CHAPTER ONE

PREFACE

This thesis is composed of two separate projects. The first is centered around the development of a supported catalyst system for Shilov oxidation of alkanes. It entails looking for methods in which a homogeneous system can be transformed into a heterogeneous system to achieve the advantages therein without losing too much activity. This work is arranged as follows:

Chapter 2 introduces alkane oxidation and some of the problems encountered. Shilov oxidation is also introduced as a possible route to products without oxidizing to carbon dioxide. Finally several techniques for methods to create heterogeneous reaction systems from homogeneous systems are described.

Chapter 3 details the experimental methods used in Part I of the thesis, both the procedures for preparing the three catalyst systems and the reactor systems used to test them.

Chapter 4 describes the work done with Wacker oxidation of alkenes to aldehydes. It is here that the supported molten salt, supported aqueous phase, and ion-exchanged zeolite catalyst are compared. The impact of water concentration in the feed stream is introduced.

Chapter 5 moves from the Wacker system to the Shilov oxidation. Trials with ion-exchanged zeolites are described, as well as with the supported Shilov catalyst. Tests are run in the plug-flow reactor for the oxidation of ethane. The oxidation of ethanesulfonate is also utilized in the batch system to explore parameters of the catalyst.

Chapter 6 presents a summary of the work on the development of a supported Shilov oxidation catalyst.

The second project, while still utilizing the reactor system, shifts from the development of catalysts for the production of desired species to the use of reactions as a characterization tool. One class of important catalysts are zeolites which have a defined uniform structure. This structure can provide useful shape-selectivity in reactions and separations. Multiple techniques exist for characterizing the structures of zeolites, especially for new materials. One such test is the Constraint Index test which classifies the pore size of structures based on the competitive cracking of n-hexane and 3-methylpentane. However structures have been recently found that are exceptions to this classification. This project looks at how the presence of large internal cages in these structures contributes to their anomalous Constraint Index test results. Part Two is structured similarly to Part One, as follows:

Chapter 7 provides an introduction to the Constraint Index test. A description of the development of structures with large internal cages is included as well. Also some of the issues surrounding hydrocarbon cracking are touched on. Chapter 8 then provides some experimental details.

Chapters 9 through 11 describe the results of the investigation. Chapter 9 explores the role of the external surface, while Chapter 10 describes methods for looking at both the accessibility provided by the structures for molecules to enter through the pores and the accessibility to bulkier transition states. Chapter 11 highlights an observation that by looking at the Constraint Index over a longer time on stream it may be possible to see evidence of multiple structure features. Chapter 12 provides an overall summary.

PART ONE

SYNTHESIS AND TESTING OF A SUPPORTED SHILOV CATALYST

CHAPTER TWO

SHILOV OXIDATION

For many decades society has consumed products derived from petrochemicals, mainly from oil. However demand has risen for these products to be produced in a more environmentally clean manner. Natural gas has become an alternative to oil as both an energy source and chemical feedstock, due to its large supply and clean burning properties. Natural gas, however, is typically composed of methane and other light alkanes for which there is no industrially practical direct process for converting them to more valuable products.[1] The activation of the C-H bond, especially for direct functionalization at mild conditions, remains a challenge.[1–4]

2.1 Methane

Methane is an example where direct functionalization could make a substantial improvement in terms of cost savings and efficiency. Currently there are over 5000 trillion cubic feet of proven natural gas reserves in the world or, in other words, enough to meet the current consumption rate for the next 200 years.[5] This abundance of natural gas reserves, along with its characteristics of being a cleaner fuel than oil, have inspired effort into developing technologies to utilize this resource as a fuel and a chemical feedstock, just like oil. Industry not only wants to harness the energy stored in natural gas as a fuel source but to develop technologies to move it into other markets much the same way oil derivatives are used today.[6]

Natural gas is mainly composed of alkanes; in fact over 80% is methane.[6] Unfortunately, there are very few direct process for converting it to a valuable product industrially.[1] The C-H bonds of a methane molecule have no empty low energy orbital or filled high energy orbital to easily participate in chemical reactions like unsaturated hydrocarbons can.[1] However, methane has still found industrial value as the precursor to the formation of synthesis gas, a mixture of CO and H_2. Synthesis gas is then used to make products such as methanol, ammonia, and other alcohols. Methanol production is one of the primary uses of synthesis gas.

Methanol is used across a wide variety of industries. Methanol serves as a precursor of formaldehyde, which is used to make urethanes and plastics. These make many of the items we use—from seat cushions, to the plastic in cars, to engineered wood products, to synthetic fibers. Also methanol can be used in the production of acetic acid, which is used in the production of many paints and adhesives, as well as the polyethylene terephthalate (PET) plastic that makes up so many of the items we use every day. Every time one wash their windshield or their car starts on a cold morning, they are using methanol, a major component of windshield-washing fluid and antifreeze. Previously, one of methanol's biggest markets was the production of methyl tertiary butyl ether, MTBE, a fuel additive. However, due to environmental and health concerns, the use of MTBE has been phased out. Even with the reduction in MTBE usage, the transportation market still has potential as a large methanol user in the future. Much of the work on fuel cell technology involves the use of methanol as a fuel source, and dimethyl ether, DME, can be produced from methanol to be used as a power source or to make cleaner diesel fuels.

More than 30,000 metric tons of methanol were produced in 2003 worldwide.[7] BP and Methanex operate a plant in Trinidad that can produce 1.7 million tons per year.[8] A simplified process diagram of the methanol production process as described on the Methanex website is shown in Figure 2.1. In the process, methane is fed first through zinc oxide pellets to remove sulfur before being preheated. After the sulfur removal, steam is added to the reactant stream and the mixture is heated to facilitate the reforming. In the reformer the methane/steam mixture passes over a nickel oxide catalyst at ~900°C where it is converted to synthesis gas: carbon monoxide, dihydrogen, carbon dioxide, and water. Then the water is removed from the synthesis gas and the dry gas is sent to a compressor to increase the pressure for the methanol conversion reaction. The stream is then fed to the methanol reactor, where it is passed over a copper-containing catalyst and converted to methanol and water. Finally the product stream must be separated to remove the water and unreacted gases from the methanol.

As one can see, this process is heavy in capital investment, with the multiple stages in the production as well as high energy cost to operate at high temperatures and elevated pressures. This economic motivator has spurred research into direct methods of methane-to-methanol conversion. Removing the synthesis gas production route and lowering the pressure of the methanol conversion reaction could greatly alter the economics of methanol production and thus alter the end use, making it both a more viable feedstock and fuel source.

2.2 Shilov Oxidation

Much research has gone into the area of the direct partial oxidations of alkanes, for which several reviews can be found.[1,3,9] The research ranges from organometallic catalysts to the use of enzymes. One example is the work of Periana using mercury-mediated oxidation of methane by sulfuric acid.[10] However, while this provides production of methanol at lower temperatures, it introduces the problem of dealing with the corrosive sulfuric acid. One of the earliest reported mechanisms for direct methane conversion is that reported by Shilov and coworkers in 1972.[11] No other method has been able to achieve the conversion under the mild conditions of Shilov's approach. It is this chemistry that this study will try to utilize.

In 1972, Shilov and coworkers reported the selective oxidation of methane to methanol at 130°C using aqueous salts of $PtCl_4^{2-}/PtCl_6^{2-}$. [11] Later he proposed a three-part mechanism for this partial oxidation.[12] The first step is the activation of the C-H bond to produce an alkylplatinum(II) species. It is then followed by an oxidation to an alkylplatinum(IV) species, and finally a reductive elimination results in the product and the return to the platinum(II) catalyst. The nature of the first step has proven difficult to study[3] and is still not clearly defined as it may progess in either an associative or disassociative manner[21]. In the second step, oxidation is achieved by a two-electron transfer from the $PtCl_6^{2-}$ to the alkylplatinum(II) species. Finally the reductive elimination occurs by a nucleophilic attack of water- or chloride resulting in the oxidize or chlorinated product respectively via an S_N2 mechanism. It is also accompined by the loss of another chloride ligand resulting in the return to the platinum(II) species. [13] Since then work has gone into determining the mechanism of each step and the C-H bond activation has been shown to be the rate-determining step.[13]

However the Shilov chemistry suffers the drawback of the use of platinum(IV) as an (expensive) oxidant. It would be highly more attractive to use molecular oxygen as the overall oxidant. In 2001, Sen and coworkers reported such a modification to the Shilov chemistry.[14] In their work, they replaced the $PtCl_6^{2-}$ salt with $CuCl_2$ and demonstrated that in the presence of molecular oxygen they were able to oxidize alkanesulfonates and ethane in water. They also provided support that the addition of a second metal does not greatly alter the proposed mechanism. The modified Shilov cycle is shown below in Figure 2.2. In this study we work with Sen's modified Shilov system using copper(II); however recent work by Weinberg [15] demonstrates several possible alternatives to copper (II) and some of the conditions another oxidant would need.

While the Shilov oxidation provides the desired selectivity not seen in many other C-H bond oxidation processes, the homogeneous system has several drawbacks. These include the low solubility of alkanes in water and the corrosive nature of the metal salts. Another drawback of running the homogenous system is the difficulty of separating the desired products from the aqueous catalyst solution. Separations with the homogenous system would require more investment in process equipment that would be exposed to the catalyst solution. Also the C-H bond activation of the alkane and desired alcohol products are similar which leads to more over-oxidation of the products and less alkane conversion as the concentration of the product increases in the solution.[16] It would be advantageous to be able to run the reaction in a continuous flow system with a heterogeneous catalyst where product is continually being removed and reactant added to maintain a high alkane/low product concentration on the catalyst.

2.3 Supported Catalysts

A heterogeneous catalyst can be developed by immobilizing the catalyst on a selected support system. The common method for accomplishing this task is to covalently bond a catalyst to the support.[17] However, in this work the desire is to use the transition metal salts which don't lend themselves to covalent bonding without the addition of new ligands. Also utilizing covalent bonding to immobilize a catalyst may result in a loss of the effectiveness of the catalyst due to decreased mobility.[17] Other methods for immobilizing the catalyst are through hydrogen bonding or ionic, hydrophobic/hydrophilic, or fluorous interactions.[17] The supported molten salt and supported aqueous phase catalysts make use of the hydrophilic/hydrophobic interactions, whereas the ion-exchanged zeolite relies more on the ionic interactions of the materials. Each of these will be discussed further in the context of their use in this work.

