>Carbon Balances</th>
</tr>
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<tbody>
<tr>
<td>$C_{in}$, g</td>
</tr>
<tr>
<td>$C_{out,gas\ phase\ using\ Eq.\ C.4}$, g</td>
</tr>
<tr>
<td>$C_{out,gas\ phase\ using\ Eq.\ C.5}$, g</td>
</tr>
<tr>
<td>$CB_{level\ 1\ using\ Eq.\ C.4,\ %wt}$</td>
</tr>
<tr>
<td>$CB_{level\ 1\ using\ Eq.\ C.5,\ %wt}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sulfur Balances</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_{in}$, mg</td>
</tr>
<tr>
<td>$S_{out,gas\ phase\ using\ FID\ results\ and\ n_p\ from\ Eq.\ C.4}$, mg</td>
</tr>
<tr>
<td>$S_{out,gas\ phase\ using\ FID\ results\ and\ n_p\ from\ Eq.\ C.5}$, mg</td>
</tr>
<tr>
<td>$S_{out,gas\ phase\ using\ FPD\ results\ and\ n_p\ from\ Eq.\ C.4}$, mg</td>
</tr>
<tr>
<td>$S_{out,gas\ phase\ using\ FPD\ results\ and\ n_p\ from\ Eq.\ C.5}$, mg</td>
</tr>
<tr>
<td>$S_{out,gas\ phase\ using\ MSD\ results\ and\ n_p\ from\ Eq.\ C.4}$, mg</td>
</tr>
<tr>
<td>$S_{out,gas\ phase\ using\ MSD\ results\ and\ n_p\ from\ Eq.\ C.5}$, mg</td>
</tr>
<tr>
<td>$S_{ads}$, using FID $n_p$ from Eq. C.4, wt%</td>
</tr>
<tr>
<td>$S_{ads}$, using FID $n_p$ from Eq. C.5, wt%</td>
</tr>
<tr>
<td>$S_{ads}$, using FPD $n_p$ from Eq. C.4, wt%</td>
</tr>
<tr>
<td>$S_{ads}$, using FPD $n_p$ from Eq. C.5, wt%</td>
</tr>
<tr>
<td>$S_{ads}$, using MSD $n_p$ from Eq. C.4, wt%</td>
</tr>
<tr>
<td>$S_{ads}$, using MSD $n_p$ from Eq. C.5, wt%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Coke distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coke in the FCC catalyst, wt%</td>
</tr>
<tr>
<td>Coke in the additive, wt%</td>
</tr>
<tr>
<td>Sulfur in the FCC catalyst, mg</td>
</tr>
<tr>
<td>Sulfur in the additive, mg</td>
</tr>
</tbody>
</table>
Table C.4. Product distribution after applying sulfur modified respond factor for Run PP1ZN9A using 1.2 wt% 2MTh in TMB at 530 °C, reaction time 5 s, 0.1g of Zn(3.5wt%)-OFF additive for total evacuation

