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

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

Thesis by

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# 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

# LIST OF FIGURES

LIST OF FIGURES (CONTINUED)

LIST OF FIGURES (CONTINUED)

# LIST OF TABLES