In general those catalysts that are supported based on the hydrophobic/hydrophilic interactions are depicted in Figure 2.3, in which we see a porous catalyst particle provide a large surface area for increased reaction surface. Here the catalyst phase is a thin layer of a hydrophilic liquid supported on a hydrophilic surface and the reactant phase is a hydrophobic organic phase. In this setup, the actual catalyst molecules are free to move in the immobilized liquid layer and the reaction takes place at the interface of the hydrophobic and hydrophilic phases.

A similar system to the Shilov oxidation of alkanes is the Wacker oxidation of alkenes on a $PdCl_2/CuCl_2$ catalyst system. This system has been demonstrated for the supported molten salt catalyst [18], supported aqueous phase catalyst[19], and ion-exchanged zeolite[20]. These will serve as the starting point in this work that tries to use the lessons of these systems to make a heterogeneous system for Shilov oxidation. Wacker oxidation of alkenes and Shilov oxidation of alkanes share many similarities that make using the Wacker system as a starting model attractive. The both work with a transition metal from the same family as well as operate at temperatures between 100°C and 200°C in conditions exposed to oxygen and water. They both undergo a two-electron oxidation of the metal species by 2 $CuCl_2$ and in both nucleophilic attack of water on the hydrocarbon coordinated with the metal result in the product. A couple difference do exist in that the Wacker system is Pd(II)/Pd(0) system while the Shilov system is Pt(II)/Pt(IV) also the order of the reductive elimination and oxidation are reversed between the two. As Periana points out [22] Wacker oxidation using Pd^{2+} is not a viable route for alkane oxidation since the catalyst is not a powerful enough electrophile to activate the Ch bond in alkanes. Shilov oxidation is attractive as an alkane oxidation route for many of the reasons that have made Wacker oxidation of alkenes successful. Shilov oxidation provides a direct route for methane to methanol conversion that uses oxygen as the ultimate oxidant, operates at lower temperatures (below 200°C), lower pressures than the synthesis gas route, and is water tolerable. Also the selectivity limit the over oxidation to CO2 and CO that afflict many oxidation strategies. In fact Shilov oxidation has the potential to meet many of the requirements described out in a recent report from Periana for a successful direct route catalyst for methane conversion.[22]

2.4 References

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Figure 2.1: Simplified process diagram of Methanex's process for the production of methanol from methane via synthesis gas

Synthesis Gas reactions

$CH_4 + H_2O \longrightarrow CO + 3H_2$

$CO + H_2O \longrightarrow CO_2 + H_2$

Methane Conversion reactions

$CO + 2H_2 \longrightarrow CH_3OH$

$CO_2 + H_2 \longrightarrow CO + H_2O$

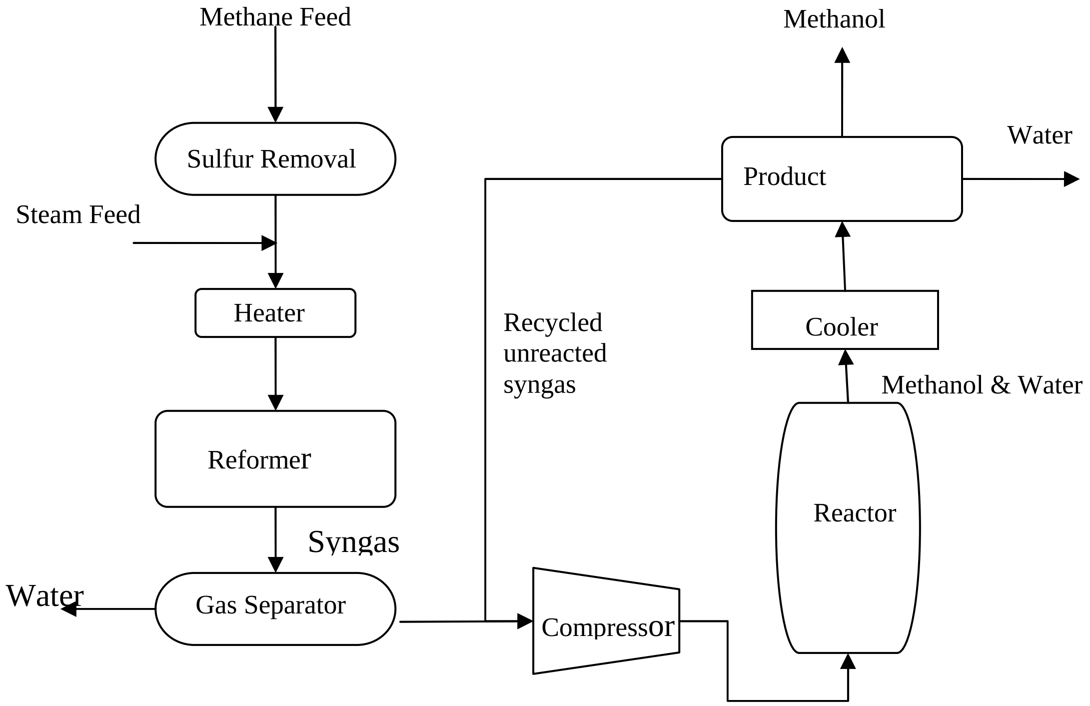


Figure 2.2: Schematic of the mechanism of modified Shilov oxidation detailing the three main steps 1) C-H bond activation 2) oxidation and 3) reductive elimination. In the oxidation step, the modification to use Copper (II) and thus molecular oxygen as the overall oxidant has been included.

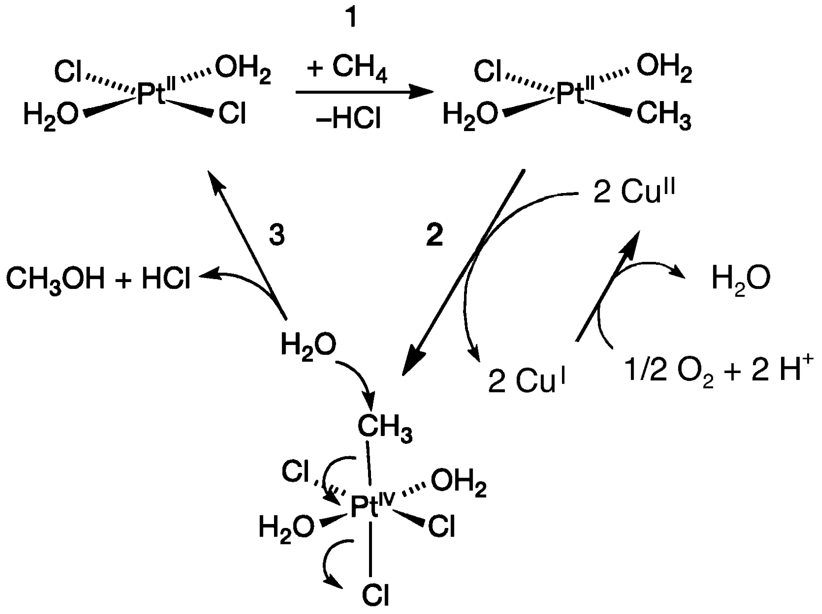
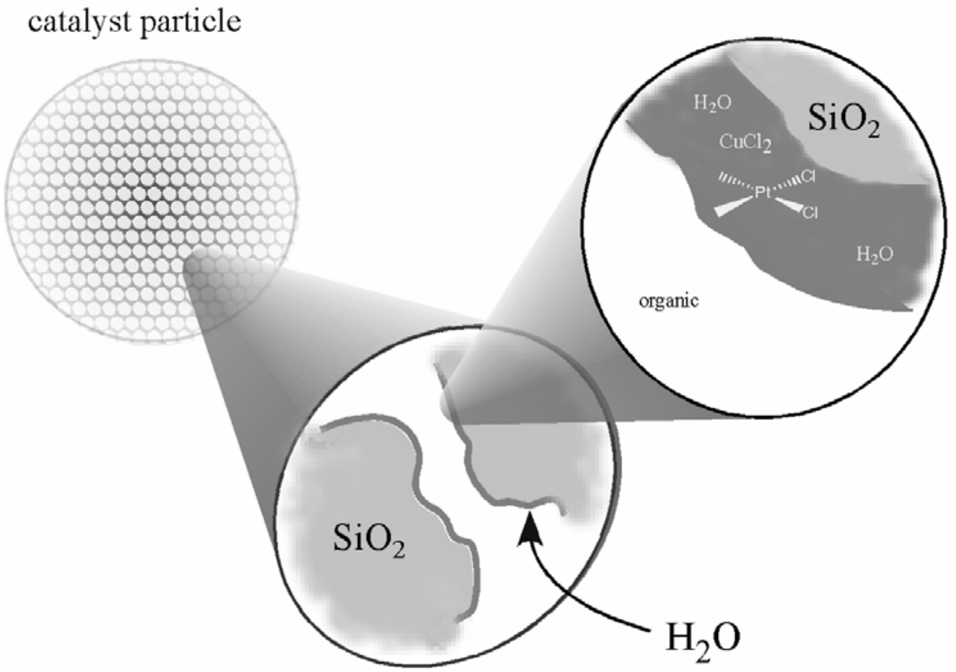


Figure 2.3: Depiction of a supported catalyst solution. In this case the solution is depicted as an aqueous solution but the water could also be a eutectic melt of molten salts.



CHAPTER THREE

EXPERIMENTAL METHODS FOR SYNTHESIS AND TESTING OF SUPPORTED SHILOV OXIDATION CATALYST

3.1 Supported Molten Salt Catalyst

The supported molten salt catalyst (SMSC) was prepared following the work of Rao and Datta.[1] Palladium chloride(≥ 98%), copper(II) chloride dehydrate (≥ 99.0%), copper (I) chloride(≥ 98%), potassium chloride (≥ 99.0%), and hydrochloric acid (1.0N) were used as purchased from Sigma-Aldrich. Controlled Pore Glass from CPG, Inc., with pores of 240 nm, was used as the support. The desired amount of metal salts required to achieve the desired loading on the support were dissolved in dilute (0.1N) HCl. The desired amount of support was dried under vacuum overnight before the vacuum was broken by introduction of the catalyst solution. The sample was evacuated to a pressure of less than 150 millitorr on a Schlenk line using a DUO Seal ™ Mechanical vacuum pump and monitored with a VH-3 Hastings vacuum gauge. Unless otherwise specified this is the system used in this rest of this work. The solution was stirred under nitrogen for 24 hours. The water was removed using a rotary evaporator.

3.2 Supported Aqueous Phase Catalyst

The supported aqueous phase catalyst (SAP) was prepared in a similar manner to the SMSC, and follows the procedures of both Hanson [2] and Butt [3]. Desired amounts of the catalyst ($PdCl_2$/$CuCl_2$ for Wacker oxidation and K_2PtCl_4(Reagent Grade 98%)/$CuCl_2$ for Shilov oxidation), enough to typically achieve approximately 5% by weight salt loading on the CPG, were dissolved in water. In the cases of ethanesulfonate oxidation, the sodium salt of ethanesulfonate was also dissolved in the solution. CPG was measured out into a round bottom flask and evacuated for several hours using the same vacuum system as described in Section 3.1. The solution of metal salts was then transferred to the flask containing the CPG, breaking the vacuum. The flask was then backfilled with nitrogen and the slurry was then stirred for at least 2 hours before the water was removed by using a rotary evaporator. The catalyst obtained was a free-flowing light green powder and was stored at room temperature. Thermogravimetric analysis determined the catalyst to maintain 2–3% by weight of water after the rotary evaporation.

3.3 Ion-Exchanged Zeolites

The ion-exchanged zeolites for Wacker oxidation were prepared based on the work of Jacobs.[4] BEA* and Ultrastable Zeolite Y (USY), a faujasite-type zeolite, from Tosoh were calcined as received. The parent materials were in the sodium form with BEA* having a Si/Al ratio of 13.5 and USY having a Si/Al ratio of 2.75. The USY is similar to that used for the highest conversions reported by Jacobs [4] and the BEA was the lowest ratio available from the company. They were then exchanged at room temperature for 24h in a 1M $Cu(NO_3)_2$ ($\geq$ 98%) solution with a solid to liquid ratio of 1g/L. After filtering and drying, the Cu(II)-Y and Cu(II)-BEA* were exchanged with aqueous solutions containing the desired amount, assuming all Pd is exchanged, of $Pd(NH_3)_4Cl_2$. The solution was allowed to stir at room temperature for 24 hours before filtering and washing with three times the exchange solution volume of water. The material was then dried in air at 100°C and stored in a desiccator until used. No attempts were made to determine the oxidation state of the copper after either exchange step; however the sample remained a light blue color. This is consistent with reports on Cu^{2+}-

exchanges into zeolite Y and BEA* where the copper remains in the Cu^{2+} state after exchange. [5,6]

3.4 Supported Catalyst Batch Reactions

All batch reactions were carried out in a stainless steel 25mL Parr mini reactor. The reactor is equipped with a pressure gauge, gas inlet and outlets, and a rupture disk. The desired amount of supported catalyst, usually 0.5g, was loaded into a glass liner and then hydrated by the addition of the desired amount of water. This mixture was stirred until all the water was taken up by the catalyst and the catalyst was a homogeneous powder. The glass liner was placed into the reactor and the reactor sealed. The reactor was then charged with the desired pressure of oxygen and placed in an oven. Heating to reaction temperature took approximately two hours in the oven. After the desired reaction time, the reactor was removed from the oven and allowed to cool to room temperature. Then a GC/MS analysis of the overhead was performed, and the catalyst was collected for NMR analysis in order to quantify the species remaining in the liquid phase on the CPG. This was accomplished by extracting those species in D_2O with a small addition of DMSO added as an external standard. The slurry was stirred for 1h and then sonicated for 1h before decanting the liquid. The decanted liquid was then centrifuged to remove any remaining CPG from solution before a proton NMR was taken to quantify the products of the reaction on a Varian Mercury 300 MHz spectrometer at 23°C. The signals at 1.25 ppm, 3.1 ppm, and 3.4 pmm were quantified in comparison to the DMSO signal at 2.7ppm for ethanesulfonate, 2-hydroxyethanesulfonate and 2-chloroethanesulfonate respectively in D_2O.

3.5 Supported Catalyst Flow Reactions

Reactions were carried out in a BTRS Jr. single pass vertical reactor system (Autoclave Engineers) with a ½" stainless steel reactor tube. 0.5g of catalyst was loaded into the reactor tube packed between glass wool. A thermocouple extended to the middle of the catalyst bed to measure reaction temperature. The water feed was fed as a liquid by syringe pump into a mixing assembly where it was vaporized with a sweep gas of 5% argon in helium (AirLiquide, 99.999%) in a mixing assembly at 150°C. The He/Ar , oxygen, and ethane flows were controlled by Brooks mass flow controllers. All reactions were run at concentrations above the upper flammable limit of the hydrocarbon in use. Products were analyzed by online GC/MS (Agilent GC 6890/MSD 5973N) with a Plot-Q capillary column. Products were identified from the GC/MS results by both the MS results for each peak as well as retention times from injections of individual components purchased from Sigma-Aldrich (99%+ purity). The retention times were argon, oxygen and carbon monoxide at 1.7 min and were quantified on the basis of distinct fragment counts in the MS 32 for oxygen, 40 for Ar, and 28 for carbon monoxide. The other retention times were carbon dioxide at 1.8 min, methane at 1.85min, ethene at 1.95min, ethane at 2.1min, water at 2.4min, acetaldehyde at 4.4 min, methanol at 4.8 min, ethanol at 6.8 min and acetic acid at 11.65min. The GC program had a start temperature of 150°C with a 2°C a minute ramp and a column flow of 2ml/min. The results were quantified using the argon in the He/Ar sweep gas as an internal standard. Calibration curves on the basis of mols product/mols Ar vs. MS counts product/MS counts of Ar for each of the products were generated by flowing various concentrations of the known product mixtures with various sweep gas flow rates through the system in bypass mode

3.6 **References**

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CHAPTER FOUR

SUPPORTED WACKER OXIDATION CATALYST

The similarities between the Wacker chemistry and the Shilov chemistry, along with the work on supported Wacker catalyst, make it attractive as a first step screening for the development of a supported catalyst for performing the Shilov chemistry. In 1959, Smidt and coworkers discovered the oxidation of olefins to ketones or aldehydes in a palladium/copper aqueous solution.[1] The Wacker oxidation cycle can be described by the following reaction set (Figure 4.1).

One can notice right away the similarities between the two mechanisms: the use of copper(II) as the oxidant of the transition metal and the use of molecular oxygen as the overall oxidant; the fact that the added oxygen to the hydrocarbon actually comes from the water molecule even though molecular oxygen is the overall oxidant; and the two-electron oxidation. Also this system is derived from a mixture of the salts $PdCl_2$ and $CuCl_2 \cdot 2H_2O$, similar to the salts used in the Shilov cycle. The Wacker system has been adapted to several supported systems: supported molten salts, supported aqueous phase, and ion-exchanged zeolites.[3–10]

4.1 Supported-Molten Salt Catalyst

The first supported catalyst looked at was a supported molten salt Wacker catalyst. Rao and Datta reported their development of a supported molten salt catalyst (SMSC) for the Wacker process and its use for the oxidation of ethylene to acetaldehyde in 1987.[2] The main characteristic of the SMSC is the use of a eutectic melt as the reaction medium as opposed to an aqueous phase. This is important since with an aqueous phase catalyst, evaporation of the solvent will lead to catalyst deactivation. Thus the low-volatility of a eutectic melt made it an attractive choice.

Rao and Datta investigated several choices of eutectic melts and found that a melt of 65 mol% CuCl and 35 mol% KCl at 195°C had good activity and selectivity similar to an aqueous phase catalyst.[2] This eutectic melt has a melting point of 150°C; thus operating at 195°C insures the mixture is in the liquid phase. Rao and Datta supported this eutectic melt on silica pellets with catalyst concentrations in the melt of 7 mol/m^3 $PdCl_2$ and 130 mol/m^3 $CuCl_2$. Rao and Datta's work took utilized a Berty reactor at 195°C and atmospheric pressure with a flow rate of 1.2×10^{-6} m^3/s and a feed composition of 5 mol% ethylene and 95 mol% air and the catalyst spread as a thin layer in a crucible which sat in the catalyst basket.[2]

In this study the method Datta reported for producing a SMSC was adapted to use controlled pore glass (CPG) as opposed to the silica pellets. The SMSC-CPG was prepared as follows: (1) the CPG was washed and dried under vacuum (i.e. pressure less than 150 millitorr per section 3.1 vacuum system description and the same for the following steps) over night; (2) the catalyst and solvent salts were dissolved in aqueous hydrochloric acid; (3) the vacuum on the CPG was broken by adding the required amount of the catalyst/solvent solution to the CPG; (4) the solution and CPG were stirred for 24 hours; (5) the CPG were dried on the rotovap. The initial attempt saw the catalyst/solvent solution turn from a dark green color initially to a blue color overnight. TGA/DSC experiments were unable to observe the melting transition of the catalytic phase with the prepared SMSC-CPG or with the unsupported eutectic mixture. It is possible that the color change may have arisen from changes to the copper species, though that was not investigated, and the use of catalysts prepared from these solutions were not active.[11] Due to the inactivity of the catalyst from the solutions prepared in air, subsequent catalyst preparations were performed under inert conditions. With this change the solution color, dark green, and the final catalyst, a light brown, are more in line with those reported by Datta[2] and Byers[11]. Also TGA/DSC experiments with the unsupported mixture show a melting point around 150°C, as seen in Figure 4.2. However, the SMSC-CPG showed much smaller effects, if any, probably due to the small amount of material actually undergoing the transition in a SMSC-CPG sample.

Most of the reactions run in this study using Wacker oxidation as a model substitute for Shilov oxidation were exploratory for developing technique and basic operating conditions as opposed to detailed studies of reaction variables and mechanism. The data for many of these runs either shows trace or no activity. For this reason only a few representative runs are detailed in Table 4.1. All reactions were run at 195°C and atmospheric pressure. The catalyst used was loaded to 20% liquid loading with the catalyst solution similar to the conditions Datta reports.[2] Besides the products acetaldehyde and carbon dioxide, dichloroethane was also produced in all runs of the SMSC likely arising from the high concentration of chloride and the use of cupric chloride at near 200°C [14]. A sample of CPG with no metal salts loaded was run and showed no products other than the feed composition.

In comparison Datta reports ~25% conversion of ethylene with a 95% selectivity to acetaldehyde.[2] As can be seen, the SMSC produced in this study perform nowhere near this level. One large difference in the two studies is the reactor type and the contact time — Datta uses a Berty reactor and this study uses a fixed-bed flow reactor. While every effort was taken to maintain identical conditions between this work and the work of Datta; i.e the same temperature, pressure, and catalyst loadings, in Datta’s study the space time is ~170s whereas the highest our current plug-flow reactor can achieve is approximately 25s. The Berty reactor Datta uses is more approximate of a continuously-stirred reactor (CSTR) than a plug-flow reactor (PFR). Typically a lower space time is required in a PFR to achieve the same conversion compared with a CSTR. The extremely large difference in the space times here however would lead to an expected lower conversion that is seen. In an ideal approximation (i.e. assuming all conditions are identical, the systems are isothermal, Datta's Berty reactor is an ideal CSTR and our PFR is an ideal PFR) for a first order reaction, which the Wacker system is under these conditions [2], a PFR with a space time of 145s would be needed to match the 25% conversion Datta achieves in the Berty reactor. Hence the large difference in the space time is likely a major cause for the lower conversions experienced in this study. Another observation that was made is that Datta claims all runs are dry except those investigating the feed of water into the system.[2] In this study, reactions with the SMSC and water in the feed had very little activity and favored the production of carbon dioxide over acetaldehyde. The physical appearance of the catalyst at different stages indicate changes in the catalyst, but these changes have not been determined as of yet. The catalyst as made and stored is a light brown color; after a reaction the removed catalyst is a more vivid brownish-orange. However if left exposed to air over time (several days), the catalyst will turn to a green color. It has also been seen that unreacted catalyst will turn to a light green if left open to air. The color change is a result of the hydration of the catalyst due to exposure to air. The CPG support is known to by hydrophilic and when exposed to air will have a 1-2 wt% of water content. The cupric chloride is hygroscopic as well. When dried the KCl and CuCl are colorless and the $CuCl_2$ will be a yellowishbrown while the palladium chloride is a reddish brown. This is the color observed after drying. After a reaction the catalyst is dried during the cool down when dry nitrogen is flowing over the catalyst as the reactor cools before it can be unloaded. When exposed to air the green color arises from the hydration of the $CuCl_2$.$CuCl_2$ in highly concentrated aqueous solutions appears green. The green of the CuCl2 likely dominates the reddish brown of the palladium chloride as the $CuCl_2$ is present in concentrations 20 times higher than the palladium chloride. It should also be noted that it is possible that some of the CuCl is converted to cupric oxychloride as well which is also green.

4.2 Supported Aqueous Phase Catalyst

In 1989 Davis and coworkers reported on a class of supported catalysts called supported aqueous phase catalyst (SAP), [12] in which a catalyst is dissolved in water and supported on a hydrophilic material and the combination is used in an organic solvent that is immiscible in water, thus maintaining the thin layer of water on the support and the catalyst in it, with the reaction occurring at the interfacial area of the organic and aqueous phases. Low solubility of methane in water makes this an attractive catalyst. These SAP catalysts differ from previously reported supported liquid catalysts because of the loss of liquid phase when a liquid substrate is used in the reaction. Thus the supported liquid phase catalysts are mainly designed for gas phase reactions. Even though this work will be dealing with a gas phase reaction the SAP catalyst is mentioned because in 1991 Davis and coworkers reported the development of a SAP Wacker catalyst for the oxidation of 1-heptene to 2-heptanone.[3] It is their procedure that will be used for the production of a SAP catalyst in this work. However the work will be comparable to other reported studies of supported liquid catalyst Wacker oxidation experiments.[3,9,13]

The SAP catalyst in this study was prepared according to the procedure laid out in Davis's work on Wacker SAP catalyst.[3] The catalyst was prepared as follows: (1) the CPG was washed and dried under vacuum overnight (i.e. pressure less than 150 millitorr per section 3.1 vacuum system description and the same for the following steps), (2) a desired amount of $PdCl_2$ was dissolved in ethanol, (3) the vacuum on the CPG was broken by adding the ethanol/$PdCl_2$ solution to the CPG and stirred, (4) the ethanol was removed by use of the rotovap and then placed back under vacuum, (5) a desired amount of $CuCl_2 \bullet 2H_2O$ was dissolved in water, (6) the vacuum on the $PdCl_2$/CPG was broken by addition of the $CuCl_2$/water solution and stirred, (7) the solution was dried under vacuum leaving the $PdCl_2$ and $CuCl_2$ deposited on the CPG. TGA/DSC experiments of the SAP catalyst showed that after drying the catalyst still maintained 2 – 3 wt% water. The catalyst was prepared to have 5 wt% metal salts with a Pd:Cu ratio of ~20 as is the ratio of the SMSC.

A sample of results for the SAP catalysts is also listed in Table 4.1. The reaction conditions are somewhat different than the SMSC due to trial and error to find good working conditions. One major difference is the reduction in temperature. With no requirement to reach the melt point of metal salts, the reaction can be carried out at lower temperatures, which improves the ability to maintain the water loading on the catalyst.[9] Looking at Table 4.1 comparing SAP7a and SAP7b the only difference is the amount of steam fed into the system, which when doubled increased the conversion of ethene from 34% to 56%. Increases in the water content of the feed leads to a increase in the liquid loading on the catalyst.[9] As described previously with the SAP catalyst, as the liquid loading increases initially the mobility of the individual catalyst molecules increases leading to an increased activity till a maximum is reached. After the maximum is reached, increased water feed leads to pore flooding that can lower the interfacial surface area and increased diffusional limitations that lower the activity. Thus based on the increased conversion from 34% to 56%, it should be expected that the optimal liquid loading was not fully reached. At 125°C an increase in the steam showed little change suggesting this is near the optimal steam feed for running the Wacker oxidation. The main products seen were acetaldehyde and trace carbon dioxide, while acetic acid was also seen occasionally, but none of the chlorinated products that were seen with the SMSC were observed.

One of the dominating factors in the activity of the supported aqueous phase catalyst is the liquid loading on the catalyst.[9] Shaw shows a sixfold increase in the reaction rate by increasing the liquid loading(fraction of pore volume filled with liquid) on the catalyst from 0.05 to 0.1, and a similar reduction in activity at higher loadings going from 0.1 to 0.5.[9] Multiple factors control liquid loading on the catalyst in a flow system, such as reaction temperature, support material, support pore size, and feed water concentration. This study used controlled-pore glass pores of either 240 nm or 500 nm (the CPG has a pore distribution of ±5%) as opposed to the alumina supports with 4 – 8 nm pores Shaw used. Larger pores would be expected to need more water in the feed to achieve the same liquid loading as is seen in this work where a higher water feed rate is need to see activity than in Shaw’s work.[9] Different supports will exhibit different optimal liquid loadings for maximum activity dependant on both the characteristics of the support and the reaction.[9] Larger pores and higher reaction temperatures are expected to require more water in the feed to reach op. Figure 4.3 shows the variation in activity over both the 240 nm and 500 nm CPG over 3 different reaction temperatures. The SAP catalyst loaded for each run was adjusted between the 240nm-pore CPG supported catalyst and the 500nm-pore CPG supported catalyst to maintain equal pore surface areas and loading amounts of palladium chloride and copper chloride were in each test. The larger pore size required higher feed water content to reach similar activity as the small pore size, and higher reaction temperatures also required higher feed water contents. The required feed water content needed to reach the maximum activity was not investigated nor was pore filling, due to concerns of flooding the reactor resulting in corrosion from the chloride salts on the CPG.

It is difficult to compare these results to some of the results of published data since the work by Davis was on 1-heptene[6] and work by Shaw used a flow rate 4 times slower with different feed compositions.[9] However both report on the observed peak in a plot of reaction rate versus water feed. [3,9] Both show an increasing reaction rate with an increased water feed, which eventually peaks and then decreases as the water feed continues to increase. As the water feed increases, the liquid layer of the SAP catalyst increases, so initially the increase in water allows more mobility of the catalyst particles and greater reaction rate. However, further increasing the water feed begins to fill the pores, decreasing the surface area for reaction and increasing diffusional limitations. More work is required to find the optimal water feed for these conditions.

4.3 Ion-Exchanged Zeolite

The final catalyst type that was pursued is an ion-exchanged zeolite. There are several reports on the use of Cu/Pd exchanged zeolites to perform Wacker oxidation of alkenes to aldehydes or ketones.[4 – 8] In this catalyst the cations that act as the catalyst are held in the zeolite by the ionic interaction with the zeolite lattice. In some of the more recent work on these catalysts, Jacobs and coworkers have attempted to establish the mechanism of the Wacker oxidation and determined it to be similar to that of the homogenous reaction.[4,5] They have also demonstrated that only the faujasite type zeolite, zeolite Y, provides high activity, and that activity has a dependence on the Si:Al ratio.[4]

The procedure used in this study for producing the Cu/Pd exchanged zeolite was adapted from the work of Jacobs.[5] The procedure involved mixing a sample of NaY zeolite for 24 hours at room temperature with an excess of a .01M solution of $Cu(NO_3)_2$ and then filtering and washing the sample until there were no nitrates detectable in the wash water. The Cu-exchanged zeolite was then mixed with a solution of $Pd(NH_3)_4Cl_2$ containing a molar amount of Pd that was less than twice the estimated amount of Cu in the zeolite. The solution was then allowed to once again stir at room temperature for 1 day, after which the zeolite was filtered and washed. It was then dried overnight at 100°C. The catalyst was then tested in the same reactor as the previous catalyst. Table 4.1 also contains several results from those runs.

The conversion of ethene on these Pd/Cu-exchanged zeolites is comparable to the reports from Jacobs[5]. In the run ZEO2 high conversion of ethene is seen with high selectivity toward acetaldehyde. Over the run on ZEO2 the conversion and selectivity remain constant. In ZEO4 and ZEO5 is set of back to back runs using the same sample of the catalyst. Runs ZEO4 and ZEO5 should results consistent with ZEO2 and the catalyst was still active at the same levels after 8 hours when the combined ZEO4 and ZEO5 runs are considered. All reaction runs were performed at atmospheric pressure and 105°C. Also each reaction was run so as to match the weight hourly space velocity and feed compositions used by Jacobs.[4] Each reaction also saw trace amounts of various other products, including acetone, acetonitrile, and acetic acid.

An initial reaction run at 195°C to match the similar temperature and pressure conditions of the SMSC only produced carbon dioxide. This is consistent with previous work on the oxidation of propylene by a Cu/Pd exchanged zeolite in which increasing the reaction temperature showed an increased selectivity to carbon dioxide and a decreased selectivity toward acetone.[6] The other reaction runs were run at a much lower temperature of 105°C, closer to the 100°C that Jacobs used.[4,5] Each of these runs shows good activity toward ethylene conversion; in fact they appear a little higher than the 50% conversion Jacobs reports [4,5]; however he does not report the product distribution for comparison of selectivity.

The low conversion and chloride products of the SMSC make it an unlikely candidate for the development of a supported Shilov oxidation catalyst, while both the supported aqueous phase catalyst and ion-exchanged zeolite may be useful techniques.

4.4 References

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Figure 4.1: Reaction scheme for the Wacker oxidation of olefins

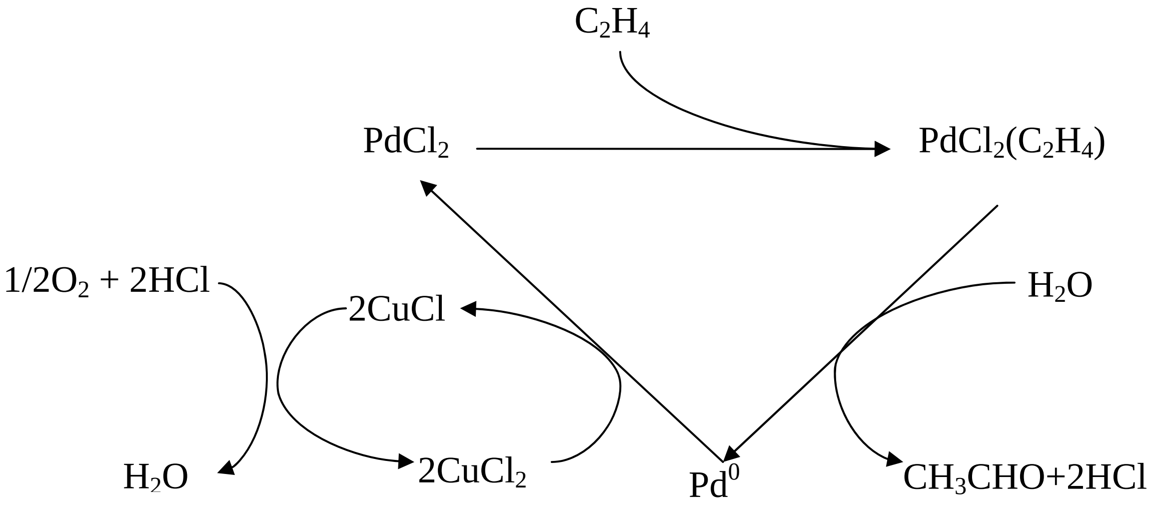


Figure 4.2: TGA/DSC analysis of the molten salt Wacker catalyst showing an endotherm beginning at approximately 150°C indicating the melting point

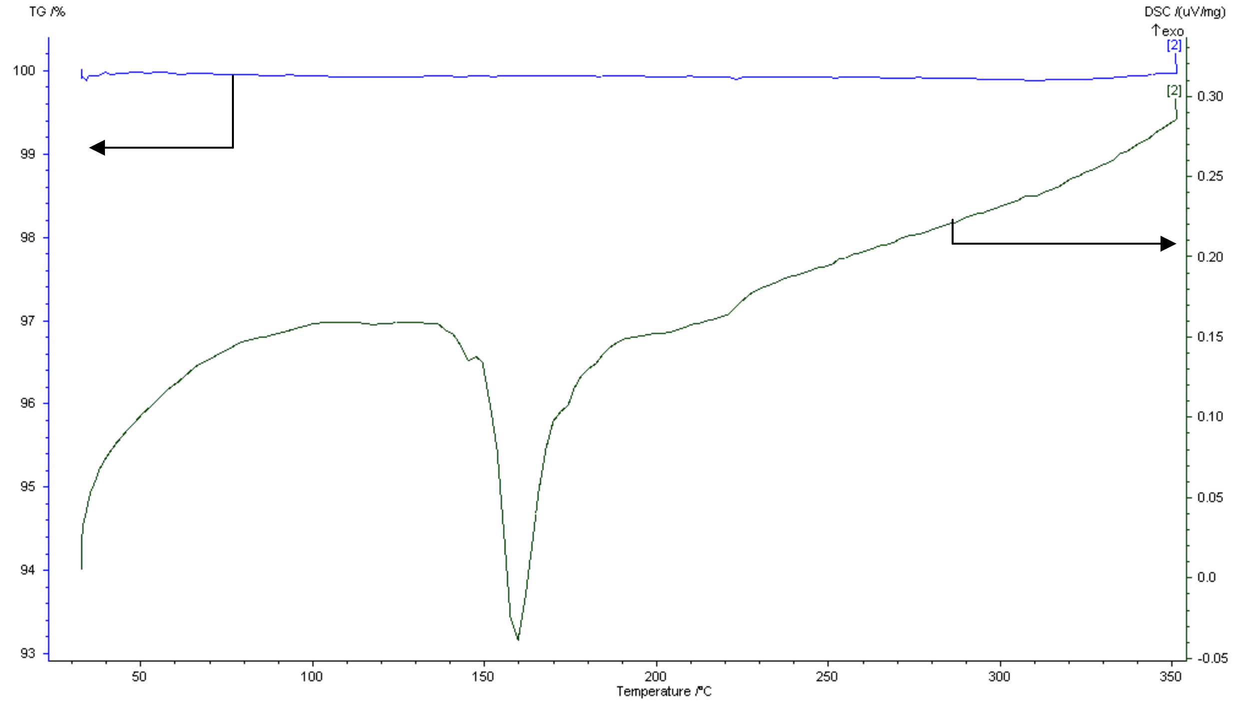
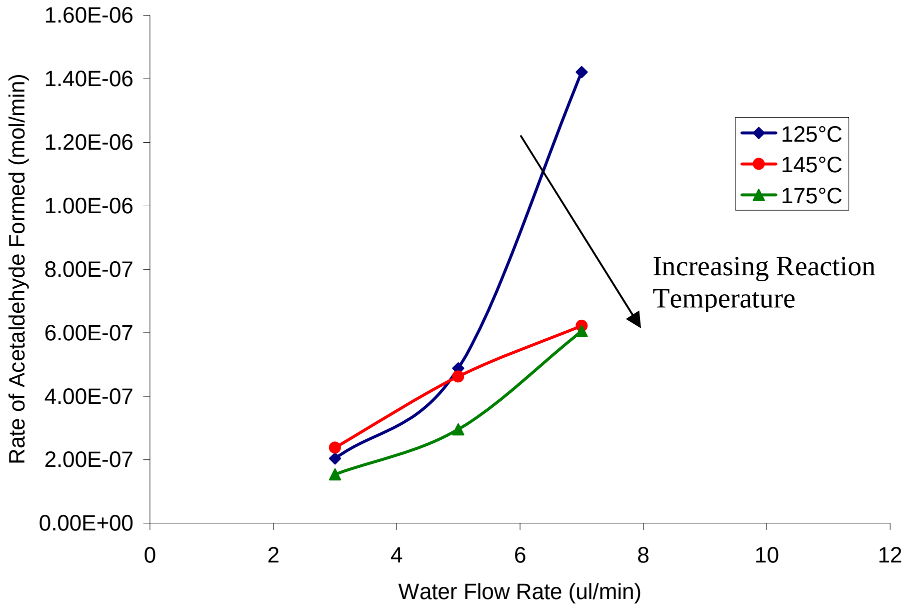


Figure 4.3: Comparison of acetaldehyde production on SAP catalyst at varying reaction temperatures and water flow rates on a) CPG with pores of 240 Å and b) CPG with pores of 500 Å

a) 240 Å CPG



b) 500 Å CPG

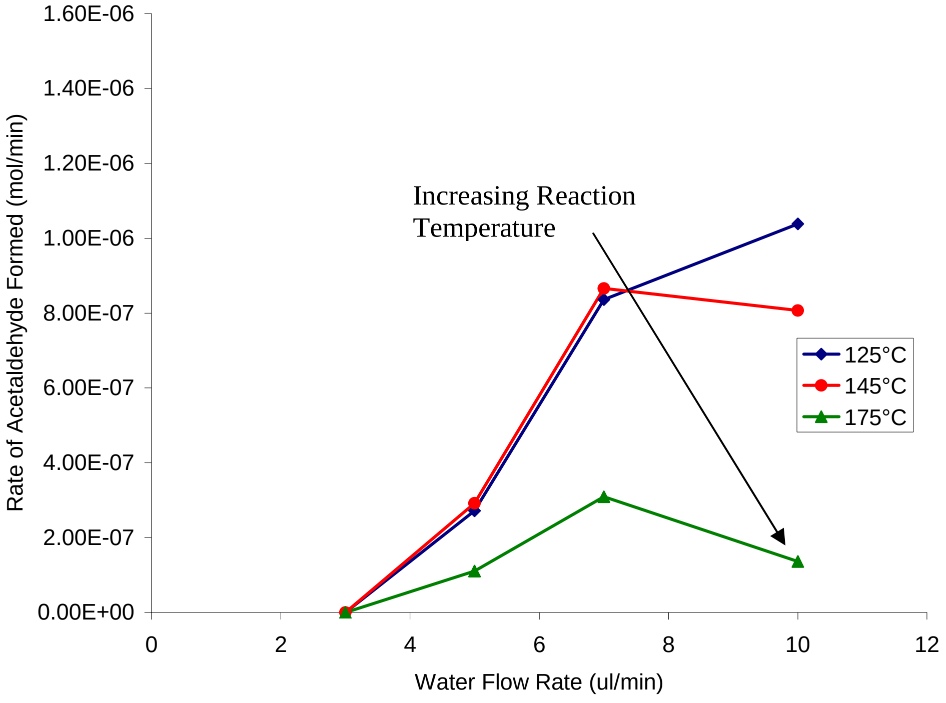


Table 4.1: Review of Wacker Catalysts used for the gas-phase flow oxidation of ethylene to acetaldehyde. SMSC=Supported Molten Salt Catalyst, SAP=Supported Aqueous Phase Catalyst

Run	Cat. Vol. (ml)	Cat. Mass (g)	Flows (ml/min) HC:O2:He/Ar: steam	Vol Cat./ Vol. Flow Rate	Conv. Ethene	Conv. O2	Selectivity Acetaldehyde
SMS Catalyst - 195°C, atm. pressure, 20 wt% loading of melt, 130 and 7 mol/m3 of CuCl2 and PdCl2 in the melt							
SMSC 8[a]	3.6	1.78	0.7: 3.0: 10.5:5.4	0.18	1.10%	0.20%	64%
SMSC 9[a]	3.75	1.82	0.7: 3.0: 10.5: 5.4	0.2	1.60%	0.50%	31%
SMSC 11[a]	3.7	1.8	0.4: 1.5: 3.1: 4.3	0.4	1.10%	0.30%	51%
SAP Catalyst - 115°C(runs 7&8), 125°C(runs 10&11), atm. pressure, 15wt% loading, Cu:Pd=3							
SAP7a[b]	3.9	1.53	0.3: 4.9: 5.4: 2.0	0.31	34.5%	1.55%	>99%
SAP7b[b]	3.9	1.53	0.3: 4.9: 5.4: 4.0	0.27	56.0%	2.52%	>99%
SAP8b[b]	3.9	1.53	0.6: 9.9: 10.9: 8.0	0.13	39.5%	1.7%	>99%
SAP10[b]	3.7	1.45	0.3: 4.9: 5.4: 4.0	0.25	47.4%	2.0%	>99%
SAP11[b]	3.7	1.45	0.3: 4.9: 5.4: 6.8	0.21	47.1%	1.8%	>99%
Zeolite Catalyst - 105°C, atm. pressure							
ZEO2[b]	2.5	1.067	0.3: 4.9: 5.4: 2.5	0.19	88%	5.80%	78%
ZEO3[b]	2.5	1.067	0.3: 4.9: 5.4: 2.5	0.19	6-20%	0.5-1.2%	42-65%
ZEO4[b]	2.4	1.012	0.3: 4.9: 5.4: 2.5	0.18	81%	5.50%	66%
ZEO5[b]	2.4	1.012	0.3: 4.9: 5.4: 2.5	0.18	81%	6.60%	75%

[a] Data is averaged over online time of hour 5 – 6 for run SMSC9 and from 4.5 – 5.5 for SMSC11 and 2 – 3 for SMSC8.

[b] Data is averaged over online time of hour 2.5 – 3.5 for all runs.

CHAPTER FIVE

SUPPORTED SHILOV OXIDATION CATALYST

From the Wacker oxidation study, the ion-exchanged zeolites and the supported aqueous phase catalyst seemed to have the most promise of providing good activity with limited undesired products such as carbon dioxide and chlorinated products.

5.1 Ion-Exchanged Zeolites for Shilov Oxidation

Using the process for the preparation of the ion-exchanged zeolites for Wacker oxidation, $Pt(NH_3)_4Cl_2$ was substituted for $Pd(NH_3)_4Cl_2$ to attempt to make a Shilov oxidation catalyst analog of the Wacker catalyst. The uptake of $Pt(NH_3)_4^{2+}$ was observed by UV-Vis. However reactions at a variety of temperatures, pressures, and feed concentrations saw no activity toward the oxidation of methane or ethane. In the Wacker system where $Pd(NH_3)_4Cl_2$ is exchanged into the zeolite in place of $PdCl_2$ used in the homogenous form, the ion-exchanged zeolite is active for the oxidation of ethene. However in the Shilov system, $Pt(NH_3)_4Cl_2$ appears to be inactive for alkane oxidation. The amine ligands appear to kill the activity of Pt(II) species in the Shilov cycle as use of $Pt(NH_3)_4Cl_2$ to oxidize ethanesulfonate supported on CPG was also inactive.

A second method of platinum addition to the copper-exchanged zeolite was the vapor deposition of platinum acetylacetonate. Reaction runs only showed an initial CO_2 product stream, not the desired products. Most of the CO_2 is attributed to the decomposition of the platinum species, as Pt^0 was observed by XRD on the spent catalyst.

A suitable method to introduce an active form of platinum into the zeolite was not found as there was concern that impregnation methods would leave the K2PtCl4 on the external surface as opposed to internal cages in proximity to the copper species. Further studies into obtaining a Pt(II) species inside a zeolite such as other potential ligands or manipulations could provide further interesting studies. However, we chose to devote our resources to the SAP catalyst at this time.

5.2 Supported Aqueous Phase Catalyst for Shilov Oxidation

The Supported Aqueous Phase Catalyst was expected to provide a better route to a heterogenized Shilov catalyst as there was already a homogeneous aqueous system. Initial tests of the supported aqueous phase catalyst were done following the work of Sen [1] working with the terminal oxidation of ethanesulfonate. The use of ethanesulfonate provides several advantages: it provides direct comparison with the homogenous system Sen used, reduces flammability/explosion concerns as opposed to a methane/oxygen mixture, and, as a water soluble reactant already on the support, limits issues related to pore flooding. Supporting the reaction solution on the controlled pore glass gives comparable activity to that reported by Sen [1] for the homogeneous reaction. Table 5.1 details examples of both reactions. The homogenous reaction produces species of further oxidation while the SAP catalyst produces only 2-hydroxyethanesulfonic acid and 2-chloroethanesulfonic acid. The SAP system is slower than the homogenous system, at the 4h reaction times point, the SAP system has achieved 49 turnovers with respect to Pt while Sen and Byers reported turnovers of 53 and 102, respectively. The reaction system used with the SAP system seems to have a 2 hour induction period before any products are observed, attributed to the heating to reaction temperature; it is unknown from Sen's report whether a similar period is observed. Also in the homogeneous system the total pressure is 1200psi with additional nitrogen while the SAP system was run under pure oxygen at 400psig, though the total pressures differ the oxygen pressures are similar and the pressure difference is expected to have little effect. Overall similar conversions are obtainable in the supported system as the homogeneous system.

Previous studies using a supported liquid system for catalysis have shown the importance of the thin film size on the ability of the reaction to proceed.[2,3] A minimum level of hydration is needed to maintain the mobility of the catalyst in the aqueous phase in order to achieve good activity. On the other hand, high levels of hydration lead to pore filling that reduces the interfacial area between the aqueous phase and the substrate leading to a reduction in activity.[2,3] The supported aqueous phase systems for Wacker oxidation require a liquid loading of approximately 10% of the pore volume for maximum activity on alumina support[3].

In this case, the reactant, ethanesulfonic acid, is easily dissolved in the water layer and oxygen more easily diffuses into the system than the olefins used in Wacker oxidation. With the reactant in the aqueous phase, pore flooding is not as large a concern with ethanesulfonic acid oxidation as is the need to hydrate the system to a level that provides sufficient mobility for all species, but pore filling must be considered in attempts to convert alkane feeds. Figure 5.1 shows the effect of initial catalyst hydration on the conversion of the ethanesulfonic acid and selectivity to 2-hydroxyethanesulfonic acid. The initial catalyst hydration is defined as the percent of the pore volume filled with water before the reaction begins. Some water is lost to the vapor headspace by evaporation when heating the system, meaning the actual water loading on the catalyst during reaction is lower. The controlled pore glass needs to be hydrated to between 10 –

18% of the pore volume filled before conversion of ethanesulfonic acid is observed, and selectivity improves up to between 25 – 30% pore volume filled (Figure 5.1). The onset of activity in the Shilov oxidation of ethanesulfonic acid is similar to the loading reported for ethylene oxidation on various supports at 10 vol.% [3] but lower than that required for heptene oxidation[2]. In respect to these observations further experimentation was carried out with a system hydrated to at least 25% of the pore volume filled with water.

Oxygen concentration had little effect on the system. Table 5.2 shows results for increasing the oxygen pressure from 60psig to 500psig. A small increase in conversion is noted between 60psig and 140 psig of oxygen with no additional increase to 250 psig of oxygen. This is similar to Sen’s observation in the homogenous system where an increase of the oxygen pressure from 300psig to 1300psig resulted in only a doubling of the reaction rate.[1] Looking at the analogous Wacker oxidation of ethylene on supported liquid phase catalyst, Shaw determined the reaction to be zero order with respect to oxygen.[3] This suggest that in both systems the oxygen reoxidizing the copper species is rapid compared to the other steps of the reaction.

While not affected by the oxygen concentration, the turnover frequency has a strong dependence on the concentration of the organic substrate. Increasing the organic substrate/Pt ratio from 84 to 152 increased the turnovers from 72 to 120, with both reactions reaching around 80% conversion with similar selectivities of approximately 94% to 2-hydroxyethanesulfonic acid after 9 hours. This suggests that little deactivation is occurring in the batch system and in these tests the limit to turnovers is the amount of organic substrate loaded into the system.

Another important aspect of the Shilov oxidation with the Pt/Cu system is the influence of the chloride ion. Similarly to the Wacker oxidation [5], this system requires an excess of chloride ions to reoxidize the platinum species and prevent platinum metal formation, but excess chloride concentration inhibits the organic substrate oxidation. It is presumed that the excess chloride inhibits C-H Bond activation by reducing accessibility of the metal substrate to the substrate. [1] In a similar manner, recent DFT studies by Zeigler have suggested how presence of different platinum species and the amounts of each in the solution can effect the rate of the methane uptake/activation rates. The chloride concentration may cause shifts to larger population of less active species. [6] Figure 5.2 shows the product evolution over time for the batch reaction of the SAP catalysts with Cu/Pt ratios of 10, 26, and 37. Increasing the Cu/Pt ratio in the SAP catalysts slows the reaction — increasing the time before products are observed and increasing the time to reach a similar level of conversion as that observed with the catalyst with Cu/Pt ~10. Another unique feature is the presence of chlorinated products. Sen does not report the formation of chlorinated products in the homogeneous system.[1] However using the SAP catalyst as shown in Figure 5.2, chlorinated products appear to be formed and then are consumed as the reaction proceeds. At a Cu/Pt ratio of 10, chlorinated products are seen from the beginning but only decline over time. At Cu/Pt of 26, there is a quick build-up of chlorinated products that disappears over the rest of the run and at Cu/Pt of 37 the build-up is slowed down as well as the disappearance.

The appearance and disappearance over time of the chlorinated species was not reported in the work on the homogenous system by Sen.[1] The chlorinated species likely arise during the final step of the Shilov mechanism, as shown in Figure 2.2 step 3, when instead of H_2O, Cl^- acts as the nucleophile in the reductive elimination. As seen in Figure 5.2, increases in the Cu/Pt ratio, and thus increases of the Cl^- concentration in the system, lead to a higher level of chlorinated species observed. The disappearance of the chlorinated species is likely due to hydrolysis. Table 5.3 details chloroethanesulfonate conversion to the desired 2-hydroxyethanesulfonic acid, indicating that 2-hydroxyethanesulfonic acid can be derived via the chlorinated species. The amount of 2-hydroxyethanesulfonic acid arising from oxidation via the Shilov mechanism as opposed to hydrolysis of the formed chloroethanesulfonate was not determined.

The ability of the supported aqueous phase system for Shilov oxidation of ethanesulfonic acid to reach similar conversion levels as the homogeneous system, and Sen's observation for the homogeneous system of ethane being as reactive as the ethanesulfonic acid in solution [1], makes the supported system a good candidate for the direct oxidation of light alkanes to alcohols in a flow reactor. However, using a variety of reaction conditions resulted in no measurable product by GC/MS or offline NMR of captured effluent. The reaction pressure was maintained at 500 psig over all tests with varying oxygen, ethane, and helium concentrations in the range above the upper flammability limit for ethane. A wide range of water feed rates were also used to vary the liquid loading on the catalyst. The catalyst was the 5 wt% metal salt loading with a Cu/Pt ratio of 25. In all instances the catalyst changed color from a light green to grey color, probably indicating the formation of platinum metal. Another sign of the deactivation is the detection of chloride in the trapped effluent by precipitation with silver nitrate addition. It appears that the supported catalyst is losing a large amount of its chloride concentration quickly in the flow setup and the reaction is unable to proceed. In the Shilov reaction while the conditions are at a mild reaction temperature of 150°C, this temperature is still above the boiling point for any aqueous HCl solution. While the steam fed to the system maintains a vapor pressure of water above the supported film, the feed contains no chloride and thus by equilibrium some of the HCl in the film is being lost to vapor that is then swept from the system in the effluent. In the Shilov system, chloride is released in both the C-H bond activation and the reductive elimination step. These ions are then reused in the oxidation of the cuprous chloride to cupric chloride. However any HCl loss to the vapor phase before the oxidation occurs is swept away with the effluent. The loss of chloride ions leads to the loss of cupric chloride as an oxidant and eventually the Pt(II) species can also be consumed as an oxidant resulting in the formation of platinum metal and shutting down the system. It is plausible that the system actually undergoes a few turnovers which we do not observe and in those processes the chloride is lost

The initial inactivity of the flow system does not preclude this from being a useful catalyst or technique. While probably not advantageous for light alkane oxidation, a system where the chlorine concentration can be replenished by added HCl may prove active for various terminal oxidations. Similarly systems with other ligands that are not swept away like the chloride ions in the Shilov system, either by quicker uptake with the metal centers or less volatility, could work well as a supported system for chemical transformations.

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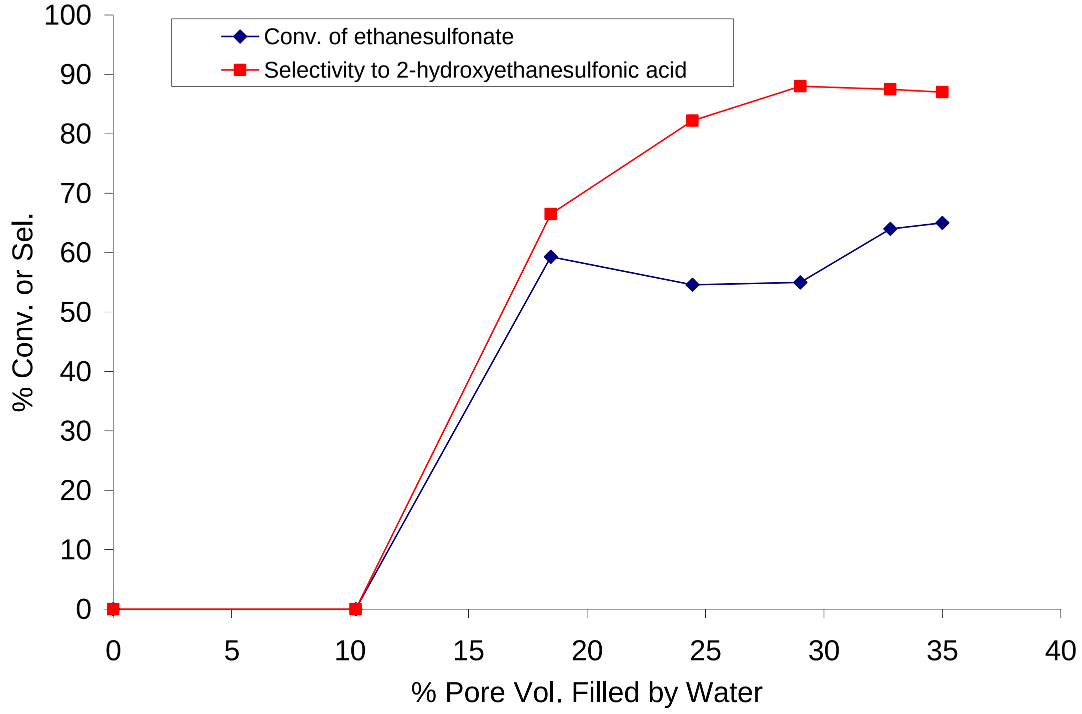
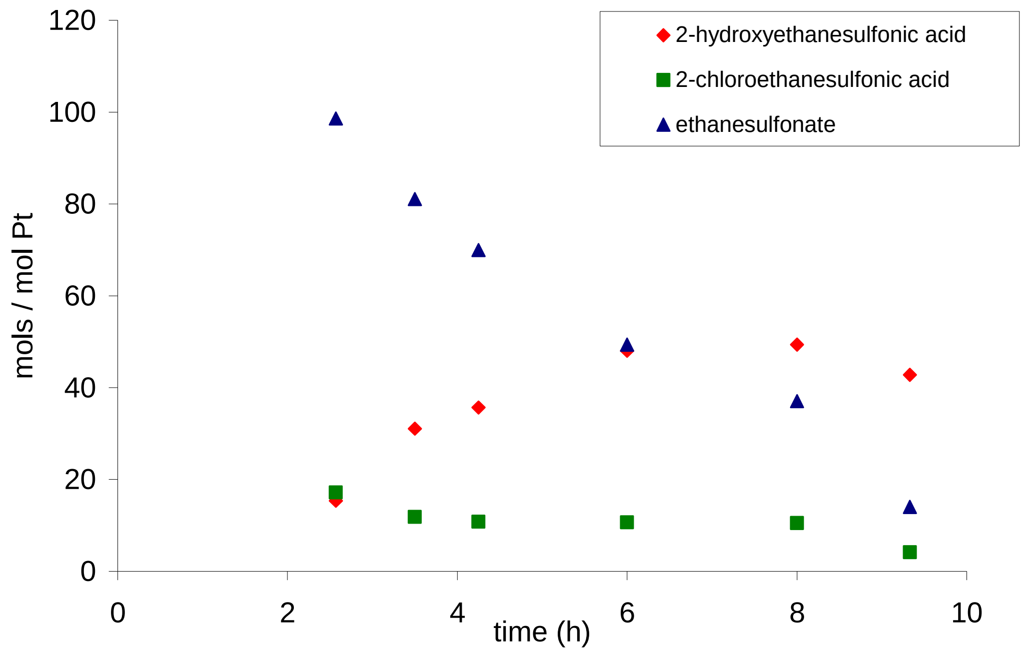
Figure 5.1: Oxidation of ethanesulfonate over various levels of liquid loading on the catalyst



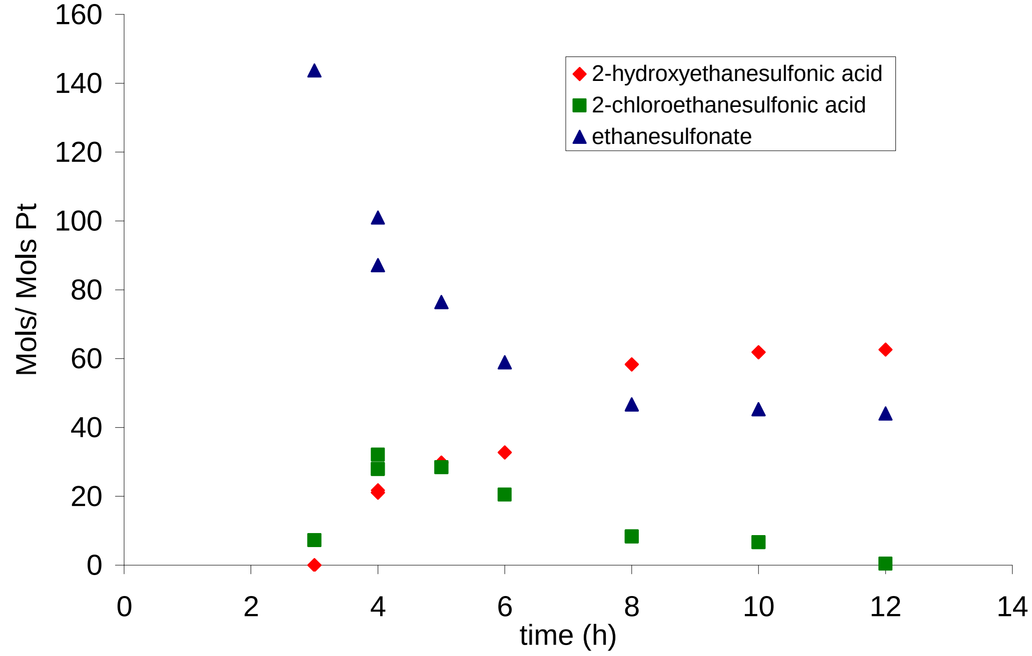
Reactions conditions: Cu/Pt ~10, $C_2H_5SO_3^-$/Pt ~80, 500psig O_2 @ RT, 160°C, 6h

Figure 5.2 Profile of reaction species on a per mol Pt basis over time for varying Cu/Pt ratios

A) Cu/Pt ~10



B) Cu/Pt ~26



C) Cu/Pt ~37

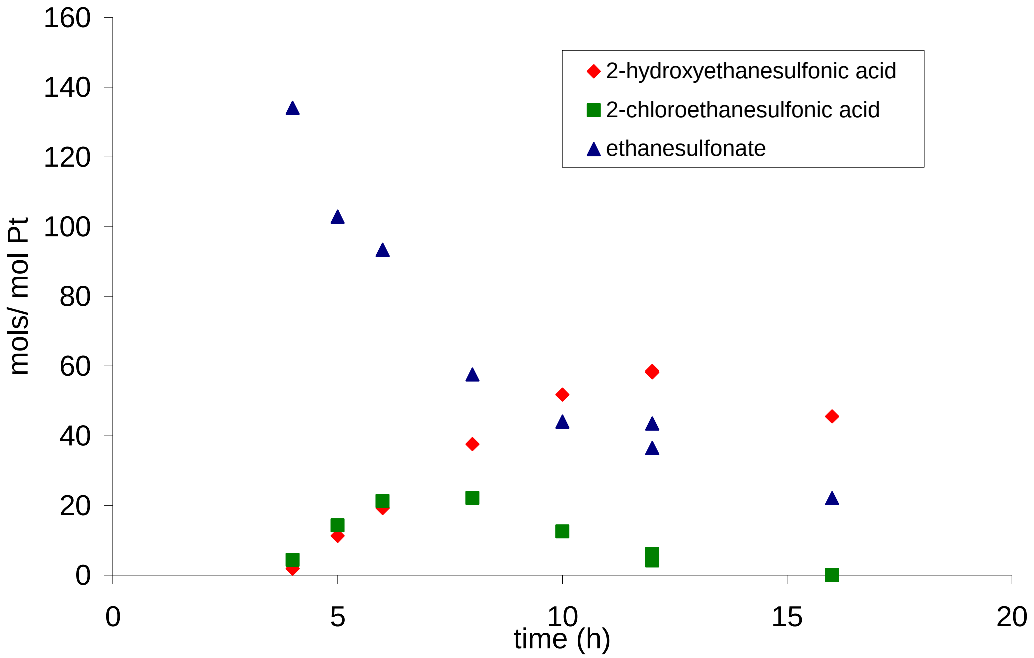

160
140
120
100
80
60
40
20
0
mols/ mol Pt
0
5
10
15
20
time (h)
◆ 2-hydroxyethanesulfonic acid
■ 2-chloroethanesulfonic acid
▲ ethanesulfonate

Table 5.1: Comparison of supported aqueous phase Shilov catalyst with the homogenous system

		Reagent Ratios (mol/mol)			Products (% based on total liq. products)							
Catalyst	Type	Substrate/ Pt	Cu/Pt	O_2/Cu	1	2	3	4	5	6	Conv.(%)	TO/Pt
Sen[1]	Homogenous	167	6	203	78	0	19	2	2	0	32	53
Byers[2]	Homogenous	194	7	212	88	tr	0	0	11	tr	61	102
Byers[3]	CPG	82	9	1517	47	45	0	0	0	6	29	24
Carpenter[4]	CPG	152	10	850	76	23	0	0	0	0	33	49

1. 2.0mmol substrate; 2.0ml water; 0.1ml H_2SO_4; 300psi O2; 1200psi N_2; 160°C; 4h. [1]
2. 2.0mmol substrate; 2.0ml water; 160°C; 4h. [4]
3. 0.0109mmol (Pt)/g(CPG); 0.103(Cu)/g(CPG); 0.891(substrate)/g(CPG); 160°C; 4h. [4]
4. 0.011mmol (Pt)/g(CPG); 0.29(Cu)/g(CPG); 1.7(substrate)/g(CPG); 150°C; 4h. – mass loss to vapor phase

Products:
1=$HOCH_2CH_2SO_3^-$
2=$ClCH_2CH2SO_3^-$
3 = $(HO)_2CHCH_2SO_3^-$
4=$HOCH_2COOH$
5=CH_3COOH
6= $CH_3CH(OH)SO_3^-$

Table 5.2: Variation in oxygen pressure in the oxidation of ethanesulfonate on a supported aqueous phase Shilov catalyst

		Reagent Ratios (mol/mol)			Products (% based on liquid products)					
Run	mass used (g)	Substrate /Pt	Cu/ Pt	O_2/ Cu	$HOC_2H_4SO_3^-$	$ClC_2H_4SO_3^-$	other	Conv. (%)	TO/ Pt	% vol Added H_2O
60 psig	.61	77	10	42	87	13	tr	55	42	30
140 psig	.51	77	10	117	87	13	tr	64	50	33
250 psig	.60	77	10	178	86	14	tr	65	50	35
500 psig	.59	77	10	363	78	22	0	62	48	24.5

Table 5.3: Conversion of chlorinated products to desired products over time

Reaction Time (h)	Initial Reagent Ratios					Mass Balance	**Final mols $HOEtSO_3$/ mols Pt**	**Final mols $ClEtSO_3$/ mols Pt**
	Pt mmol/ g cat	Cu mmol/g cat	$ClEtSO_3$ mmol/g cat	Cu mol/ Pt mol	$ClEtSO_3$ mol/ Pt mol			
0	0.0170	0.2130	2.25	12.55	132.39	100	**0.0**	**132.4**
5	0.0170	0.2130	2.25	12.55	132.39	86	**55.2**	**59.2**
10	0.0170	0.2130	2.25	12.55	132.39	86	**105.7**	**8.6**

CHAPTER SIX

CONCLUSIONS ON SUPPORTED SHILOV OXIDATION CATALYST

In Part One three different techniques for creating a heterogeneous catalyst system were investigated. Methods for preparing Wacker oxidation catalysts in the forms of a supported molten salt catalyst [1], as a supported aqueous phase catalyst [2,3], and as an ion-exchanged zeolite[4] were explored. Comparisons of these catalysts under similar reaction conditions for the oxidation of ethene to acetaldehyde were made in a plug-flow reactor system. Due to the need to reach the melting point of the eutectic mixture of KCl and CuCl, the supported molten salt catalyst system required a higher temperature, 195°C, than the supported aqueous phase system or ion-exchanged zeolites, 100°C – 125°C. Also the supported molten salt system showed lower conversion of ethene than those systems (1 – 2% versus 55+ %) and a higher selectivity to chlorinated products (50% versus less than 25% on the zeolites or virtually none in the supported aqueous phase catalyst). The supported aqueous phase system demonstrated the previously reported [2, 3] importance of the concentration of water in the feed stream. Increasing the steam fraction of the feed from .15 to .4 increased the conversion of the ethene from 35% to 87%. The supported aqueous phase catalyst and ion-exchanged zeolites met the criteria of mild operating temperature with good activity and high selectivity toward the desired products.

Attempts were made to use an analogous ion-exchanged zeolite in the Shilov oxidation by changing the $Pd(NH_3)_4Cl_2$ to $Pt(NH_3)_4Cl_2$. Unfortunately over various reaction conditions — increased pressure, various feed concentrations, multiple temperatures, and heeding the lesson of Wacker oxidation, different water concentrations by varying the steam feed — no oxidation products of ethane were detected. The lack of activity is not from a lack of Pt; following the UV-Vis spectra shows almost complete uptake of the platinum species during the exchange process, much like that reported by Jacobs for the palladium species. [4] Unlike with the Wacker oxidation of ethylene, the use of a Pt(II) species with amine ligands and/or supporting the catalyst in the cages of a zeolite resulted in no products from Shilov oxidation of alkanes or ethanesulfonate. Other attempts to introduce different platinum species were also unsuccessful, as vapor phase deposition of platinum acetylacetonate only resulted in the formation of Pt^0 upon testing.

In the supported aqueous phase system, the homogenous reaction solution that has been shown to work by Sen[5] is dispersed as a thin layer on a hydrophilic support. This allows the system to maintain many of the characteristics of a homogeneous solution by not having to add extra ligands to an organometallic catalyst with which to anchor it, but at the same time massively increasing the surface area for interaction between aqueous and gaseous species. Also it provides the potential to contain potentially corrosive species on the support as opposed to being in close contact with a reactor wall.

Initial work was successful in following Sen [5] in oxidizing the terminal methyl group of ethanesulfonate with dioxygen as the ultimate oxidant, except doing it on the controlled pore glass support. Similar turnovers of the platinum were seen in both systems. Sen achieved 53 turnovers to products of platinum [5] while similar conditions on the supported aqueous phase system saw 62 turnovers on platinum. Higher turnovers of platinum, 102, were achieved in the homogenous system with some changes in reaction conditions. [6] Various reaction parameters were investigated with the ethanesulfonate oxidation to provide guidance for alkane oxidation. As with the Wacker system, a minimum amount of liquid loading was required to achieve activity, in this case the required loading seems to be between 15 % and 20 % of the pore volume. Similar to Sen [5] little dependence on the oxygen concentration was observed. The platinum species was required to see oxidation. Unlike in Sen's work [5], the SAP catalyst did not require a spike of sulfuric acid in the system to observe oxidation, and the presence of sulfuric acid did not enhance the activity. The increase in chloride concentration by increasing the copper(II) chloride slowed down the reaction and increased initial formation of chlorinated products. However the chlorinated products disappeared with increased reaction time. Some were converted to increasing carbon dioxide concentration in the head space but some were converted to the desired isethionic acid product. This was observed by loading the catalyst with only the chlorinated species and following the conversion to isethionic acid over ten hours. This raises questions as to the true mechanism occurring in the supported system, as there may be a second pathway to the product than directly through the Shilov mechanism.

With a successful oxidation of ethanesulfonate on the supported aqueous phase system, trials were run for the oxidation of ethane in a plug-flow reactor system. Using the lessons learned from both the Wacker oxidation and the ethanesulfonate work, reaction conditions were varied within safety limits and no oxidation was observed. The catalyst changed color from a light green to a grey color, leading to suspicion about the formation of Pt^0. At the same time chloride ions were detected in the trapped effluent. It seems the catalyst, when used in the flow system, lost chloride ions rapidly leading to deactivation before any products were detected. In the batch system with ethanesulfonate, it is likely that this was not as noticeable, as chloride loss was minimized by using a static system.

While the oxidation of a small alkane on heterogeneous system in a flow mode was not achieved, a supported system catalyst that performed similar to the homogeneous system was demonstrated for ethanesulfonate oxidation. This system remains a highly viable route for creating a heterogeneous system provided a catalyst species can be identified that overcomes the problem of ligand loss. Similarly a future direction could be in the application of this catalyst to more specialty chemical applications such as a liquid/liquid phase oxidation in batch systems where the mobility of the chloride ion and its corrosiveness can be better contained.

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