

**I. SYNTHESIS AND TESTING OF A SUPPORTED SHILOV OXIDATION
CATALYST**

&

**II. INFLUENCE OF STRUCTURAL FEATURES ON ZEOLITE
CHARACTERIZATION BY CONSTRAINT INDEX TESTING**

Thesis by

John Reeves Carpenter III

In Partial Fulfillment of the Requirements for the

degree of

Doctor of Philosophy



CALIFORNIA INSTITUTE OF TECHNOLOGY

Pasadena, California

2010

(Defended May 28, 2009)

© 2010

John Reeves Carpenter, III

All Rights Reserved

ACKNOWLEDGEMENTS

Behind any achievement is a group of people whose contributions either directly or indirectly provide the support necessary to reach the goal. This work is no different. I am indebted to many people for helping me along my path of learning and discovery. I will attempt to acknowledge many of those people here but am sure to miss some for which I apologize but assure your interactions were appreciated.

First I would like to thank Dr. Mark Davis for the opportunity to be a member of his research group. He has provided support and guidance that has allowed me not only to advance my knowledge scientifically and perform research but also learn on a more general level how to better attack problems and manage work processes. In his lab I have had the opportunity to mature and grow as a research engineer. Watching the various work in the lab has been exciting and I will continue to look back to see what the future holds for this lab. I also would like to thank the other members of my thesis committee: Dr. Jay Labinger, Professor Richard Flagan, and Dr. Stacey Zones. Their time, advice, and support have been invaluable to me as I have worked to complete my thesis.

Part one of this thesis received financial support from BP through the Methane Conversion Cooperative. The MC² program provided a unique opportunity to experience a larger effort to research between multiple academic institutions and industry. It was a program with a diverse set of views on the issues around methane activation and a interesting set of ideas. Dr. Labinger, Dr. John Bercaw, and Dr. Tom Baker from the program provided helpful guidance and suggestions to this work.

Part two of the thesis was financially supported by the Chevron Energy Technology Company with collaboration with Dr. Zones. I would like to express my gratitude to Dr.

Zones for the multitude of assistances he provided, from access to his resources to valuable insight into the issues surrounding zeolite structure and activity to his wonderful patience. Besides financial support and Dr. Zones several other members of the Chevron Energy Technology Company were helpful in this endeavor. Dr. Shelia Yeh provided her expertise on the XPS analysis of samples and Dr. C.Y. Chen provided use of his equipment and time on the adsorption measurements. Also I thank the other colleagues of Dr. Zones—though I can not name them all—for their assistance in the procurement of several zeolite samples and facilitation of this collaboration.

During my time as a member of the Davis lab, many good people have come and gone from the family. Each has played a role in my life for which I thank them. Dr. Andrea Wight, Dr. Jonathan Galownia, and Dr. Victor Diakov were senior members when I arrived and helped my transition into the group. Heather Hunt has been a constant office mate who has shared in the attempts to maintain sanity. Dr. Yuriy Roman Leshkov, a recent addition to the lab, has proved to be a wonderful asset sharing ideas as our projects have taken similar tracks. Raymond Archer deserves lots of gratitude. He joined the lab at the same time as I and has been a solid person to lean on for technical advice, as a sounding board, or even ranting. He has done all of this with great openness and expected little back. I can continue naming all of the people but then this would never end. So to everyone in the Davis lab past and present thank you.

Finally I must thank my family without whose support this would not have been possible. I know the long distance from my parents, siblings, and extended family has been tough on them as it has been on myself, but they have remained supportive throughout, recognizing the opportunity presented to me. Also my wife Catherine: she is my constant

support providing a listening ear when needed, providing encouragement when things were not going well, providing a distraction away from work when fun was required, and tolerating my moments of stressed craziness. I only hope I can return the support.

To everyone I offer my sincere gratitude and best wishes for success.

ABSTRACT

This thesis is composed of two separate projects invoking the use of heterogeneous catalyst. However that is the point where they diverge. Part One details work on the development of a heterogeneous system for the direct oxidation of alkanes. Part Two explores the use of competitive catalytic cracking of 3-methylpentane and n-hexane as a tool for the characterization of zeolites.

Part One is about the development of a heterogeneous system for alkane oxidation. Three techniques for creating heterogeneous catalyst from homogeneous systems without adding anchoring ligands are investigated: supported molten salts, supported aqueous phases, and ion-exchanged zeolites. Each of these has been used to create Wacker oxidation catalysts, in literature and in this work, for comparison purposes. From the study of Wacker oxidation the ion-exchanged zeolites and supported aqueous phase catalyst were identified as potential methods for developing a Shilov oxidation catalyst. The supported molten salt was eliminated because of high levels of chlorinated products and low activity. Attempts were made with ion-exchanged zeolites to oxidize ethane to ethanol but no products were detected.