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Fraction by FID corrected, wt%</th>
<th>MW, g/mol</th>
<th>Mole Fraction, mol%</th>
<th>#Ci in mol C/mole specie i, (calculated Eq. C.4)</th>
<th>Cm of each specie i, (calculated Eq. C.5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2S</td>
<td>0.00</td>
<td>34.05</td>
<td>0.000</td>
<td>0</td>
<td>0.0000000</td>
</tr>
<tr>
<td>Ethane</td>
<td>0.00</td>
<td>28.12</td>
<td>0.000</td>
<td>2</td>
<td>0.0000000</td>
</tr>
<tr>
<td>Propene</td>
<td>0.00</td>
<td>42.08</td>
<td>0.000</td>
<td>3</td>
<td>0.0000000</td>
</tr>
<tr>
<td>Propane</td>
<td>0.00</td>
<td>44.10</td>
<td>0.000</td>
<td>3</td>
<td>0.0000000</td>
</tr>
<tr>
<td>Ethanethiol</td>
<td><strong>0.00</strong></td>
<td><strong>62.13</strong></td>
<td><strong>0.000</strong></td>
<td><strong>2</strong></td>
<td><strong>0.0000000</strong></td>
</tr>
<tr>
<td>Isobutane</td>
<td>0.00</td>
<td>58.12</td>
<td>0.000</td>
<td>4</td>
<td>0.0000000</td>
</tr>
<tr>
<td>1-propene-3-Methyl</td>
<td>0.01</td>
<td>58.12</td>
<td>0.016</td>
<td>4</td>
<td>0.0000111</td>
</tr>
<tr>
<td>1-propene-2-Methyl</td>
<td>0.00</td>
<td>58.12</td>
<td>0.006</td>
<td>4</td>
<td>0.0000004</td>
</tr>
<tr>
<td>Butane</td>
<td>0.00</td>
<td>58.12</td>
<td>0.000</td>
<td>4</td>
<td>0.0000000</td>
</tr>
<tr>
<td>Butane-2-Methyl</td>
<td>0.00</td>
<td>72.15</td>
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<tr>
<td>2-Butene-2-Methyl</td>
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<td>70.15</td>
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<td>0.0000000</td>
</tr>
<tr>
<td>Pentane</td>
<td>0.00</td>
<td>72.15</td>
<td>0.000</td>
<td>5</td>
<td>0.0000000</td>
</tr>
<tr>
<td>Pentane-2-Methyl</td>
<td>0.00</td>
<td>86.18</td>
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<td>0.0000000</td>
</tr>
<tr>
<td>Butane-2,3-DiMethyl</td>
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<td>86.18</td>
<td>0.000</td>
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<td>0.0000000</td>
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<tr>
<td>Thiophene-2-Methyl</td>
<td><strong>1.09</strong></td>
<td><strong>98.17</strong></td>
<td><strong>1.331</strong></td>
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<td><strong>0.001107</strong></td>
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<td><strong>98.17</strong></td>
<td><strong>0.009</strong></td>
<td><strong>5</strong></td>
<td><strong>0.000008</strong></td>
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<tr>
<td>1,3-Dimethyl Benzene</td>
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<td>106.18</td>
<td>0.142</td>
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<tr>
<td>Thiophene-3,4-dimethyl</td>
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<td><strong>112.17</strong></td>
<td><strong>0.000</strong></td>
<td><strong>6</strong></td>
<td><strong>0.000000</strong></td>
</tr>
<tr>
<td>Thiophene-2,5-dimethyl</td>
<td><strong>0.00</strong></td>
<td><strong>112.17</strong></td>
<td><strong>0.000</strong></td>
<td><strong>6</strong></td>
<td><strong>0.000000</strong></td>
</tr>
<tr>
<td>p-Xylene</td>
<td>0.00</td>
<td>106.18</td>
<td>0.006</td>
<td>8</td>
<td>0.0000008</td>
</tr>
<tr>
<td>Thiophene-2,4-dimethyl</td>
<td><strong>0.00</strong></td>
<td><strong>106.18</strong></td>
<td><strong>0.000</strong></td>
<td><strong>6</strong></td>
<td><strong>0.000000</strong></td>
</tr>
<tr>
<td>Benzene-propyl</td>
<td>0.00</td>
<td>120.19</td>
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<tr>
<td>Thiophene-2,3,4-Trimethyl</td>
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<td><strong>126.17</strong></td>
<td><strong>0.000</strong></td>
<td><strong>7</strong></td>
<td><strong>0.000000</strong></td>
</tr>
<tr>
<td>Benzene-1-ethyl-3-methyl</td>
<td>0.04</td>
<td>120.19</td>
<td>0.037</td>
<td>8</td>
<td>0.000049</td>
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<tr>
<td>1,2,3-Trimethylbenzene</td>
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<td>120.19</td>
<td>0.352</td>
<td>9</td>
<td>0.000527</td>
</tr>
<tr>
<td>1,2,4-Trimethylbenzene</td>
<td>0.01</td>
<td>120.19</td>
<td>0.008</td>
<td>9</td>
<td>0.000012</td>
</tr>
<tr>
<td>Thiophene-2-(1-methyl)-ethyl</td>
<td><strong>0.00</strong></td>
<td><strong>126.17</strong></td>
<td><strong>0.000</strong></td>
<td><strong>7</strong></td>
<td><strong>0.000000</strong></td>
</tr>
<tr>
<td>1,2,4,5-Tetramethylbenzene</td>
<td>0.00</td>
<td>134.22</td>
<td>0.003</td>
<td>10</td>
<td>0.0000004</td>
</tr>
<tr>
<td>1,2,3,4-Tetramethylbenzene</td>
<td>0.01</td>
<td>134.22</td>
<td>0.012</td>
<td>10</td>
<td>0.000019</td>
</tr>
<tr>
<td>1,2,3,5-Tetramethylbenzene</td>
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<td>134.22</td>
<td>0.009</td>
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<td>0.000015</td>
</tr>
<tr>
<td>Pentamethyl Benzene</td>
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<td>148.24</td>
<td>0.000</td>
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</tr>
<tr>
<td>Naphthalene-x-methyl</td>
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<td>156.00</td>
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<td>0.000000</td>
</tr>
<tr>
<td>Naphthalene-x,y-dimethyl</td>
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<td>0.000</td>
<td>12</td>
<td>0.000000</td>
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<td>Naphthalene-x,y-trimethyl</td>
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<td>0.000000</td>
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<tr>
<td>2,4,6-Tri-t-butylbenzene</td>
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<td>278.00</td>
<td>0.000</td>
<td>15</td>
<td>0.000000</td>
</tr>
<tr>
<td>Ethan 1,1-di-3,4-Xylyl</td>
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<td>238.37</td>
<td>0.298</td>
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<td>0.000744</td>
</tr>
<tr>
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<td>238.37</td>
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<td>0.000000</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>0.149216</td>
<td>0.152302</td>
<td></td>
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</tr>
</tbody>
</table>
C.3. Balance Level 3

Chapter 4, section 4.1.3, reports the carbon balance for the Balance Level 3. Sulfur and Carbon Balances Based on Solid Residues Left or Stripping 2:

\[ SB_{\text{level 3}} = S_{\text{stripping 2}} = \frac{m_{\text{add, e}} MW_S}{S_{\text{in}} + AW_C + C/S} \times 100 \]  
\[ C_{\text{stripping 2}} = \text{coke yield} = \frac{m_{T,C}}{c_{in}} \times 100 \]

\[ SB_{\text{level 3}} = \text{Sulfur left as coke in the additive or catalyst (Level 3), wt\%} \]
\[ C/S = \text{Carbon}/\text{Sulfur molar ratio typical expected value of 5 (1 mol S = 5mol C)} \]

In Table C.5 is reported sulfur and Carbon elemental balances level 3 example for the same experimental results reported in Table C.3-C.4.

Table C.5. Sulfur and Carbon Balances Level 3 for Run PP1ZN9A using 1.2 wt\% 2MTh in TMB at 530 °C, reaction time 5 s, 0.1g of Zn(3.5wt\%)-OFF additive (Total evacuation)

<table>
<thead>
<tr>
<th>Run</th>
<th>PP1ZN9A</th>
</tr>
</thead>
<tbody>
<tr>
<td>( m_{T,C} = m_{\text{add, e}}, \text{mg} )</td>
<td>0.018</td>
</tr>
<tr>
<td>( SB_{\text{level 3}} = S_{\text{stripping 2}}, \text{wt%} )</td>
<td>1.487</td>
</tr>
<tr>
<td>( C_{\text{stripping 2}} = \text{coke yield}, \text{wt%} )</td>
<td>0.012</td>
</tr>
</tbody>
</table>

C.4. Conversions

The conversion of thiophenic species and TMB were assessed as follows:

\[ X_j = \frac{m_{j,i} - m_{j,p}}{m_{j,i}} \times 100 \]  \hspace{1cm} (Eq.C. 19)

Where
\[ X_j = \text{conversion of the compound J, wt\%} \]
\[ m_{j,i} = \text{mass of the compound J injected to the reactor, g} \]
\[ m_{j,p} = \text{mass of the compound J in the products, g} \]

The thiophene and TMB conversion calculated with equation C.19 with the data reported in Table C.4 is presented in Table C.6.
Table C.6. Conversion for Run PP1ZN9A using 1.2 wt% 2MTh in TMB at 530 °C, reaction time 5 s, 0.1g of Zn(3.5wt%)-OFF additive (Total evacuation)

<table>
<thead>
<tr>
<th>Run</th>
<th>PP1ZN9A</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-methylthiophene conversion, $X_{2\text{MTh}}$, %</td>
<td>10.58</td>
</tr>
<tr>
<td>TMB Conversion, $X_{\text{TMB}}$, %</td>
<td>2.33</td>
</tr>
</tbody>
</table>
Appendix D: BHJ Method