The supported aqueous phase system, however, provided more promising results. Initial work focused on oxidation of ethanesulfonate loaded onto the controlled pore glass support along with the catalyst. Similar turnovers were achieved on the supported aqueous system as had been seen in the homogeneous system. The reaction parameters of liquid loading, oxygen pressure, reactant concentration, copper(II) chloride concentration, and acid addition were investigated. While the supported aqueous system was successful in the

oxidation of ethanesulfonate, attempts to perform ethane oxidation in a flow system were not. The loss of chloride ions from the system is believed to lead to the deactivation.

Part Two investigates anomalous Constraint Index results for small and medium pore zeolites containing cages that are relatively larger than the pore (i.e., cages similar in size to large pore zeolites). The Constraint Index test was developed as the competitive cracking of 3-methylpentane and n-hexane for the classification of structures as having small, medium, or large pores. Small pores are defined as 8-ring pores or smaller; medium pores are 10-ring pores; and large pores have 12-rings or larger. 10-ring structures like SSZ-25 and SSZ-35 that contain cages in the structure had Constraint Index results consistent with a large pore classification and 8-ring structures with cages like SSZ-23 and SSZ-28 have Constraint Index results consistent with medium pore zeolites.

Incomplete cages on the external surface have been shown to be active in other reactions. These hemi-cages may provide a nonselective active site that would result in lower Constraint Index results. This work looks at this possibility by comparing four zeolites, ZSM-5 and BEA* as normally behaving medium- and large-pore structures, and SSZ-35 and SSZ-25 as zeolites with structures containing 10-ring pores and cages. The surface is passivated by a dealumination treatment and tested by isopropanol dehydration. Then the Constraint Index test is performed and compared on calcined samples of both the parent and treated samples. No evidence of activity on the external surface having an influence on the Constraint Index test is observed. Several techniques are used to investigate accessibility are also looked at but only indirect hypotheses can be drawn. Finally it is reported that for structures with two or more distinct features, different fouling

rates in each feature may result in observable changes in the Constraint Index value over time on stream.

TABLE OF CONTENTS

Acknowledgements	iii
Abstract	vi
Table of Contents	ix
List of Figures	xi
List of Tables	xiv
 Chapter 1: Preface	 1
 Part One: Synthesis and Testing of a Supported Shilov Catalyst.....	 4
 Chapter 2: Shilov Oxidation	 5
2.1 Methane	6
2.2 Shilov Oxidation.....	8
2.3 Supported Catalysts	10
2.4 References.....	13
 Chapter 3: Experimental Methods for Synthesis and Testing of Supported Shilov Oxidation Catalyst	 18
3.1 Supported Molten Salt Catalyst	19
3.2 Supported Aqueous Phase Catalyst	19
3.3 Ion-Exchanged Zeolites	20
3.4 Supported Catalyst Batch Reactions.....	21
3.5 Supported Catalyst Flow Reactions	22
3.6 References	24
 Chapter 4: Supported Wacker Oxidation Catalyst.....	 25
4.1 Supported Molten Salt Catalyst	26
4.2 Supported Aqueous Phase Catalyst	30
4.3 Ion-Exchanged Zeolites	34
4.4 References	36
 Chapter 5: Supported Shilov Oxidation Catalyst.....	 41
5.1 Ion-Exchanged Zeolites for Shilov Oxidation.....	42
5.2 Supported Aqueous Phase Catalyst for Shilov Oxidation.....	43
5.3 References	49
 Chapter 6: Conclusions on Supported Shilov Oxidation Catalyst.....	 56
6.1 References	61
 Part Two: Influence of Structure Features on Zeolite Characterization by Constraint Index Testing.....	 62

Chapter 7: Constraint Index Testing of Zeolites	63
7.1 Constraint Index Test	64
7.2 Structures Containing Internal Cages	66
7.3 Zeolite Catalyzed Hydrocarbon Cracking	68
7.4 References	72
 Chapter 8: Experimental Methods for Investigation of Constraint Index Testing	 79
8.1 Zeolite Synthesis	80
8.2 External Surface Modification	82
8.3 Reactivity Tests	82
8.4 Zeolite Characterization	84
8.5 n-Hexane and 3-Methylpentane Adsorption	85
8.6 References	86
 Chapter 9: Effect of External Surface Activity on Constraint Index Testing .	88
9.1 Characterization.....	90
9.2 Isopropanol Dehydration.....	91
9.3 Constraint Index Testing.....	92
9.4 References	95
 Chapter 10: Evidence of Increased Accessibility in the Interior of Structures with Large Cages.....	 106
10.1 Adsorption of n-Hexane and 3-Methylpentane	107
10.2 Deactivation Characteristics of Caged Structures	108
10.3 Hydrocarbon Cracking on Caged Structures.....	111
10.4 References	114
 Chapter 11: Evidence of Multiple Structure Features in Constraint Index Testing.....	 121
11.1 References	126
 Chapter 12: Conclusions on Structure Effects in Constraint Index Testing for Zeolite Characterization	 131

LIST OF FIGURES

<i>Figure</i>		<i>Page</i>
Figure 2.1.	Simplified Process Diagram of Methanex's Process for the Production of Methanol from Methane via Synthesis Gas	15
Figure 2.2.	Schematic of the mechanism of modified Shilov oxidation.....	16
Figure 2.3.	Depiction of a supported catalyst solution	17
Figure 4.1.	Reaction scheme for the Wacker oxidation of olefins.....	37
Figure 4.2	TGA/DSC analysis of the molten salt Wacker catalyst.....	38
Figure 4.3	Comparison of Acetaldehyde Production on SAP catalyst at varying reaction temperatures and water flow rates	39
Figure 5.1	Oxidation of ethanesulfonate over various levels of liquid loading on the catalyst.....	50
Figure 5.2	Profile of reaction species on a per mol Pt basis over time for varying Cu/Pt ratios	51
Figure 7.1	Examples of two structures whose CI values fall outside expected ranges for their pore size	75
Figure 7.2	Examples of structures with pores opening into larger cages.....	76
Figure 7.3	Structure Directing Agents used to make the 4 structures with cages in figure 7.2.....	77
Figure 8.1	Flow diagram of BTRS Jr. reactor system for isopropanol dehydration and hydrocarbon cracking.	87

LIST OF FIGURES (CONTINUED)

<i>Figure</i>		<i>Page</i>
Figure 9.1	Ammonium hexafluorosilicate dealumination scheme	96
Figure 9.2	Aldol XRD patterns of ZSM-5, BEA*, SSZ-35 and SSZ-25 before and after dealumination treatment.....	97
Figure 9.3	SEM images of ZSM-5, BEA*, SSZ-35, and SSZ-25 before and after dealumination procedure	99
Figure 9.4	TGA/DSC of ZSM-5, BEA*, and SSZ-35 demonstrating SDA degradation above 350°C	100
Figure 9.5	TGA/DSC of SSZ-25 demonstrating SDA degradation below 350°C.....	101
Figure 9.6	Isopropanol dehydration activity on the external surface of ZSM-5, BEA*, and SSZ-35.....	102
Figure 9.7	Aldol Constraint Index testing on zeolites before and after dealumination treatment	103
Figure 10.1	Adsorption of n-hexane and 3-methylpentane on 10-ring pore structures	115
Figure 10.2	Adsorption of n-hexane and 3-methylpentane on small pore structures	116
Figure 10.3	Constraint Index and Conversion of Individual Pure Reactants over Time on Stream for the small pore structures	117
Figure 10.4	Comparison of mass accumulation on structures with the amount of C ₆ cracked on those structures during Constraint Index testing	119

LIST OF FIGURES (CONTINUED)

<i>Figure</i>		<i>Page</i>
Figure 11.1	Constraint Index test over time on stream for various zeolite structures	127
Figure 11.2	Fraction of n-hexane and 3-methylpentane remaining during the Constraint Index test on MOR, FER, and SSZ-25	128
Figure 11.3	Constraint Index testing on partial Na-exchanged MOR and FER.....	129
Figure 11.4	Constraint Index test on at 425 °C and 375 °C on ferrierite	130

LIST OF TABLES

<i>Table</i>		<i>Page</i>
Table 4.1.	Review of Wacker catalyst	40
Table 5.1.	Comparison of supported aqueous phase Shilov catalyst with the homogenous system	53
Table 5.2.	Variation in oxygen pressure in the oxidation of ethanesulfonate .	54
Table 5.3.	Conversion of chlorinated products to desired products	55
Table 7.1	Examples Constraint Index Values	78
Table 9.1	Characterization data of zeolite samples before and after dealumination treatment.	105
Table 10.1	Characterization of mass deposition from samples at the 1h and 6h time point in the Constraint Index test	120