The calculation method follows generally described by Barret, Joyne and Halenda, called BHJ method (Webb and Orr 1997). The pore volume distribution is established using the N$_2$ isotherm data for each material. To calculate the radius, the Kelvin equation was affected:

$$\ln\left(\frac{P^*}{P_o}\right) = -\left(\frac{2\gamma\theta \cos \theta}{RT r_m}\right) \quad (D.1)$$

Where $\theta$ stands for the wetting angle, $\gamma$ represents the surface tension for nitrogen, and $v$ is nitrogen molar volume, $r_m$ representing the radius of the meniscus, $R$ is the gas rate constant and $T$ denotes temperature.

To apply BHJ Method in Kelvin equation $r_m$ is substitute by $(r_c-t)$, where $t$ is the thickness of the adsorbed layer, and $r_c$ the radio of capillarity.

$$r_c = -\frac{2\gamma \theta \cos \theta}{RT \ln\left(\frac{P^*}{P_o}\right)} + t \quad (D.2)$$

The thickness of the adsorbed layer can be calculated via a number of semi-empirical equations. In this documents, the following relationship was considered:

$$t = \left[\frac{13.99}{0.034 - \log_{10}\left(\frac{P^*}{P_o}\right)}\right]^{1/n} \quad (D.3)$$

Then, using the correlation factors of $1/n=1/2$ (Webb and Orr 1997). In addition, some other considerations were affected such as: a) $\theta$ is near to zero so the $\cos \theta$ is essentially the unity, b) 0.00894 N/m of the nitrogen surface tension at 77K, c), d) 34.7cm$^3$/mol of nitrogen molar volume. Then, one substitutes all the values the resulting equation was:

$$r_c = -\frac{9.7}{\ln\left(\frac{P^*}{P_o}\right)} + \left[\frac{13.99}{0.034 - \log_{10}\left(\frac{P^*}{P_o}\right)}\right]^{1/2} \quad (D.4)$$

Table D.1 shows and example of the results obtained applying equation D.4.
Table D.1. Distribution Function Data and BHJ calculation Method

<table>
<thead>
<tr>
<th>Relative Pressure (p/p₀)</th>
<th>Quantity Adsorbed (cm³/g STP)</th>
<th>rc (Å)</th>
<th>Pore Width (Å)</th>
<th>ΔVabs/Δlnrc</th>
</tr>
</thead>
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</table>
# Curriculum Vitae

**Name:** Yira Aponte  

**Post-secondary**  
Universidad de Carabobo  
Carabobo, Venezuela  

The University of Western Ontario  
London, Ontario, Canada  
2010-2012 M.E.Sc. in Chemical and Biochemical Engineering.  

The University of Western Ontario  
London, Ontario, Canada  
2012-2016 Ph.D in Chemical and Biochemical Engineering  

**Honours and Awards:**  
Western Research Graduate and CREC Lab Scholarships for Ph.D degree studies for 4 years (Canada). 2012-2016  
Ontario Graduate Scholarship (Canada). 2015-2016  
Petroleos de Venezuela S. A.(PDVSA), Scholarship for MESc degree studies for 2 years (Venezuela). 2010-2012  
2nd prize award of best presentation in the Sarnia Research Bridges (Sarnia, Canada). 2011  
BSc research thesis Honorable Mention granted by Universidad de Carabobo (Carabobo, Venezuela). 2000-2001  

**Related Work Experience**  
The University of Western Ontario, London, Ontario.  
Graduate Teaching Assistant in the Chemical and Biochemical Engineering Department  
2010-2016  
PDVSA INTEVEP, Los Teques, Venezuela.  
Research Process Engineer in Technical Support/ Project Management/Analysts to refinery planning LP model. Areas of expertise: FCC, Alkylation, Naphtha Reforming, Hydro-processes, catalysis evaluations, troubleshooting, turnaround and startup of FCC plants  
2001-2012
PDVSA INTEVEP, Los Teques, Venezuela.
Internship, BSc Thesis. Synthesis and evaluation of novel catalytic systems to improve the catalytic cracking naphtha quality in hydrotreating units (ISAL process).
2000-2001

Universidad de Carabobo, Carabobo, Venezuela
Teaching Assistant in the Chemical Engineering Department
1998-2000

Publications:


