DEOXYGENATION CATALYSIS ON TITANIA FOR RENEWABLE FUEL APPLICATIONS

By

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This research studies the use of titania (titanium dioxide, TiO₂) as a catalyst for deoxygenation of syngas derived oxygenates. These oxygenates are formed as byproducts when biomass derived syngas (CO & H₂) is converted to ethanol on Rhodium or Molybdenum based catalysts. Conversion of these oxygenates to hydrocarbon would enhance the viability of syngas to gasoline technology. This study revealed that titania can indeed be used to convert syngas derived oxygenates to hydrocarbon at high temperature and pressure. Acetone condensation to mesitylene was studied very closely. The study revealed that the acid-base dual nature of titania is key for the success of this reaction. When titania was combined with the zeolite H⁺/ZSM-5, a broad range of gasoline type hydrocarbon could be produced. Ethanol conversion to higher alcohols was studied as part of a partial deoxygenation of ethanol research. While this conversion was possible on titania, zirconia proved to be a better catalyst. Ethanol could be converted to 1-butanol and other higher alcohols at high temperature and pressure. The mechanism by which this occurs was studied as well.
DEDICATION

I would like to dedicate this work to my mother Bharathi and father Francis Jayaraj Daggolu whose support, prayers and encouragement was of utmost importance during the course of this study. Also, I would like to extend this dedication to my brother Benjamin and sister Jerusha.
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CHAPTER I

INTRODUCTION

The growing demand for liquid fuels has placed an enormous pressure on oil supplies around the world. This increased demand for oil has been responsible for the sharp rise in crude oil prices in 2008. The United States Department of Energy, US-DOE, expects the price of the crude oil to increase by 100% by 2035 compared to 2010 price (Fig 1.1, [1]). The world energy consumption is expected to increase by about 40 % from 2009 to 2030 (fig 1.2). It is clear that without the unexpected discoveries of enormous oil reserves, non-renewable fuel sources such as petroleum, would not be a solution for the world energy needs in general and that of the United States’ in particular in the long term future. There are some viable sustainable fuel options in this regard including: solar energy, wind energy, biofuels and fuel cells. Of these options biofuels alone can be used as a replacement for petroleum-derived liquid transportation fuels with little or no changes in the present infrastructure for fuel production, delivery and usage.
Figure 1.1  Trends and projection of energy prices from 1980 to 2035 (Source: United States Energy Information Administration).

Figure 1.2  World Energy Consumption from 1980 – 2006 (actual) and 2010 – 2030 (Projected), (Source: United States Energy Information Administration).
Biofuels have numerous advantages for the United States. The development of biofuels would significantly decrease the oil imports giving US the energy self-reliance and hence strategic advantage. It would decrease the trade deficit and generate new jobs. Biofuels can be engineered to reduce CO₂ yields relative to fossil fuels, hence reducing green house effect. Also there would be reduced incentives for oil drilling which would reduce the environmental risks to oceans resulting from oil exploration and deep water drilling. Hence biofuels would not only replace fossil fuels for transportation but also have positive environmental, political and economic impact on US policies.

1.1 Production of Bio-fuels

Much research has been concentrated in the production of biofuels. Many biomass sources have been studied for potential use as starting material for biofuels. Biofuels are classified into two main branches: primary and secondary fuels [2]. Primary fuels are those which utilize biomass directly. Burning of wood to make fire in fire places is an example of primary fuels. These were historically used for cooking and heating. But these cannot be used for transportation fuels. A secondary fuel is processed biomass. Naturally occurring materials are taken and processed using thermo chemical or microbial methods and converted into useful fuels.
Figure 1.3 Classification of Biofuels

All biofuels that can be used for transportation fall in this category. The secondary biofuels are further classified into 1\textsuperscript{st} generation (1G) biofuels, 2\textsuperscript{nd} generation (2G) biofuels [3], and 3\textsuperscript{rd} generation Biofuels (3G)[4] based on the evolution of technology in the past years. The 1G biofuels utilize simple processes to convert mainly sugars [5-8] or seeds [9-11] into fuels. The classic example of this generation of technology is bioethanol production [12, 13]. This has been practiced to make potable alcohol from sugar containing materials for centuries and recently for fuel purposes. This generation also includes transesterification techniques of sugars [14]. While there is no question about the viability of these technologies technically, they utilize food sources to make fuels. In the long term this leads to a conflict between food market and fuel market making it unsustainable. The 2G biofuels utilize lignocellulosic material from the plants as the carbon source. Biological or thermo-chemical methods are used to convert lignocelluloses into useful fuel. Since these biofuels do not employ edible sugar parts of the plants, a conflict with food market is avoided. Conversion of biomass to gasoline via syngas or pyrolysis routes falls in this category [15]. Conversion of lignocellulose to
alcohols using fermentation is also part of this generation of Biofuels [16]. One important factor in both 1G and 2G Biofuels is that they need large amounts of land to produce sufficient amount of fuels for the market. This problem can be avoided in 3G fuels. These fuels are produced from microbes and algae [17]. These fuels neither compete with food market nor with land utilization like 1G and 2G fuels.

Biomass can be converted to fuel by 2 main methods: pyrolysis and gasification. Pyrolysis is a high temperature, short residence thermal process for the liquefaction of biomass in the absence of air. One product of this process is a chary liquid which then can be treated further to produce fuels. Gasification is a high temperature, longer residence time thermal process controlled burning of biomass in air or pure oxygen. A major product of this process is synthesis gas (shortly called syngas) which is a combination of carbon monoxide, CO, and hydrogen, H₂. Syngas can be converted to hydrocarbons using several thermal catalytic processes. One process that has been practiced commercially is the well known Fisher Tropsch technology using Fe or Co catalysts [18]. Another process for converting the syngas is the conversion to methanol over CuO/ZnO/alumina catalysts [19]. Alternatively, syngas can be converted to ethanol on Rh catalysts and to many other chemicals [20]. The pyrolysis process mainly yields a chary liquid which is mainly a mixture of oxygenates, some of which are not easily converted to liquid hydrocarbons suitable for use as a fuel [21, 22]. But the pyrolysis process uses less energy than gasification. On the other hand, while gasification uses more energy than pyrolysis, its products can be easily converted to liquid hydrocarbon by well established methods.
1.2 Conversion of Syngas to gasoline

1.2.1 Fisher Tropsch Technology

The well known Fischer Tropsch Technology (FTT) was invented by Franz Fischer and Hans Tropsch in 1920s [23]. In its most pristine form, it utilized Fe catalyst to convert syngas to paraffins. But over the years FTT has undergone many modifications and new catalytic systems have been discovered to get better results in terms of product distribution and quantity.

The recent surge in alternative fuel research has led to researchers taking a new look at FTT [24]. Syngas required for FTT can be obtained from either coal gasification [25, 26] or biomass gasification [27, 28]. FTT produces linear hydrocarbon and hence is a good route to make high quality diesel [29]. A recent study showed that iron supported on alumina resulted in higher activity for olefin formation [27].

Figure 1.4 Schematic showing possibilities available for biomass conversion to fuels.
Basic equations governing FTT are:

\[
\begin{align*}
nCO + 2nH_2 & \rightarrow (-\text{CH}_2^-)_n + nH_2O \quad (1.1) \\
nCO+(2n+1)H_2 & \rightarrow C_nH_{2n+1}+nH_2O \quad (1.2) \\
nCO+(n+m/2)H_2 & \rightarrow C_nH_m+nH_2O \quad (1.3)
\end{align*}
\]

Where \( n \) is the average chain length of the hydrocarbon and \( m \) is the number of hydrogen atoms per carbon. The formation of \(-\text{CH}_2^-\) is the building block for the hydrocarbon [30].

Co catalyst gives higher CO conversion than Fe catalyst [31]. Co is more active as a hydrogenation catalyst and hence forms mostly saturated hydrocarbon. Several reactors and conditions have been studied for FTT application. It was found that reaction temperature, pressure and residence time influence the quality of liquid product formed [32, 33]. But there are some downsides to the FTT Process. It does not produce gasoline range hydrocarbon i.e. no aromatics. Since gasoline is the highest used transportation fuel today FTT cannot cater to all transportation needs. There is poor control on the usage of carbon in FTT. Once the reaction is initiated, the \(-\text{CH}_2^-\) hydrocarbon back bone keeps growing based on residence times. But even at low residence times, it is difficult to produce only low carbon number liquid hydrocarbon and avoid wax formation. Also low residence times would result in less conversion. These are some of the present challenges in FTT to be overcome for full scale commercialization.

### 1.2.2 Alcohol intermediate Technology

In order to avoid the problems associated with Fischer Tropsch Technology, a new route for converting syngas to fuels is being explored. Syngas can first be converted
to alcohols. Then the alcohols can either be converted to gasoline, used directly as fuels or as additives to fuel. Syngas can be converted to methanol on a CuO/ZnO/Alumina Catalyst. However this reaction is equilibrium limited.

\[
CO + 2H_2 \rightleftharpoons CH_3OH
\]  

(1.4)

Hence present research efforts are concerned with making higher alcohols. Another advantage with higher alcohols is that they have higher heat value than lower ones.

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>Heat value, MJ/kg</th>
<th>Fuel</th>
<th>Heat value, MJ/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>22.7</td>
<td>Natural Gas</td>
<td>54.0</td>
</tr>
<tr>
<td>Ethanol</td>
<td>29.7</td>
<td>Gasoline</td>
<td>46.5</td>
</tr>
<tr>
<td>1-Butanol</td>
<td>36.1</td>
<td>Kerosene</td>
<td>46.4</td>
</tr>
<tr>
<td>1-Octanol</td>
<td>40.7</td>
<td>Fuel Oil</td>
<td>40.9</td>
</tr>
</tbody>
</table>

Presently, ethanol \([35, 36]\) and 1-butanol \([37, 38]\) are being produced by fermentation reaction of sugars. Fermentation is a very slow process compared to thermochemical reactions. Present catalytic processes to produce higher alcohols from syngas yield many unwanted side products. Syngas can be converted to ethanol on Rh based catalytic systems \([20]\). But this yields acetic acid, acetaldehyde and methyl acetate as major side products. In a Mo catalytic system also oxygenated by products are seen. Effective utilization of carbon by converting these by products also into useful fuel range hydrocarbon is a key to making this technology viable.
1.3 Catalytic de-oxygenation to fuels

1.3.1 Complete de-oxygenation

The most common type of complete de-oxygenation is removal of oxygen as water using an acid catalyst. Complete de-oxygenation of some oxygenates was studied on zeolite ZSM-5 and found that long chain oxygenates are easier to de-oxygenate than short chain hydrocarbon. Shorter chain oxygenates tend to produce coke on the catalyst. Fuhse and Bandermann [39] attempted to quantify this phenomenon using various oxygenates. They found out that after oxygen is removed as water, the left over hydrocarbon can form carbon if its C/H ratio is greater than 0.62. For example, when acetone (CH3COCH3) is dehydrated (-H2O), it results in CH3COCH. It contains 3 C and 3 H. The resultant C/H ratio is 1.0 which is greater than 0.62. Hence when acetone is reacted on H-ZSM-5, it forms coke and not any useful gasoline range products. Compounds such as acetaldehyde, acetic acid and methyl acetate have a C/H ratio greater than 0.62. As stated previously, these are the main by-products along with acetone when syngas is converted to alcohols. All primary alcohols have a C/H ratio of 0.5 Alcohols a can be converted to gasoline range hydrocarbon on H-ZSM-5 quite easily. A recent study by Gujar et al [40], showed that higher the alcohols, the better were the yields of gasoline when reacted on zeolite. This is an incentive to make higher alcohols from syngas rather than just methanol or even ethanol.

1.3.2 Partial de-oxygenation of ethanol to higher alcohols.

Ethanol could be converted to 1-butanol using well known Guerbet Chemistry [41].

\[ 2CH_3CH_2OH \rightarrow C_4H_9OH + H_2O \] (1.5)
According to this mechanism, an alcohol is first oxidized to an aldehyde. Then two molecules of aldehyde undergo aldol condensation with water removal to form an unsaturated aldehyde with double the carbon atoms as the initial alcohol. In the final step this aldehyde is reduced to an alcohol with double carbon atoms to that of the initial alcohol. This chemistry is mainly used to produce large branched alcohols and has not yet been exploited to make butanol from ethanol. Guerbet chemistry is known to occur on a variety of catalysts such as lead, tungsten, molybdenum and manganese [42]. So far there is no literature to show that titania would catalyze this reaction.

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{OH} & \rightarrow \text{CH}_2\text{CH(OH)}\text{CH}_2\text{OH} + \text{H}_2 \\
2\text{CH}_2\text{CH(OH)}\text{COH} & \rightarrow \text{CH}_2=\text{CHCH(OH)}\text{COH} + \text{H}_2\text{O} \\
\text{CH}_2=\text{CHCH(OH)}\text{COH} + 2\text{H}_2 & \rightarrow \text{C}_4\text{H}_{10}\text{OH}
\end{align*}
\]

Figure 1.5 Reaction mechanism of 1-butanol formation from ethanol using Guerbet chemistry

1.4 Titanium dioxide (Titania)

Titanium dioxide (TiO₂), generally called titania, is a strong base catalyst when suitably dehydrated and it has also shown Lewis acidity. It’s oxygen, having a lone pair of electrons which can be donated, makes it a Lewis base. Adding alkali metals like Cs, K can further increase the basicity. But oxygen deficiencies on the titania surface can cause coordinate un-saturation. These vacancies can accept a pair of electrons rendering some Lewis acidity to titania surface. This, in general, is not a property of titania but
arises due to surface defects. This dual acid base property of titania is established in literature [43]. This is of importance because the Lewis base site could catalyze aldol condensation reactions while acid sites could catalyze dehydration of ethanol to ethylene.

Titania is known to dehydrate and perform aldol type condensation reactions to convert acetone to trimethylbenzene [44]. This reaction is quite similar to Guerbet chemistry. In acetone condensation two acetones undergo aldol condensation to remove water and form mesityl oxide, a C₆ ketone. This C₆ ketone further undergoes the same reaction with acetone to form trimethylbenzene. This reaction is very similar to Guerbet chemistry since here two aldehydes condense to form an aldehyde with twice the number of carbons. Hence titania should be able to catalyze a critical step, aldol condensation, of Guerbet chemistry. This is possible due to the basic oxygen on titania which can extract a OH group from the substrate leading to dehydration.

Titania being primarily a base catalyst, generally, is not expected to coke during dehydration reactions at low temperatures (<400 °C) [45]. Also, it cannot be reduced to titanium metal, instead it loses oxygen to form sub stoichiometric titanium dioxide which can act as semi conductor [45, 46]. Hence the destruction of the catalyst is expected to be minimal. The regeneration of the catalyst, usually, is not necessary. But if required, it can be accomplished by heating the catalyst in air to remove coke formation.

1.5 Conclusion

The rising fuel demand and diminishing oil supplies call for an effective action and development of biofuels, which are sustainable and feasible, is the best way forward. Biomass (ligno-cellulosic material) conversion to fuels would not compete with food market and also would build on existing technologies. Biomass can be pyrolyzed to bio-
oil or gasified to syngas. Syngas can be converted to hydrocarbons using Fischer Tropsch technology. Converting syngas to alcohols and then converting alcohols to fuel would facilitate forming products very close to gasoline range hydrocarbon. Also, alcohols can be used as additives to gasoline or as direct fuels (in particular, higher alcohols, >C_3).

Syngas can be converted to methanol on copper based catalysts. But this is equilibrium limited. Syngas is converted to ethanol on Rh or Mo based catalytic systems[47]. This results in formation of oxygenated by products such as acetic acid, acetone, methyl acetate and acetaldehyde. These oxygenates could be converted to fuel range hydrocarbon using titanium dioxide (titania). Higher alcohols have higher heating values. Hence ethanol should be converted to 1-butanol on titania.
1.6 References


CHAPTER II

PROJECT OBJECTIVES

The broad goal of the project was to study the use of titania as catalyst to remove oxygen from syngas derived oxygenates. This could be achieved either by removing such oxygen as water and convert the oxygenate into a hydrocarbon which would be ‘complete deoxygenation’ or by converting the oxygenate into a longer hydrocarbon chain oxygenate which would be ‘partial deoxygenation. The oxygenates considered here are: ethanol, acetaldehyde, acetone, methyl acetate and acetic acid. The broad objective was realized by completing the following step-wise experimental work:

- Model compound study
  - Batch reactor studies with each of the oxygenates separately
  - Batch reactor studies with 2 oxygenates at a time to understand their interaction
  - Flow reactor studies with all 5 oxygenates in one stream

- Acetone condensation (a key reaction)
  - Effect of pressure on the reaction
  - Effect of temperature on the reaction
  - Effect of acetone flow rate on the reaction
  - Reaction kinetics
  - Effect of titania modifications on the reaction
  - Combination studies of titania and H⁺/ZSM-5
• Ethanol up-gradation to higher alcohols
  o Effect of catalyst amount in batch reactor
  o Effect of reaction times in batch reactor
  o Comparison of similar metal oxides for catalysis of this reaction
  o Flow reactor studies for the effect of pressure
  o Flow reactor studies for the effect of temperature
  o Flow reactor studies for the effect of ethanol flow rate
  o Flow reactor studies with higher alcohols as reactants
CHAPTER III
DE-OXYGENATION OF SYNGAS DERIVED OXYGENATES ON TITANIA: A QUALITATIVE ANALYSIS

3.1 Introduction

Acetone, acetic acid, methyl acetate, acetaldehyde are the major byproducts when syngas is converted to gasoline [1-2]. Conversion of these compounds to liquid hydrocarbons or other useful fuels will greatly enhance the viability of syngas to alcohols/fuels technology. Also these compounds along with ethanol are representative of the 4 major classes of oxygenates – ketones, carboxylic acids, aldehydes and alcohols. Hence acetone, acetic acid, methyl acetate, acetaldehyde and ethanol were used as model compounds to study their de-oxygenation reaction pathways, activity, and selectivity on titanium dioxide. Much research has been conducted on conversion of oxygenates to fuels on acid catalysts, in particular, zeolites. Only alcohols have proved to be amenable for this reaction. Fuhse and Bandermann showed that non-alcohol oxygenates of short carbon chain do not convert to useful hydrocarbons [3]. This result was explained in detail in the previous chapter. Titanium dioxide (Titania) in the anatase phase with its dual acid-base chemistry could be a useful catalyst to convert oxygenates to hydrocarbons. This hypothesis is explored here by performing batch reactor. Oxygenates also form a major component of pyrolysis oil from biomass. Hence, this study could help understand some of the possibilities of converting pyrolysis oil into liquid hydrocarbons.
3.2 Materials and Methods

All batch reactor studies were run in a 450 cc Parr batch reactor made of Hastelloy C. Titania was used as bought from Fisher Scientific after pelletizing into 30-50 mesh size. All the reactants were used as received from Fisher Scientific, Inc. without further purification. The catalyst pellets were placed in a catalyst basket attached to the reactor stirrer. After the reaction assembly was fixed with catalyst, the reactor was purged with Argon and the reactant was transferred into the reactor using slight vacuum (about 30 mm Hg). Hence no air was present in the reactor. All the reactions were performed at 350°C and at room atmospheric pressure. Initially each reactant was reacted separately over the catalyst. Then, binary-pair reactions were performed where 2 reactants were introduced into the reactor. This binary pairs study would help in understanding the influence of one reactant on the other. The reactor stirring was set at 200 rpm and after the reaction temperature was reached (about 60 minutes), the reaction was continued for 5 hours. After the completion of the reaction, the liquid product was analyzed using a gas chromatograph with a mass spectrometer. Only the liquid product was analyzed in this part of research as the goal was to understand the formation of liquid hydrocarbons from oxygenated compounds.

3.3 Results and Discussion

Table 2.1 shows the main components in the liquid product as analyzed by GC-MS. The component in red is the largest peak on the chromatogram other than unreacted reactant. The principal diagonal of the matrix shows experiments with single component reactants. The upper triangle matrix in the table shows the results when 2 components were reacted on the same catalyst, simultaneously. While the single component reactions followed along expected lines as per literature, the results of studying the binary pairs
showed unexpected products when compared to the single component reaction studies. This study helped us to understand the influence of one reactant on the other which most model compound studies found in literature do not take into consideration. In a possible industrial scenario when syngas is converted to alcohols, the product stream also contains oxygenated by-products. It would be cost effective to convert the stream directly into hydrocarbons rather than distill and separate compounds prior to reaction. Hence the importance of this study can be understood.

When acetone was reacted over titania it formed mesitylene (1,3,5-trimethylbenzene) as a major product. This is a well known reaction reported in literature (Equation 2.1) and it is speculated to be the result of a direct dehydration of acetone molecules in a sequence. The first step is the condensation of two acetone molecules to give a mesityl oxide intermediate, a C₆ ketone. Mesityl oxide, MO, further condenses with another acetone to form mesitylene (1,3,5 trimethyl benzene). Hence, some unreacted MO is also seen which is listed as C₆ ketone on the table. The rest of the compounds, such as phenols are side products of the reaction which are discussed by Salvapati, et al [4].

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\[ 3 \text{O} + 3 \text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_8 + 3 \text{H}_2\text{O} \]  \hspace{1cm} (3.1)

\[ 2 \text{H} + \text{O} \rightarrow \text{C}_6\text{H}_8 + \text{H}_2\text{O} \]  \hspace{1cm} (3.2)
Ethanol can be easily converted to gasoline on a catalyst showing Brønsted and Lewis acidity, such as H⁺/ZSM-5 [5]. Hence it is important that ethanol does not undergo any adverse reaction on titanium dioxide. There was only a minor conversion of ethanol on the anatase phase of titania. It resulted in the formation of 1,1, diethoxy ethane as a major compound. This compound is a diethyl acetal formed by a reaction between ethanol and acetaldehyde [6]. The acetaldehyde required for this reaction is simultaneously generated by dehydrogenation of ethanol to acetaldehyde.

\[
2 \text{CH}_3\text{OH} + \text{CH}_3\text{CH}_3 \xleftrightarrow{\text{H}^+} \text{CH}_3\text{CH}_3\text{O} + \text{H}_2\text{O} \quad (3.3)
\]

\[
\text{CH}_3\text{OH} \xrightarrow{\text{H}^+} \text{CH}_3\text{CH}_2\text{H} + \text{H}_2 \quad (3.4)
\]
<table>
<thead>
<tr>
<th>Compounds</th>
<th>ETAcetate, Butanol, C5 ketone and alcohol, cyclohexenes, xylene, toluene, phenole, TMB and sub phenols and benzenes, 1,1 diethoxyethane</th>
<th>C5 ketone, Butenal, xylene, toluene, aceto phenone, sub. benzenes, cyclohexenes, sub. phenols.</th>
<th>Mesitylene, C6 ketone, C4 HC</th>
<th>Ethyl acetate, C6 ketone, Mesitylene, Acetic acid, ET formate, cyclohexenes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Butanol, 1,1 diethoxyethane, methyl propanol, ethyl acetate</td>
<td>1,1 diethoxyethane, ET acetate, Butenal, benzene, BXT, EB, hexyl e thanoate and ethyl hexanoate.</td>
<td>ETHYL ACETATE, Acetone, 1,1 diethoxythane</td>
<td>ETHYL ACETATE, Acetic acid, Methanol, Ethylether</td>
</tr>
<tr>
<td></td>
<td>Degradation</td>
<td>Acetone, Butyaldehyde, Methylacetate, TINY amounts of BXT and other sub Benzenes</td>
<td>Very Small amount of Acetone otherwise can be considered inert</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Acetone</td>
<td>Propenyl acetate and acetone (both small amounts)</td>
<td>Acetic acid and Methanol</td>
</tr>
</tbody>
</table>

Figure 3.1 Matrix showing the reaction products of batch reactor runs when oxygenates were reacted on titania catalyst. The principal diagonal shows individual compound reactions and the upper triangular matrix shows binary pair reactions.
Acetaldehyde when reacted alone, produced a chary thick liquid which showed no components except some unreacted acetaldehyde on the chromatogram. This result has been reported as the degradation of acetaldehyde when reacted on titania [7]. But when acetaldehyde was reacted with any other oxygenate on titania, this degradation was arrested. This result will be explained in some detail later.

When acetic acid was reacted on titania, it formed acetone as a major product. The ketonization of acetic acid has been studied in detail in literature [8-11]. But the unique ability of titania is that it can both ketonize acetic acid to acetone and also catalyze acetone condensation to mesitylene. This is of importance because, acetic acid does not produce hydrocarbons on Brønsted acid zeolites traditionally used to convert alcohols to gasoline. In fact the presence of acetic acid in the stream will coke up the catalyst causing deactivation. Due to the dual acid-base nature of titania, the basic oxygen on titania can react with acetic acid forming acetone and avoiding any deactivation of the catalyst. Also, acetic acid is a component in pyrolysis product of biomass and hence bio-oil can also be treated with titania to remove acetic acid. Once an acetic acid containing stream is treated with titania, it then can be passed over zeolites to produce hydrocarbon based on the composition of the stream.

\[
2 \text{CH}_3\text{CO}_2\text{OH} \rightarrow \text{CH}_3\text{CO}_2\text{H} + \text{CO}_2 + \text{H}_2\text{O}
\]  
(3.5)

Methyl acetate when reacted on titania formed small amounts of acetic acid and methanol. This product distribution can be explained by the reaction between methyl acetate and surface bound water leading to a reverse esterification.
As stated previously, when just acetone was reacted on titania, mesitylene was the major product. But when it was mixed with ethanol, 1,1 diethoxyethane was the major product. This result shows that ethanol has a greater affinity for the titania surface than acetone. When acetone was combined with acetaldehyde, the reaction manifold of acetone to mesitylene was blocked. Instead, acetone reacted with acetaldehyde to form a \( \text{C}_5 \) ketone. Acetone seems to have a greater tendency to condense with acetaldehyde than with another acetone molecule. When acetone was reacted with acetic acid or methyl acetate, the intermediate mesityl oxide was the major product and not mesitylene.

Ethanol by itself when reacted on titania produced 1,1 diethoxyethane. Since this is a product of ethanol and acetaldehyde, acetaldehyde being formed by the dehydrogenation of ethanol; this product was reinforced when ethanol was reacted on titania with acetaldehyde. Ethanol when reacted with acetic acid on titania produced ethyl acetate, a product of esterification reaction. Ethanol when reacted with methyl acetate produced ethyl acetate as a main product. This is a two step reaction. The methyl acetate reacted with surface bound water to produce acetic acid and methanol. Then acetic acid reacted with ethanol to produce ethyl acetate.
When acetaldehyde was reacted on titania, it basically degraded. But when reacted with other compounds as explained earlier, the degradation was arrested. With ethanol, acetone and acetic acid, it formed 1,1, diethoxyethane, a C_5 ketone and acetone as major products respectively. With acetic acid, acetone being formed as a major product is a direct result of ketonization of acetic acid on titania as reported in literature. But butyraldehyde was seen as a side product which is a reaction between acetaldehyde and acetic acid. When reacted with methyl acetate on titania it was largely inert.

\[
\text{HO} + \text{H}_2\text{O} \rightarrow \text{HO} + \text{H}_2\text{O}
\]

(3.8)

Acetic acid when reacted with alcohol resulted in ester as expected. Otherwise, acetic acid ketonized to form acetone. Methyl acetate largely was neutral unless reverse-esterification reaction was possible.

The main conclusion from the above study is that the binary pair reactions are not merely the sum reaction of individual reactants on titania. Most model compound studies in the literature are performed with single compound on a particular catalyst. This may not capture the complete picture when the final goal is to react all the compounds being studied simultaneously on the catalyst in one stream. In fact when all the reactants were combined and reacted in a flow reactor, the esterification reaction between ethanol and acetic acid dominated the products. However, it should be noted that the residence time in flow reactor was in the order of few minutes while in batch reactor where binary pairs were studied, it was 5 hours. The carrier gas used in the flow reactor run was argon. Another run was made using syngas as carrier gas. No major difference in product
distribution was seen. However, the ethanol to butanol reaction seemed to have been favored in syngas flow. 1-butanol and side product of pentenone was seen on chromatogram, Figure 2.2.

3.4 Conclusion

The deoxygenation chemistry of small organic oxygenates formed as by products when syngas is converted to alcohols is studied on titania. The model compound study clearly shows that titania can be used as a catalyst for conversion of these oxygenates into useful hydrocarbon for fuel purpose. However, it should be born in mind that multiple oxygenate stream can react differently on catalyst surface than individual compounds. Hence this is needs to be taken into account while designing a final titania based catalytic system.
Figure 3.2  The chromatogram of the products when all the 5 oxygenates (acetone, acetaldehyde, ethanol, methyl acetate and acetic acid) were reacted on titania in a flow reactor at 500°C and 1000 psig pressure in (a) argon flow, (b) syngas flow of 150 cc/min. Figure C shows an overlay of (a) and (b) for comparison.
3.5 References


CHAPTER IV
LIQUID HYDROCARBON FORMATION IN HIGH-PRESSURE ACETONE
CONDENSATION ON TITANIA- H+/ZSM-5 CATALYTIC SYSTEMS

4.1 Introduction

Acetone was one of the oxygenated byproducts (OBPs) formed when syngas (CO and H₂) was reacted on Mo-based catalytic systems[1]. Converting these OBPs into fuel grade hydrocarbon can economic feasibility of syngas conversion to gasoline. Hence we decided to revisit the well-known condensation reaction of acetone to mesitylene (1,3,5-trimethylbenzene, TMB), which has been converted at low pressures (vide infra), and test it at high pressure (~70 bar) and high temperature conditions (350-500°C). These conditions were chosen because syngas conversion to mixed alcohols (or even the well-known methanol synthesis reaction) requires pressures in excess of 50 bar. Moreover, we have reported the beneficial effect of high pressure upon the alcohols-to-gasoline reaction [2]. Others also showed how higher pressures favored the conversion of i-propanol of liquid hydrocarbons over H⁺ZSM-5 vis-à-vis the conversion of methanol to liquid hydrocarbons [3]. Apart from that, we tested the acetone conversion on H⁺/ZSM-5 in conjunction with titania, which is a novel attempt. This new catalyst combination showed formation of gasoline range hydrocarbon from acetone, which suggests a new technology for converting ketones to gasoline.

Acetone when reacted on H⁺ZSM-5 showed deactivation of catalyst due to coking. As an example of this technology, consider the empirical studies reported by
They showed that an oxygen-containing, organic molecule with C/H ratio greater than 0.62, after removal of oxygen as water, results in coking of the catalyst. According to this criterion, then acetone, which has a value of 0.75, should be a candidate for reaction over the zeolite with formation of coking. Hence, we studied the possibility of using base catalysis and a combination of base and acid catalysis to make gasoline-range products from acetone. We studied the possibility of using the acetone condensation to mesitylene reaction to convert acetone into a useful gasoline range hydrocarbon. Acetone is known to convert to mesitylene using homogenous catalysts such as HCl [5-6], and H2SO4 in combination with H3PO4 [7]. Moreover, the reaction was reported to occur on solid catalysts, such as aluminosilicate, alumina and Nb2O5 [8]. In the present studies, acetone was reacted over base catalysts, such as magnesia, and Lewis acid catalysts, such as titania, and found to be useful to produce mesitylene. At higher temperatures, ca. > 475°C, titania may act as a strong Lewis base, because it can catalyze the acetic acid ketonization to acetone [9]. Acetic acid is a side product when syngas is reacted on Rh-based catalytic systems [10]. The work presented here can aid in developing a single-step conversion of acetic acid to mesitylene, and thus be a method to deoxygenate a stream containing low-molecular weight oxygenates. The well known mechanism by which acetone can be converted to mesitylene begins with (Figure 1.) [8]two molecules of acetone condensing with a removal of water molecule to form a C₆ ketone: mesityl oxide, (MO). The MO further dehydrates and combines with another acetone molecule to form mesitylene. This mechanism was confirmed in a C-13 NMR study reported by Bell and Gold [11].
4.2 Experimental

4.2.1 Materials

Acetone and titania (both Fisherbrand) were the main chemicals in the research. Titania was made into pellets of the mesh size 30-50. Magnesium Oxide (Fisherbrand), CBV 2314 NH$_4^+$/ZSM-5 (Silica/Alumina=23:14; Zeolyst) were also used in some tests. Zirconia (E101) was obtained from Magnesium Electronics, Incorporation (Marietta, GA). Hydrogen gas (Nexair) was used as a carrier gas in all the experiments. All of the NH$_4^+$/ZSM-5 used in these studies were first heated to 550°C for over 12 hrs prior to use, so as to convert it into H$^+$/ZSM-5. Titania depositions on alumina, silica and H$^+$/ZSM-5 supports were performed using the incipient wetness technique. The titania precursor is titanium(IV) bis(ammonium lactato)dihydroxide complex with the flowing structure:

\[
2\text{NH}_4^+ \begin{array}{c}
\text{O} \\
\text{OH} \\
\end{array} \begin{array}{c}
\text{O} \\
\text{C} \\
\end{array} \begin{array}{c}
\text{O} \\
\text{O} \\
\end{array} \\
\text{NH}_4^+ \\
\end{array} \text{OH}^{2-}
\]

The above complex was purchased from Sigma Aldrich as an aqueous solution, containing 14% wt. titania. The solution was added to the support, dropwise, to make a barely wet paste, mixed well and then dried at 120°C for about 5 hours and then calcined at 550°C for about 12 hours. Then the catalyst was pelletized and used. For the experiment where potassium was used as promoter on titania, a similar procedure was followed with potassium acetate as starting material to deposit K on titania.
4.2.2 Reaction system

The flow reactor was made of 316 Stainless steel with a diameter of ¼ inch and 2 feet length. 2.5 g of fresh catalyst was introduced for each run and the rest of the space of the reactor was filled with glass beads (Fisherbrand). The liquid flow was pumped separately from the carrier gas. This liquid flow was merged with gas flow and fed into the reactor. The reactor space above the catalysts bed was filled with glass beads served as a preheating zone. All the liquid analysis was performed on a GC-FID (Agilent) system with a mass spectrometer used for compound identification (Agilent 7495). HP-5MS column (Agilent) was used for chromatographic analysis of the liquid samples whereas a GS-GASPRO (Agilent) column was used for gas analysis.

There was negligible gas formation when titania was used and coke formation was not significant. Each gas product chromatogram was carefully analyzed. However,
no substantial gas formation was seen as the total gas yields were always less than 0.1% and the composition of these samples showed negligible amounts of CO, \( \text{CO}_2 \) and methane. Hence, the yields and selectivities of only liquid products was reported. The yield and selectivity were calculated based on carbon balance.

\[
\begin{align*}
\text{Conversion} &= \frac{\text{moles of acetone reacted}}{\text{moles of acetone fed}} \times 100 \\
\text{Yield} &= \frac{\text{moles of product formed} \times \text{moles of carbon in one molecule of product}}{\text{moles of acetone fed to the reactor} \times \text{moles of carbon in one molecule of acetone} (= 3)} \times 100 \\
\text{Selectivity} &= \frac{\text{moles of product formed} \times \text{moles of carbon in one molecule of product}}{\text{moles of acetone converted} \times \text{moles of carbon in one molecule of acetone} (= 3)} \times 100
\end{align*}
\]

Five main product streams were analyzed. They were: (1) Mesitylene, (2) Mesityl Oxide, (3) Isophorone, (4) Other oxygenates and (5) Higher hydrocarbon (see fig 4.2). Other oxygenates are all oxygen containing compounds in the product except isophorone,

![Figure 4.2](image_url)

**Figure 4.2** Structures of products formed when acetone was reacted on titania. (a) Mesitylene, (b) Mesityl Oxide, (c) Isophorone, (d) examples of ‘other oxygenates’ and (e) examples of ‘higher hydrocarbon’.
mesityl oxide and unreacted acetone. ‘Higher Hydrocarbon’ refers to all compounds containing only carbon and hydrogen except mesitylene. These 5 streams capture the total picture of the reaction manifolds when acetone was reacted on titania. The structures of some of these compounds are shown in fig 3.2.

4.2.3 Catalyst Characterization

Powder X-ray diffraction spectra were recorded for all of the solids used in this study. The instrument was a Rigaku Ultima III. XRD characterization was performed on titania and it was confirmed that it was the anatase phase (fig 2a). No rutile was observed in titania (compare fig 2a with fig 2b, an XRD of pure Degussa P25). These data were compared with the literature for the powder diffraction data of crystalline solids to confirm the presence of crystalline anatase and rutile phases. ZSM-5 (fig 2c) was used in protonated form. In the case of ball milled ZSM-5, it was crushed in a ball mill (Fristch Pulverisette 6 mono mill) for 10 hrs at 200 rpm. The XRD pattern showed some destruction of the zeolite structure (compare fig 2c with fig 2d). The results are discussed in detail in later sections.

The surface area of the titania was 9.5 m$^2$/g as determined by the BET method using the services of Micromeretics, Inc (Norcross, GA). The ZSM-5 samples before and after ball-milling were also examined by nitrogen adsorption using the services of Micromeretics to show surface area, total pore volume, and pore volume distribution. The manufacturer of the zirconia, MEI, reported a BET surface area of 20 m$^2$/g and a NH$_3$ temperature programmed desorption amount equaling 0.022 +/- 0.002 millimoles NH$_3$/g of solid.
4.3 Results and discussion

4.3.1 Effect of Pressure

Acetone was reacted on fixed bed titania catalyst (30-50 mesh) at a temperature of 375°C and an acetone flow rate of 1 cm\(^3\)/min. The Argon gas, which was used as carrier gas, was fed at 150 STP cm\(^3\)/min. The pressure was varied between 0, 250, 500, 1000, and 1500 psig. The conditions resulted in GHSV of \(~11000\) h\(^{-1}\) for Ar and LHSV of \(~75\) h\(^{-1}\) for acetone (calculated at atmospheric pressure and room temperature). The same catalyst bed was used for running all the five experiments. There was very little coke formation observed at the end of the runs.

When the reaction pressure was increased, the acetone conversion also increased (Fig 3.3a). But the conversion showed a small decrease between 1000 and 1500 psig. There is a considerable increase in yield of mesitylene and a decrease in yield of mesityl oxide (MO) with increasing pressure (Fig 3b). The yield of isophorone generally increases with pressure whereas that of higher hydrocarbon first decreases and then increases (fig 3.3c). The yields of Other Oxygenates were generally unchanged with increasing pressure (fig 3.3c). At high acetone conversions (achieved at high pressures), there is higher selectivity to mesitylene (fig 3.4 d). As seen from fig 3.4 (b) and (c), the trends in selectivity are quite similar to that of yields with an increase in pressure.
Figure 4.3  Graphs showing the effect of pressure on (a) acetone conversion, (b) yields of mesitylene and mesityl oxide and (c) yields of isophorone, other oxygenates and higher hydrocarbon
Figure 4.4 Graphs showing the effect of (a) acetone conversion on the selectivity of mesitylene, (b) pressure on selectivities of mesitylene and mesityl oxide and (c) selectivities of isophorone, other oxygenates and higher hydrocarbon.

4.3.2 Effect of temperature

Acetone was reacted on fixed bed titania catalyst (30/50 mesh) at a pressure of 1000 psig and acetone flow rate of 1 cm³/min. The temperature was varied between 300,
350, 400, 450 and 500°C. The conditions are similar to the previous experiments (section 3.1) except for the fact that the pressure was maintained at 1000 psig and temperature was varied.

Higher temperatures result in higher conversions (fig 3.5a). The yields of mesitylene increased with increasing temperature and there was a general decrease in yield of MO at higher temperatures (fig 3.5b). However, there is a slight increase in MO yield at 500°C, which might be due to higher reactivity as seen from higher conversion. We observed an increase in TMB selectivity and a corresponding decrease in MO selectivity (fig 3.5b). The yield of isophorone goes through a maximum at 400°C. The yields of other compounds have a slight increase with temperature (fig 3.5c). The selectivity to mesitylene seems to be unchanged with acetone conversion obtained by increasing temperature (fig 3.6a). This is because higher temperatures result in higher activity and hence the selectivity of other products increases here. The selectivity of ‘other oxygenates’ and ‘higher hydrocarbon’ increased at high temperatures resulting in an unchanged selectivity of mesitylene. Generally, the values of selectivities followed same trends as yields of the compounds (fig 3.6b,c).
Figure 4.5  Graphs showing the effect of temperature on (a) acetone conversion, (b) yields of mesitylene and mesityl oxide and (c) yields of isophorone, other oxygenates and higher hydrocarbon
Figure 4.6  Graphs showing the effect of (a) acetone conversion on the selectivity of mesitylene, (b) temperature on selectivities of mesitylene and mesityl oxide and (c) selectivities of isophorone, other oxygenates and higher hydrocarbon
4.3.3 Effect of Acetone flow rate

Acetone was reacted over a fixed bed titania catalyst (30/50 mesh) at a pressure of 1000 psig and temperature of 400°C. The liquid acetone flow rate was varied between 0.1, 0.5, 1, 1.5 and 2 cm³/min. This corresponded to LHSV of 7.55, 37, 75, 113 and 150 h⁻¹ respectively. The gas flow (Ar) was maintained at 150 STP cm³/min. The change in total volumetric flow rate corresponds to 183, 317, 484, 651 and 818 cm³/min at 1 atm and 298 K, assuming ideal gas behavior.

As expected the conversion goes up with a decrease in acetone flow (corresponding to increased residence times; fig 3.7a). The mesitylene yields increase with a decrease in acetone flow rate due to higher residence times (fig 3.7b). At very low acetone flow rates, the MO is almost completely consumed in the reaction. Isophorone yield goes through a maximum at 1 cm³/min (fig 3.7c). The yields of other compounds increase at low acetone flow rates. At high conversions, due to low residence times, mesitylene selectivity was increased (Fig 3.8a). As before, the selectivities followed similar trend as yields for all compounds (fig 3.8b and c).
Figure 4.7  Graphs showing the effect of acetone flow rate on (a) acetone conversion, (b) yields of mesitylene and mesityl oxide and (c) yields of isophorone, other oxygenates and higher hydrocarbon
Figure 4.8  Graphs showing the effect of (a) acetone conversion on the selectivity of mesitylene, (b) acetone flow rate on selectivities of mesitylene and mesityl oxide and (c) selectivities of isophorone, other oxygenates and higher hydrocarbon

Utilizing the data generated in this set of equations, the kinetics of acetone condensation reaction were studied. Three possible rate limiting steps were examined: 1)
acetone reaction to form diacetone alcohol, 2) diacetone alcohol reaction to mesityl oxide and 3) mesityl oxide reaction with acetone to form mesitylene (see fig 3.1). Each of these rate-determining steps present a variable volume scenario, where the ε value is not equal to 1. Moreover, the inlet concentration is not constant since the acetone flow rate was varied without a change in argon flow rate. Hence different rate equations with different ε values and rate equations were studied. The equations that were employed were as follows:

First order irreversible rate equation for plug flow:

\[ k \tau = (1 + \varepsilon_A) \ln \left( \frac{1}{1 - X_A} \right) - \varepsilon_A X_A \]  

(4.4)

Second order irreversible rate equation for plug flow:

\[ k \tau C_0 = 2\varepsilon_A (1 + \varepsilon_A) \ln (1 - X_A) + \varepsilon_A^2 X_A + (1 + \varepsilon_A)^2 \frac{X_A}{1 - X_A} \]  

(4.5)

First order reversible rate equation:

\[ \frac{k \tau}{X_{Ae}} = (1 + \varepsilon_A X_{Ae}) \ln \frac{X_{Ae}}{X_{Ae} - X_A} - \varepsilon_A X_A \]  

(4.6)

When due analysis was made to find the best fit, the first order kinetics with reversible rate equation had the highest $R^2$ value (0.9344) and hence the best fit (see figure 3.9). This is also reasonable from a mechanistic point of view, as the formation of
diacetone alcohol from acetone is reversible [8]. Published data suggest that the mesityl oxide itself can be converted back to diacetone alcohol [12]. The initial activation of acetone by de-protonation might be required for the reaction to occur which might be the rate limiting step. This would result in first order kinetics. The first-order rate constant can be deduced from fig 3.9 as 508.21 min$^{-1}$ from the slope of the linear fit to the data.

The data were also fit to a Langmuir Hinshelwood (LH) model. In case of surface reaction control, the LH model can be represented as follows:

$$-r_A = \frac{k_1 C_A}{1 + k_2 C_A}$$  \hspace{1cm} (4.7)

here $r_A$ is the rate of the reaction, $C_A$ is the concentration of acetone, $k_1$ is the product of rate constant and the adsorption equilibrium constant and $k_2$ is the adsorption equilibrium constant. On integration of the rate law and when modified using fractional conversion $f$, it can be represented as:

$$-(\ln(1 - f) - \frac{k_1 \tau}{C_{A0} f}) = -k_2 + \frac{k_1 \tau}{C_{A0} f}$$  \hspace{1cm} (4.8)

If the data follow LH kinetics, the above equation should result in a linear plot and both $k_1$ and $k_2$ should be positive. A plot was made of the above equation using $X$, $Y$ as shown below:

$$X = \frac{\tau}{C_{A0} f} \hspace{1cm} Y = -\frac{(\ln(1 - f))}{C_{A0} f}$$  \hspace{1cm} (4.9)
Figure 4.9  A linear fit to an kinetic data with (a) first order reversible reaction and (b) Langmuir-Hinshelwood kinetics as a basis.

the plot is shown in fig 4.9b. While the plot is linear, the intercept is 6114.3. This results in \( k_2 \) value of -6114.3. This value of the intercept is significantly different from zero so as
to be considered a positive number. As stated previously, $k_2$ has to be positive and hence
the first-order LH kinetics do not sufficiently describe the data presented in this chapter.

4.3.4 Catalyst variations

Acetone was reacted on fixed bed titania catalyst (30/50 mesh) at a pressure of
1000 psig, temperature of 375°C and acetone flow rate of 1 cm$^3$/min. Various catalytic
systems were tested using supported and promoted titania, MgO and zirconia, while all
reactions, as stated in Materials and Methods section, were run in Argon flow. A test was
also completed using a hydrogen flow with pure titania catalyst. The supported and
promoted titania catalysts were prepared by using wet impregnation method. The results
of the reactions are shown in figures 4.10 and 4.11. Pure titania was shown to be the most
active for acetone condensation reaction to mesitylene. However all other catalysts tested
were also active in some measure for this reaction (fig 4.10a). As explained in Chapter 1,
the dual, acid-base chemistry of titanium dioxide has played a crucial role in its success
as the most effective catalyst. When 5% K was added, there was considerable decrease in
the activity of titania for this reaction (fig 4.10a and b). Potassium, being a base could
have titrated the acid sites of the catalysts thus rendering just basicity for the decorated
titania catalyst. The yields of MO were almost identical irrespective of the addition of K,
but the mesitylene yield was affected (fig 4.10b). The acidic nature of the titania seems to
play a role in MO condensation with acetone to mesitylene. When titania was supported
on acidic alumina, it seems to be more active than when supported on silica. However,
both catalysts are not as active as pure titania itself (fig 4.10a). The yield of MO with
both supported titania is comparable. But the alumina-supported titania produced higher
yields of mesitylene. Titania P25 was also tested for this reaction. P25 is a trademark
titania of Degussa Corp. (now Evonik Corp) which has both anatase (80%) and rutile phases of titania. The pure titania used in the rest of the research presented here is just anatase phase. P25, though, active for this reaction, showed lower reactivity for acetone conversion to mesitylene even though it shows a higher specific surface area of 55 m$^2$/g (Manufacturer’s literature data). This suggests that only the anatase phase of titania is active for the reaction being studied here.

When titania was reacted in hydrogen flow instead of argon, the results showed decreased conversion of acetone (58 vs 22%), and decreased yields of mesitylene (27 vs 8%). In both gas flows the yield of MO is the same (fig 4.9b). These selectivity/yields over the various catalysts and reactive atmospheres can be explained by appealing to the intrinsic chemistry of the various reaction manifolds and by what is known about the surface chemistries of the solids.

Consider first the results obtained over MgO for which only mesityl oxide, isophorone, and other oxygenates were obtained in the following yields: 4%, 2% and 4%. No hydrocarbons were formed over MgO and the overall conversion of acetone was low: 5%. MgO is a base thus, we may infer that the conversion of acetone to oxygenates are catalyzed by basic sites and that the further deoxygenation to hydrocarbons requires some types of acidic sites.
Figure 4.10 Graphs showing the influence various catalytic systems on (a) acetone conversion, (b) yields and (c) selectivities of mesitylene and mesityl oxide.
Figure 4.11  Graphs showing the influence various catalytic systems on (a) yields and (b) selectivities of Isophorone, ‘other oxygenates’ and ‘higher hydrocarbon’

Titania shows both acidic and basic sites when suitably dehydrated at high temperatures to remove some of the surface water. The conversion obtained over titania was much greater than that observed over MgO, and the yields of hydrocarbons plus
mesitylene was much greater than what was observed over MgO. We know that acetone can be converted to mesitylene using strong Brønsted and Lewis acids.

Deliberate poisoning of the acid sites with the addition of 5 wt% K dramatically reduced the conversion of acetone (58% to 12%) with a change in the selectivity that favors mesityl oxide rather than mesitylene. This selective poisoning of the acid sites by K shows almost no effect upon the isophorone selectivity, a significant increase in the selectivity to other oxygenates and a significant decrease in the selectivity to higher hydrocarbons. Taken together, these comparisons between MgO, TiO₂, and 5 wt% K/TiO₂ confirm that the reaction manifolds to convert mesityl oxide and other oxygenates to hydrocarbons required acid sites.

Consider the data for the conversion of acetone over titania supported on silica (10 wt% TiO₂). If the silica shows only neutral surface sites, then we would expect that the conversion of acetone should scale with the amount of TiO₂ present in the sample. However, the observed conversion is about twice the expected value: 12% vs. 6%. Now consider the selectivities to mesitylene and mesityl oxide (39%, 8%) obtained from the TiO₂/SiO₂ catalyst which are slightly lower than what was observed for the unsupported titania: 48% and 9%. The selectivities to other products show that the isophorone pathway is only slightly lower over the supported TiO₂ (25% vs. 21%); whereas, the selectivities to other oxygenates and hydrocarbons are much higher over the mixture of titania in silica. It appears that the surface chemistry of silica is not completely neutral.

Supporting the titania on the silica has the primary effect of dispersing the titania on a higher surface area support such as silica. This simple act alone can affect the conversion of acetone in a way not predicted from the weight loading of the titania alone. It is possible that the larger than expected conversion of acetone obtained over the
supported titania may be due to the increased dispersion of the titania on the silica. Moreover, increasing the dispersion of the titania could also influence slightly the selectivity obtained as the titania species interact with the silica to form some surface species that acts differently from either titania or silica. When the titania is highly dispersed on the silica, the interfacial area of contact is increased between silica and titania. Titania is known to have Lewis acid sites whereas silica demonstrates slightly acidic Brønsted sites. When these two sites come into close physical contact, they emulate the structure known as titanium silicate. Titanium silicate shows both strong Lewis and Brønsted acid sites. Thus, we speculate that the highly dispersed titania on silica shows some stronger protic sites that are responsible for the increased yields of higher hydrocarbons.

Consider next the data for supporting titania on alumina (10 wt% TiO₂), both of which contain acid and basic sites. The alumina-supported titania shows a conversion of acetone which is about ½ that obtained over the unsupported titania (58% vs. 30%) even though the alumina shows a surface area nearly 20 times that of the unsupported titania (200 m²/g vs. 9.5 m²/g). The decreased conversion obtained on the TiO₂/Al₂O₃, being only ½, suggests that the alumina is not completely neutral. Next, consider the selectivities to mesitylene and mesityl oxide obtained over TiO₂ (48%, 9%) and alumina-supported TiO₂ (53%, 5%). These selectivities are probably about the same considering the scatter in the yield data. Now consider the selectivities to other products obtained over the two catalysts: isophorone (24%, 5%); other oxygenates (6%, 12%); and higher hydrocarbons (7%, 25%). These numbers are significantly different and confirm the increased acidity observed for the titania/alumina over the pure titania. For the reasons
just stated for titania/silica, we speculate that the dispersed titania crystallites interact with the Lewis acid sites on the alumina to make Brønsted acid sites.

Evonik markets a higher surface area titania (~55 m$^2$/g) under the moniker P25. This material shows about 10-20% rutile phase and the balance is anatase. The acetone conversion over P25 is 38% vs. 58% for the acetone conversion over anatase. These conversion values are not explained by simple adjustments for % anatase and for surface areas: $0.8 \text{ anatase} \times 55 \text{ m}^2/\text{g} / 10 \text{ m}^2/\text{g}$. To make the observed conversion coincide with the predicted value, we must include a relative reactivity factor which accounts for the decreased reactivity of the rutile phase relative to the anatase phase. This factor is $[(0.38/0.58)(10 \text{ m}^2/\text{g}/55 \text{ m}^2/\text{g})] = 0.11$ which suggests that the presence of the rutile phase decreases the overall activity of the sample to about 10% of the pure anatase phase.

The selectivity to mesitylene, mesityl oxide, and isophorone are reduced in the P25 catalyst relative to pure anatase as follows: mesitylene (48% vs. 30%), mesityl oxide (9% vs. 2%) and isophorone (24% vs. 18%). However, the selectivity to other oxygenates (6% vs. 25% and higher hydrocarbons (7% vs. 17%) were larger in the P25 catalyst. If we can attribute higher yields of hydrocarbons to increased acidity, then the P25 catalyst could be catalyzing the higher hydrocarbons due to its increased surface acidity.

Zirconia shows lower conversion of acetone (58% vs. 11%) than titania and shows a lower selectivity to mesitylene, while showing a higher selectivity to mesityl oxide. These results could not be explained by a simple difference in surface area, since surface area of the zirconia (20 m$^2$/g) was higher than the surface area of the titania (9.5 m$^2$/g). The other products, isophorone (24% vs. 36%), and other oxygenates (5% vs. 9%) showed higher selectivities than titania. Quite surprisingly, no higher hydrocarbons were
obtained by passing acetone over ZrO₂ at these conditions. These results suggest that ZrO₂ (TPD NH₃ site density = 0.022 millimoles/g) shows fewer/less acidic sites than TiO₂.

The substitution of hydrogen for Ar as a second component in the reaction atmosphere shows quite unexpected results. We may gain further insight by examining the mesityl oxide yield which is the same with and without H₂ in the gas phase (5%). This result suggests that the sites forming MO are not influenced by the presence of hydrogen in the system. The yield of mesitylene decreases from 27% to 8% with the introduction of H₂.

The mechanism for forming isophorone from mesityl oxide may be particularly illuminating towards understanding these results (Fig. 4.12). The first step in this mechanism is the abstraction of a proton from acetone to form the anion: CH₃C=OCH₂⁻. A strong Lewis base site or a Lewis acid site is required to remove the proton from acetone. This anion then adds to the mesityl oxide via a Michael addition to form the diketone anion. The negative change is stabilized by the two electron withdrawing groups, i. e, the ketones. The final step is a self, aldol condensation to close the ring ala the Robinson annulation reaction [13]. This reaction also requires a base catalyst. Given the requirements of a base for both reactions, it seems reasonable to assert that the addition of hydrogen to the system probably neutralizes the Brønsted acid sites that are required to form mesitylene from the same two reagents (MO and acetone) that are required to form isophorone.
That is:

This mechanism can explain the higher selectivity to form isophorone when H₂ is introduced into the reaction mixture by simply altering the reaction manifold to favor isophorone rather than mesitylene. In this manner, the yields of MO don’t have to change with the introduction of H₂ into the system because the main effect occurs subsequently in the catalysis!
This suggests that the first step of acetone condensation to MO is not hindered by hydrogen flow. However, the subsequent step of condensing MO with another acetone to form mesitylene is unduly influenced by hydrogen. It can be inferred from Figs 4.11 a and b that MO is further reacting to form other oxygenates without total condensation to mesitylene. The yield and selectivity of ‘other oxygenates’ in the case of hydrogen flow is higher than that of the reaction in argon flow. Magnesium oxide and zirconium dioxide, both being metal oxides, are also active for this reaction. However, under the conditions used in this research, MgO produces only Mesityl Oxide intermediate from acetone and not the final product of mesitylene. However it does produce a higher yield of ‘other oxygenate’ compared to titania which mainly includes isomer of MO (fig 3.11a). ZrO₂, on the other hand can produce mesitylene but is highly selective to isophorone (fig 4.10b). But both catalysts are not comparable to TiO₂ in terms of reactivity for acetone condensation to mesitylene. MgO and ZrO₂ did not produce any higher hydrocarbons. Titania when supported on alumina and silica produced high yields of higher hydrocarbons. P25 also showed the same response.

Titania was also studied in conjunction with zeolite, H⁺/ZSM-5 for the conversion of acetone to liquid hydrocarbon. Pure H⁺/ZSM-5, titania supported on the zeolite were tested in similar conditions as before. Also 2 beds of titania and H⁺/ZSM-5 were reacted in that order and then in reverse fashion with fresh catalysts in 2 separate reaction tests. Two and ½ (2.5) g of each catalyst bed utilized, hence double amount of catalyst was employed in these tests compared to each of the previous experiments presented in this chapter. Finally a ball milled titania and H⁺/ZSM-5 catalyst was tested. Five (5) g of this catalyst was used for this test.
These sets of reactions with H⁺/ZSM-5 produced 3 more classes of products in addition to those already discussed in this chapter. They are: ‘Lower Hydrocarbons’, which are all hydrocarbon produced with 4-6 carbons, ‘BTX’ representing Benzene, Toluene and Xylenes, EB representing Ethyl Benzene. These 3 classes of compounds were produced only if the zeolite was used in the catalytic bed in some form.

When pure H⁺/ZSM-5 was used as a catalyst there was a much higher conversion of acetone than with titania (fig 4.13a). However there was considerable coke formation on the catalyst, which caused early termination of the run due to excessive back pressures in the catalyst bed. While all the reactions were run for 1 hour, the reactions involving pure zeolite catalyst or with zeolite as first bed had to be terminated at around 30 minutes due to coke build up in the reactor leading to substantial increase in reaction pressure. However this was not the case when titania was used as first bed and the zeolite as second as the coke deposition on the zeolite was much less than when the zeolite was placed in the bed alone. This dramatic decrease in coke yields by itself proves the value of using titania in converting oxygenates to fuel range hydrocarbon.

Supporting titania (10%) on H⁺/ZSM-5 did alter some of the product distributions (fig 4.13). All the yields and selectivities of all compounds were within a range of 5% of pure ZSM-5 except of the yield of mesitylene (fig 4.11, 47%). However, the yield of coke was significantly less; (<2%). Pure H⁺/ZSM-5 produced a higher yield of mesitylene compared to a 10 % titania impregnated zeolite (17% vs. 9%). The titania-impregnated zeolite produced a much higher yield of BTX and higher hydrocarbon (fig 4.12a). By placing the TiO₂ in with the zeolite, olefin-containing intermediates, e. g., mesityl oxide, can react with other olefins or itself, to form oligomers. It is known that H⁺/ZSM-5 converts hydrocarbon oligomers into benzene derivatives very easily. It is quite
interesting that the zeolite-supported titania shows the highest yields of BTX (40%). The commercial implication of this result is high since BTX are building blocks for the petrochemical and pharmaceutical industries.

The loading of titania (10 wt%) with this zeolite having a SiO$_2$/Al$_2$O$_3$ ratio of 23 is sufficient to replace many of the protons with (TiOOH)$^+$ species if this exchange does occur. These cationic sites will demonstrate a chemistry distinctly different from the protic site in that coking will be reduced. Moreover, the metal center will show a richer variety of catalytic reactions than the proton alone. Finally, the presence of even a few zeolite protons will produce hydrocarbons from olefins owing to the very high acidity of the protons vis-à-vis the other acid sites present in the system. In the presence of the zeolite protons, isophorone and other oxygenates will be present in low yields and selectivities because of the absence of any Lewis base sites required for their formation. The presence of the titania shows a profound effect to mitigate the coke yields either on the surface of the zeolite or as a leading catalyst bed in a two-bed sequence. The high yields of coke on the zeolite arise from the processing of small molecular weigh ketones, organic acids, and aldehydes (such as acetone, etc.) over a strongly acid surface. The role of the titania is to selectively remove these active coke precursors from the reaction zone and replace them with products which do not produce coke over the strong acid sites, such as mesitylene and other hydrocarbons.

It must be mentioned that pure titania produces the highest yields of mesitylene even in this set of reactions (fig 4.13a). Among the 2 bed catalytic reactions, the yield of mesitylene is higher for the system in which titania was the first bed. This is understandable as titania is a more active catalyst for this reaction and TiO$_2$ has just the right surface acidity/basicity to catalyze mesitylene forming reactions. Mesityl oxide was
almost entirely consumed when the zeolite was used as a second bed (fig 4.13a). There was substantial BTX formation in all reactions containing H+/ZSM-5.

While BTX is an integral part of any gasoline blend, aromatics are EPA regulated and hence their minimization is ideal. This selective decrease in the BTX yields can be achieved by a ball-milled, physical mixture of titania and H+/ZSM-5 (BM). The BM catalyst yielded fewer aromatics and showed a higher selectivity to lower hydrocarbon than all other catalytic systems that were studied with the exception of the 2 bed system with H+/ZSM-5 as the first bed (fig 4.15b). But it should be recalled that this system had coking issues leading to deactivation. However, under the reaction conditions presented in this chapter, the BM catalyst was less active for the overall acetone conversion. This could be countered by an increase in the amount of catalyst used and/or decreasing the flow rate of carrier gas resulting in an increase in residence time of acetone. The peculiar behavior of BM catalyst with low conversion activity, low aromatic selectivity and relative high ‘lower hydrocarbon’ selectivity can be attributed to loss of zeolite structure due to ball milling. The XRD patterns of some of the catalysts utilized in this part of research were studied and are presented in fig 4.15. Fig 4.16 (a) shows an XRD pattern of all the titania used in this research project and it was confirmed to be in anatase phase. Fig 4.16 (b) shows an XRD pattern of P25 which had both anatase and rutile phases. The rutile phase can be concluded from the additional peaks on the pattern, in particular, a standard rutile peak can be seen at around 28°. Fig 4.16 (c) shows a standard powder, X-ray diffractogram of fresh H+/ZSM-5 zeolite with a maximum peak intensity of 245 units at 8°. However, when titania and the zeolite where ball milled, the maximum peak intensity reduced to 121 units at 26° as can be seen on Fig 4.16 (d). This phenomenon is further investigated and shown on fig 4.15. The standard XRD pattern of H+/ZSM-5 is
Figure 4.13 Influence of various catalytic systems involving H⁺/ZSM-5 on (a) acetone conversion, (b) yields and (c) selectivities of mesitylene and mesityl oxide.
shown in Fig 4.17 (a) which is same as fig 4.16 (c). The maximum peak on this pattern, as mentioned previously, is of 245 units at 8°. Fig 4.17 (b) shows a XRD pattern of the same zeolite but after ball milling it for 5 hours. The same peak at 8° has a reduced intensity of 150 units. Fig 4.17 (c) shows a XRD pattern of the same zeolite again after further ball milling of 5 hours. This results in an effective ball milling of 10 hours. The peak intensity at 8° has further fallen to 102 units. This progressive reduction in peak intensity with increased ball milling of the zeolite clearly indicates a degradation of the structure with ball milling. This phenomenon was further investigated by studying the pore structure of the zeolite. Fig 4.18 (a) shows a study of differential pore volume as a function of pore width for a fresh zeolite H+/ZSM-5. This study was obtained from the services of Micromeritics Inc. The fresh zeolite has a maximum pore volume of 1.8 cm³/g at a pore width of 5 Å. Fig 4.18 (b) shows the same study performed for the same zeolite, which was ball milled for 10 hours. The maximum pore volume at the same pore width has reduced drastically to 0.95 cm³/g. This is a final and certain proof for the destruction of zeolite structure by ball milling. This phenomenon has been confirmed by a different set of studies in published literature [14]. This phenomenon could be exploited to engineer the reaction products.

4.4 Conclusion

Higher temperatures and pressures favor acetone condensation to mesitylene on titania. High acetone conversions in general, yield higher amounts of mesitylene. Low acetone flow rates resulting in high residence times also favor the acetone conversation to mesitylene. Pure titania is the best catalyst to convert acetone to mesitylene as compared to all the other catalysts tested in this project. A study of the promoted and supported
titania’s suggests that the dual acid-base nature of titania is central for this behavior. Zirconium dioxide also shows activity for acetone condensation to mesitylene *albeit* not at the same level as titania. Magnesium oxide also can catalyze acetone condensation to mesityl oxide but with a smaller conversion of acetone than what could be obtained over titania at the same conditions. Mesitylene formation was not seen on MgO at the conditions studied in this project suggesting that both acid and base sites could be used for its synthesis. Reacting acetone on catalysts with titania in conjunction with the zeolite H⁺/ZSM-5 produced more “lower hydrocarbons” and fewer amounts of aromatics which make a good gasoline blend. A physical mixture of titania and ZSM-5 will result in good selectivities of non aromatic hydrocarbon and limited aromatics. The special nature of ball milled zeolite arises from the partial destruction of the zeolite structure due to the ball milling activity.

Fitting the kinetic data by the integrated rate analysis method showed that the reversible, first order rate equation was a possible rate law to explain these data. Implicit in this equation, is that the rate-determining step is a first order process. With this result in mind we propose to add to the mechanism described in the literature the following steps:

Activation of the acetone:

\[
\text{Acetone} \Leftrightarrow \text{Propene-2-ol}
\]

- **CH₂CO-CH₃ over base**
- **CH₃CO-CH₃ over protic site**
Both of these species have been published as active intermediates in the catalysis of acetone to mesityl oxide then to isophorone over a base and acetone to mesityl oxide and then to mesitylene over a protic catalyst. Mesityl oxide is a common intermediate over both types of sites: acidic and basic. Thus, we see MO among the reaction products of catalysts having either type of site. Raju, et al. (Appl Catal. A: General (2000), 193, 123-128) showed that isophorone can decompose to form mesityl oxide and acetone over a silica-supported chromia. Moreover, these products can react to form mesitylene. With this reverse reaction step involving MO/acetone and isophorone, we can explain how the zirconia catalyst can produce isophorone in high yields as well as producing small amounts of mesitylene. Therefore, we incorporate this reverse reaction between isophorone and mesitylene/acetone into the existing reaction mechanism involving the same intermediates.

Propagation of acetone with intermediates:

A strong acid catalyst such as ZSM-5 is not an appropriate agent to convert small molecular weight acids, aldehydes and ketones as coke is formed in high yields and these high coke yields can develop operability problems in a fixed bed flow reactor. We established here a simple solution to this problem that does not compromise the reactivity
of the zeolite nor add much to the reactor volume: add a small titania bed upstream of the zeolite so as to convert the low molecular weight organic acids, aldehydes, and ketones. The products of this combination of two fixed catalyst beds are beneficial to the fuels and petrochemical industries.
Figure 4.14 Graphs showing the influence various catalytic systems involving $\text{H}^+/$ZSM-5 on (a) yields and (b) selectivities of Isophorone, ‘other oxygenates’ and ‘higher hydrocarbon’
Figure 4.15 Graphs showing the influence various catalytic systems involving H^{+}/ZSM-5 on (a) yields and (b) selectivities of ‘lower hydrocarbon’, BTX and Ethyl Benzene.
Figure 4.16  XRD patterns of (a) Titania used in this project, (b) Titania P25, (c) fresh H⁺/ZSM-5 and (d) ball milled mixture of Titania and H⁺/ZSM-5
Figure 4.17  XRD Patterns of H⁺/ZSM-5 which are (a) fresh, (b) ball milled for 5 hours and (c) ball milled for 10 hours
Figure 4.18  Pore volume study of H\(^+\)/ZSM-5 samples as a function of pore width which are (a) fresh and (b) ball milled for 10 hours
4.5 References


CONVERSION OF ETHANOL TO 1-BUTANOL AND OTHER HIGHER ALCOHOLS

5.1 Introduction

Ethanol has been used as a transportation fuel for quite some time now. It has been widely used as a gasoline blend and in some cases as a stand-alone fuel. However, the ethanol heating value of 29.7 MJ/Kg is much lower than that of gasoline, 46.5 MJ/Kg [1]. This difference in heating values has been discussed in detail in section 1.2a of chapter 1 (see table 1.1). However, higher alcohols (butanol and higher) have much higher heating values and hence closer to the heating values of gasoline. Hence these alcohols will make a better blend with gasoline in terms of heating value and also can be better fuels by themselves than ethanol. The conversion of alcohols to gasoline range hydrocarbon on the zeolite H+/ZSM-5 is a well known technology [2]. A recent study has shown that higher alcohols give higher yields of such hydrocarbon on this zeolite [3]. Hence the conversion of ethanol to higher alcohols holds much commercial value.

As explained in Chapter 1, ethanol and 1-butanol can be manufactured by fermentation but it is a slow process. Ethanol can be produced catalytically from syngas using Rhodium or molybdenum based catalytic systems [4-5]. There is no known procedure directly to make substantial yields of pure 1-butanol from syngas directly. Hence producing ethanol first from syngas and then converting it to butanol and even higher alcohols is a good proposition. The syngas itself can be produced by the gasification process using either coal or biomass as the feedstock. If biomass is used as a
starting material, the higher alcohols eventually produced from this process can be considered as part of renewable fuels.

Not much literature is available on the conversion of ethanol to butanols or any other higher alcohols. Nduo and others have studied the use of magnesium oxide based catalytic systems for dimerization of ethanol to 1-butanol [6]. While this effort was largely successful giving excellent yield of ~ 20% butanol, there are some limitations on this process. These limitations are: 1. There is no higher alcohols formation greater than that of butanol and hence this process cannot be used to produce even higher alcohols. 2. The reactions were performed at 1 atm pressure which is an obstacle for integration with alcohols conversion to gasoline technology which requires high pressure. Also this process uses very low flow rate of 10 cc/min of N₂ gas for 0.5 g of catalyst which places enormous constraint on large scale productivity for commercialization. The space velocity using magnesia bulk density of 3.58 g/cc amounts to 71 min⁻¹. This is very slow. Hence it would take very large amount of catalyst to maintain an industrial scale production making it very expensive. Hence a different route is investigated for conversion of ethanol to 1-butanol using other metal oxides.
Figure 5.1 Free energy of reaction is shown as a function of temperature. All values are negative suggesting thermodynamic feasibility.

5.2 Reaction Mechanisms

Before the results of the experiments are considered, the possible mechanisms are presented here. Three main mechanisms can be considered for the conversion of ethanol to butanol. The first mechanism to be considered is the direct condensation of 2 ethanol molecules to 1-butanol. That is:

\[
\text{OH} \quad \rightarrow \quad \text{OH} + \text{H}_2\text{O} \quad \text{(5.1)}
\]

This mechanism is envisaged as a surface bound ethanol directly condensing with a gas phase ethanol to form 1-butanol. This does not involve any formation of stable intermediate and hence can be considered as a 1-step reaction. This reaction is thermodynamically feasible and the free energies are shown as a function of temperature.
in figure 5.1. The free energy of reaction is well below zero and the conversions are not equilibrium limited.

The next mechanism to be considered is the reaction of ethanol with ethylene to form 1-butanol. It is well known that ethanol can be dehydrated to form ethylene on acid catalysts. Titania has a dual acid-base nature as explained in chapter 1. This leads to ethanol dehydration to form ethylene as will be discussed in results section of this chapter. Zirconia that was used in this project is reported to have an acidity of 0.022 mmol/g as calculated by NH₃ TPD performed by its manufacturer MEL chemicals [7]. With this slight acidity zirconia too can dehydrate ethanol to ethylene. Hence the possibility that is being explored is the reaction between this ethylene and ethanol to form 1-butanol. This is can be represented as follows:

$$\text{CH}_2\text{OH} + \rightleftharpoons \text{CH}_2\text{CH}_2\text{OH} + \text{H}_2\text{O}$$

(5.2)

The free energy of reaction for this mechanism is negative up to 600 K and slightly positive thereafter (fig 5.2). Hence the reaction is equilibrium limited at high temperatures (fig 5.3). However, at high pressures the fall in equilibrium conversion is not drastic and at a temperature of 800K and pressure of 70 atm, 58% conversion can be achieved.

The third mechanism to be considered is from the Guerbet chemistry [8-9]. This chemistry comprises of a reaction between an aldehyde and an alcohol to form a longer chain alcohol. The aldehyde itself can be formed by dehydrogenation of alcohol. While there is no literature support this reaction on titania or zirconia, this cannot be ruled out
from a pure chemistry point of view. The Guerbet chemistry in case of ethanol can be represented as below:

\[
\text{H}_2\text{O} + \text{O} + \text{H} + \text{H}_2 \rightarrow \text{OH} + \text{H}_2\text{O} + \text{H}_2\text{O}
\] (5.3)

Figure 5.2  Free energy of reaction is shown as a function of temperature for ethanol reaction with ethylene to form 1-butanol
Figure 5.3  Equilibrium ethanol conversion is shown as a function of temperature for ethanol reaction with ethylene to form 1-butanol

Figure 5.4  Free energies of reaction are shown as a function of temperature for the formation of 1-butanol via Guerbet chemistry
Equilibrium ethanol conversion is shown as a function of temperature for the formation of 1-butanol via Guerbet chemistry.

Acetaldehyde and hydrogen in the above reaction can be formed by a dehydrogenation step of ethanol. The free energy of reaction is negative up to high temperatures closer to 900K (fig 5.4). The reaction is equilibrium limited at high temperatures (fig 5.5). However, as in the previous case, at high pressures considerable ethanol conversion can be achieved. Even at 900 K, if pressure is increased to 70 atm, 71% ethanol conversion can be achieved.

5.3 Materials and Methods

Titania was used as purchased from Fisher Scientific Inc. after pelletizing to 30/50 mesh size. It has a surface area of 9.5 m²/g. A highly acidic form of titania called titanic acid, TiO(OH)₂, was used in some tests which was procured from BASF catalysts through Pacific Northwest National Laboratory. Zirconia was procured from MEL.
Chemicals Ltd. It has a surface area of 20 m$^2$/g and shows an acid site density of 0.022 millimoles/g as determined by NH$_3$ desorption. The heat of adsorption was titrated using NH$_3$ and found to be 130 kJ/mol. This site energy is lower than what has been established for a very strong acid such as H$^+$/ZSM-5 at 150 kJ/mol. Ethanol and other alcohols (1- & 2-propanol, 1-butanol) reacted on the catalysts were used as purchased from Sigma Aldrich. All of the analyses was performed using Gas chromatograph (GC) with Mass spectrometer (MS) and Flame ionization detectors (FID). MS was used for product identification and FID for product quantification. Agilent DB-WAX column was used for liquid analysis and GS-GASPRO column was used for gas analysis.

5.3.1 Batch reactor screening tests

Initial screening tests were performed in a batch reactor from Parr Instruments. It is made of Hastalloy C and has a volume of 450 cc. The reactor stirrer is fixed with a catalyst basket for placing the catalyst. 10 grams of ethanol was reacted with 1 g of catalyst in most cases unless specified. Reactions were performed at 350°C and 1 atm initial pressure. Before the reactant was introduced into the reactor the reactor was purged using an inert gas. Then the reactant was introduced via vacuum so that no air is present in the reactor.

5.3.2 Flow reactor studies.

A flow reactor system purchased from Parr instruments was utilized for these reactions. It is fitted with a ¼” stainless steel reactor, electric oven, mass flow controllers from Brook Instruments, a liquid pump and a temperature control system.

The catalyst bed was placed at the center of the reactor tube and glass beads were placed on either side of the catalyst bed to fill up the reactor. The reactor tube was sealed...
at both ends with glass wool. Argon with a flow rate of 150 cc/min was used as a carrier gas in all reactions. The temperature was measured at the center of the reactor and controlled using thermocouples on the outside wall of the reactor. The reaction products were condensed using an ethylene glycol-water mixture as a coolant through a jacketed condenser operated at \(-5^\circ C\). All of the system was maintained under pressure as necessary using a back pressure regulator. The gas flows were measured using a soap bubble flow meter at the end of the system.

5.4 Results and Discussion

All yields and selectivities were calculated on carbon basis. The following formulae were used for the calculation of conversion, yield and selectivities:

\[
Conversion = \frac{\text{moles of ethanol reacted}}{\text{moles of ethanol fed}} \times 100 \quad (5.4)
\]

\[
Selectivity = \frac{\text{moles of product formed} \times \text{moles of carbon in one molecule of product}}{\text{moles of acetone converted} \times \text{moles of carbon in one molecule of ethanol} (= 2)} \times 100 \quad (5.5)
\]

\[
Yield = \frac{\text{moles of product formed} \times \text{moles of carbon in one molecule of product}}{\text{moles of acetone fed to the reactor} \times \text{moles of carbon in one molecule of ethanol} (= 2)} \times 100 \quad (5.6)
\]

5.4.1 Batch reactor studies

Batch reactor runs were performed at 350$^\circ$C and 1 atm pressure using 1 g of titanic acid catalyst. Three main parameters were tested. They are: reactant to catalyst ratio, reaction time and catalysts. Apart from 1-butanol, the other compounds that were seen in the products are: CO, CO$_2$, methane, hydrocarbon of C$_2$ – C$_5$ chain length and ethers. Ethylene was a major product in almost all cases. However, for the screening test results, only the butanol yields will be discussed.
The first parameter to be studied was reactant to catalyst ratio. This ratio was varied by keeping the reactant constant and varying the amount of titanic acid catalyst used. At low reactant to catalyst ratios, a higher ethanol conversion is observed (fig 5.6a). The same trend was observed in the yields of 1-butanol (fig 5.6b). Higher concentration of catalyst compared to the reactant has a beneficial effect on the reaction. This also produced high amount of olefin hydrocarbon. This result might suggest a dissociation of alcohols to form olefins. This is an important issue that will be considered throughout this chapter.
Figure 5.6 The effect of reactant to catalyst ratio on (a) ethanol conversion and (b) yield of 1-butanol

The next parameter to be studied was reaction time. Batch reactor studies were performed using 20 g of reactant and 1 g of titanic acid catalyst at 350°C and 1 atm pressure for varying reaction times. Long reaction times, as expected, resulted in higher
ethanol conversions (fig 5.7a). However, the yields of 1-butanol continuously decreased with an increase in reaction time (fig 5.7b). An increase in reaction time resulted in a continuous increase in the yields of C₂, C₃ and C₄ hydrocarbon which mainly comprise of olefins and ethane. This again suggests a degradation of 1-butanol formed resulting in lower hydrocarbon. Rigorous reaction conditions whether due to high catalyst concentration or long reaction times seem to destroy the alcohol formed to produce light hydrocarbon. Next, 3 different catalysts were tested and compared to the results obtained on titanic acid. These catalysts are: titania, zirconia and alumina. The reaction conditions are a temperature of 350°C and 1 atm pressure. One gram (1 g) of catalyst was used with 20 g of ethanol as reactant. The reaction was run at 350°C for 5 h. Alumina showed the highest ethanol conversion among all the catalysts (fig 5.8a). However, the reaction products were from direct dehydration of ethanol. Over 40% yield of ethylene was realized. Alumina was the only catalyst among those tested that did not result in any butanol (fig 5.8b) formation. Titania demonstrated a behavior similar to that of titanic acid. Titania produced slightly higher conversion of ethanol but resulted in mildly lower butanol yields. Titania produced slightly higher ether yields compared to titanic acid. Other than this, the trend was similar to each other. Zirconia produces
Figure 5.7  The effect of temperature on (a) ethanol conversion and (b) yield of 1-butanol on titanic acid
lower conversion than titanic acid. However, it resulted in highest yields of 1-butanol (over 3.5%) among all the 4 catalysts that were tested. Low conversion but higher butanol
yields means zirconia can produce butanol with a higher selectivity. Hence it is chosen as a catalyst to perform more studies in flow reactor.

5.4.2 Flow reactor studies

All flow reactor studies were performed in 150 cc/min of argon gas flow. Ethanol was pumped at 1 cc/min unless it is the variable being studied. 2.5 g of zirconia is used as a catalyst for all the reactions. The yields and selectivities in almost all cases have similar trends and hence graphs for only yields are presented here. Selectivity can be inferred from yield and conversion data using the following equation:

$$Selectivity = \frac{Conversion}{Yield}$$

5.4.2.1 Effect of Temperature

In these studies, Pressure was maintained at 1 atm and temperature was varied between 350, 400, 450 and 500°C. Higher temperatures resulted in higher ethanol conversion (fig 5.9). Higher temperatures also favored higher yields of 1-butanol (fig 5.10a). One interesting feature of zirconia as a catalyst for this reaction is that it formed not just 1-butanol but also even higher alcohols of C$_5$-C$_8$ carbon chain length. The effect of temperature on ‘all alcohols’ is shown in fig 5.10b. All alcohols refer to all the alcohols formed in the reaction including 1-butanol. At lower temperatures, 1-butanol was the only alcohol to be formed, while at higher temperatures there were some higher alcohols formed. The high reactivity at high temperatures is expected as the reaction rate increases with temperature. Some ‘other oxygenates’ species were formed which included all oxygenates except alcohols (fig 5.10b). Their yields also increased with an increase in temperature. There was a significant increase in yield of ethylene with an
increase in temperature (fig 5.11a). This fact suggests that zirconia can catalyze the dehydration of ethanol to ethylene. At high temperature there was increase in the formation of ‘other olefins’ (fig 5.11b). This is significant as this might suggest that a higher butanol yield might be achieved in the reaction but this butanol, once formed, might be consumed by a dehydration reaction to butene. This reaction is represented as follows:

\[
\text{HOCH}_2CH\text{CH}_2OH \rightarrow \text{CH}_2\text{CH}==\text{CH}_2 + \text{H}_2\text{O}
\]  
(5.8)

The above reaction was studied using thermodynamics to analyze the equilibrium ethanol conversion at various temperatures, pressures and ratio of initial water to butanol concentration (represented as M) (fig 5.12). This reaction is clearly heavily favored by equilibrium thermodynamics at high temperatures. In fact at low pressures this reaction is significant even at low temperatures. High water concentrations considerably limit this reaction at low temperatures due to the reverse reaction to hydrate ethylene. However, at high temperatures, this reaction is inevitably favored which explains the formation of olefins at such conditions. There was some CO\textsubscript{2} formation at high temperatures (fig 5.11b). The bottom line from this part of the study is that at 500\degree C, highest possible yields of 1-butanol and other higher alcohols can be achieved even after sacrificing some of them to dehydration reactions.
5.4.2.2 Effect of ethanol flow rate

These set of reactions were performed at 500°C and all other conditions as stated previously. The acetone flow rate was varied between 0.5, 1 and 1.5 cc/min while holding the argon flow rate constant at 150 cc/min. There was considerable increase in ethanol conversion at 0.5 cc/min but the conversion was same at 1 cc/min and 1.5 cc/min (fig 5.13). The yield of butanol is at a maximum at a flow rate of 1 cc/min compared to the other flow rates (fig 5.14a). At low flow rates (high residence times), there is a significant increase in ethylene yields (fig 5.15a). Also other olefins and CO₂ yields substantially increase at such flow rates (fig 5.15b). This another confirmation of the destruction of alcohols formed to olefins under rigorous conditions. Long reaction times in batch reactor studies also showed a higher olefin formation and lower butanol formation. The ‘all alcohol’ and ‘other oxygenate’ formation followed the same trend as that if butanol with a peak yield at 1 cc/min flow rate of ethanol (fig 5.14b). There was a slightly higher yield
of ethylene and CO$_2$ at 1.5 cc/min flow rate as compared to 1 cc/min. Over the entire 1 cc/min ethanol flow rate seem to be productive of higher alcohol formation from ethanol.

Figure 5.10  Effect of temperature on (a) ethanol yield and (b) yield of ‘all alcohols’ and ‘other oxygenates’
Figure 5.11  Effect of temperature on (a) ethylene yield and (b) yield of ‘other olefins’ and \( \text{CO}_2 \)
Figure 5.12  Analysis of butanol dehydration to olefins

Figure 5.13  Effect of ethanol flow rate on its conversion.
5.4.2.3 Effect of Pressure

For this set of reactions, the conditions were maintained at a temperature of 500°C, ethanol flow rate of 1 cc/min, argon flow rate of 150 cc/min. The pressure was varied between 0, 250, 500, 750 and 1000 PSig. Two and one-half grams (2.5 g) of zirconia was used as a catalyst, as before. Higher pressures favor the ethanol conversion (fig 5.16). Generally, the yields of 1-butanol also increased with pressure (fig 5.17a). However, there was a small maximum at '500 PSig. ‘All alcohols’ also followed the same trend (fig 5.17b). The yields of ethylene also increased with pressure (fig 5.18a). There was a slight maximum at 250 Psig. Other olefins continuously had higher yields with increase in pressure (fig 5.18b). This again points to the dissociative nature of 1-butanol and other higher alcohols under these rigorous conditions. The yields of the other oxygenates’, generally, increased with increase in pressure. Higher pressures also resulted in higher yields of CO₂ (fig 5.18b). One interesting behavior of the reaction at high pressures is the formation of aromatic hydrocarbon. This mixture of aromatic hydrocarbons includes benzene, toluene, xylene and styrene. The yield of aromatic hydrocarbon was at a peak at 750 PSig (fig 5.17b). There was some yield seen at 1000 PSig as well. The zirconia used here, as stated before, was purchased from Magnesium Electronics, Limited (MEL chemical Ltd). The manufacturer reported an acid concentration as 0.022 mmol/g obtained by NH₃ TPD of this catalyst. Hence this slight acidity might be resulting in the formation of aromatics at high pressures where the adsorption is enhanced. Overall, high pressures favor the ethanol conversion to higher alcohols. In fact 1000 PSig pressure and 500°C temperature with 1 cc/min ethanol flow seem to comprise a set of optimum conditions for this reaction. This is important because these conditions are instrumental in facilitating the integration of ethanol-to-higher
Figure 5.14  Effect of Ethanol flow rate on (a) ethanol yield and (b) yield of ‘all alcohols’ and ‘other oxygenates’
Figure 5.15 Effect of Ethanol flow rate on (a) ethylene yield and (b) yield of ‘other olefins’ and CO₂
alcohol technology with syngas-to-ethanol technologies. Syngas to ethanol reactions typically need high pressured around 1000 PSI and temperature around 300°C. The ethanol conversion temperature discussed here being 500°C, is higher than syngas conversion temperature and hence the product stream must be heated before passed on to the zirconia catalyst bed. However, the reactor system pressure need not be changed. The gas chromatograms of the product when the reaction was conducted at the optimum conditions of 500°C and 1000 PSI are shown in fig 5.19, fig 5.20 and fig 5.21. Figure 5.19 represents the gas phase products and figures 5.20 and 5.21 represent the liquid products. The chromatograms are taken from a flame ionization detector. Formation of olefins including ethylene can be seen on fig 5.19. CO₂ cannot be seen on an FID signal and hence it was calculated from a thermal conductivity detector signal. Figure 5.20
Figure 5.17  Effect of Pressure on (a) ethanol yield and (b) yield of ‘all alcohols’, ‘other oxygenates’ and aromatic hydrocarbon
Figure 5.18  Effect of Pressure on (a) ethylene yield and (b) yield of 'other olefins' and CO₂
Figure 5.19  GC-FID chromatogram of gas products from reaction of ethanol on zirconia catalyst at 500°C, 1000 PSI, 1 cc/min of ethanol flow and 150 cc/min of Ar flow

Figure 5.20  GC-FID chromatogram of liquid products in organic phase from the reaction of ethanol on zirconia catalyst at 500°C, 1000 PSI, 1 cc/min of ethanol flow and 150 cc/min of Ar flow
represents the organic phase of the liquid product. The formation of liquid olefins, 1-butanol and oxygenate (2-pentanone) can be seen on the chromatogram. Figure 5.21 represents aqueous phase of liquid product and a range of alcohols from C₄ to C₆ can be seen here. Some other oxygenates can be seen as well. Tetrahydrofuran was used as an internal standard and that can seen as represented by THF(IS). The overall conclusion from this part of the study is that high temperatures and pressures favor the ethanol conversion to higher alcohols on zirconia catalyst. However, some butanol and perhaps other higher alcohols are being consumed in dehydration reactions. But zirconia can unequivocally be used as a catalyst for conversion of ethanol to higher hydrocarbon.
Figure 5.22 GC-FID chromatogram of liquid products from the reaction of 1-propanol on zirconia catalyst at 500°C, 1000 PSI, 1cc/min of 1-propanol flow and 150 cc/min of Ar flow

Figure 5.23 GC-FID chromatogram of liquid products from the reaction of 2-propanol on zirconia catalyst at 500°C, 1000 PSI, 1cc/min of 2-propanol flow and 150 cc/min of Ar flow
5.4.2.4 Other alcohol reactions on zirconia

To understand better the higher alcohol formation from ethanol, a few other alcohols were reacted on zirconia at 1000 PSI pressure and 500°C. The alcohol flow rate was maintained at 1 cc/min and argon flow rate at 150 cc/min. Two and one-half grams (2.5 g) of zirconia was used as a catalyst. 1-propanol, 2-propanol and 1-butanol were reacted in this system to study the alcohol he formation of olefins without higher alcohol formation suggests that they can be formed not just by dehydration of alcohols but also by oligomerization reactions of lower molecular weight olefins, e. g., ethylene. Also, such diverse olefins were not seen when ethanol was reacted in spite of substantial ethylene formation. This suggests that propene is much more reactive than ethylene on zirconia. Propene could oligomerize into hexadienes and substituted pentenes. The olefin products suggest that acid sites, present on the surface, are responsible for the dehydration, oligomerization, ether-forming reactions and dehydrogenation reactions.
Decyk, et al. [10], showed how strong acid sites formation. 1-propanol resulted in no other alcohol formation (fig 5.22). There were many olefins formed including dienes such as 2,4- hexadiene, some primary and tertiary pentenes formed, and propene. present in H+/ZSM-5 catalyzed the dehydration of 1-propanol and 2-propanol in substantial conversions (~40%) to olefins and ethers.

In stark contrast to these results, 2-propanol was virtually unreactive on zirconia (fig 5.23). There was some acetone formed which might be because of a keto-enol tautomerism of 2-propanol and acetone. There might have been small amount of 2-propenol formed in the reaction or as a contaminant. But the quantities are negligible. There is a very small amount of propene formed. This suggests that for an alcohol to be reactive on this zirconia, it needs a primary hydroxyl group. The secondary hydroxyl group of 2-propanol rendered the alcohol unreactive. 2-propanol is a useful probe molecule to characterize a surface for acid and base sites. The major products for acid catalysis is propene and di-isopropyl ether; whereas, base sites yields acetone as the major product. Given these literature data, it seems reasonable that base sites are active for the conversion of 2-propanol to acetone. Moreover, the acid sites present apparently show insufficient acid strength to catalyze the olefins and ethers that have been observed for the same reaction over H+/ZSM-5 [10].

1-butanol was an interesting reaction where it substantially converted to 2-propanol (fig 5.24). As in the previous case, since 2-propanol is unreactive, the reaction manifold closed there. When 1- and 2-butanol were passed over a strong solid acid such as H+/ZSM-5, the observed products were olefins and ethers. While the zirconia of this study did show some acid sites which were capable of dehydrating ethanol and 1-propanol to the corresponding olefins and ethers, it appears that those acid sites are not
responsible for the yields observed here for 1-butanol: 2-propanol! Since acid-catalyzed chemistry is not a suitable explanation, we must look for another reaction mechanism.

The only mechanism that can be envisaged for such a butanol conversion is where the 1-butanol lost –CH₂ groups to form ethylene. The reaction is represented below.

\[
\begin{align*}
2 \quad \text{OH} & \quad \rightarrow \quad 2 \quad \text{OH} \quad + \quad \equiv \\
(5.9)
\end{align*}
\]

This reaction can proceed well at high temperatures. A graph of equilibrium conversion of 1-butanol at 70 atm pressure is shown below in fig 5.25. The substantial formation of 2-propanol shows that the equilibrium favors high conversion of 1-butanol. This again proves that the primary hydroxyl group is thermodynamically feasible on this surface. The most important lesson out this part of the work is that higher alcohols (propanol or 1-butanol) do not self condense to form even higher alcohols on zirconia. Hence the formation of higher alcohols such as pentanols, hexanols, etc cannot be attributed to secondary reactions of propanols and butanols. A different set of explanations need to be considered to explain the formation of higher alcohols.
The first such explanation to be considered is one which involved activated ethanol. Since ethanol is very reactive on this surface it would be reasonable to regard it as a key player in forming higher alcohols. Ethanol could be activated by dehydration and then bound by the surface. This surface bound ethanol could then react with a gas phase 1-butanol or propanol to form respective higher alcohols. This mechanism could be extended for other alcohols to react with surface bound ethanol; one example of this mechanism is represented below:

\[
\text{CH}_3\text{CH}_2\text{OH} + \text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + \text{H}_2\text{O}
\] (5.10)

The next possible mechanism of higher alcohol formation is based on oligomerization of olefins. As shown previously, ethanol can be dehydrated to form ethylene. In fact 1-propanol was also dehydrated to form relevant olefins. These olefins could then
oligomerize to form larger olefins which can then hydrate to form higher alcohols. Based on the results of 1-propanol reaction on zirconia, there is no doubt that oligomerization of olefins can occur on zirconia and hence confirmation for this mechanism. An example of 1-hexanol formation from this mechanism is shown below:

\[
\begin{align*}
\text{OH} & \quad \rightarrow \quad \text{+ H}_2\text{O} \\
\text{3} & \quad \rightarrow \quad \text{H}_2\text{O} \\
\text{+ H}_2\text{O} & \quad \rightarrow \quad \text{OH}
\end{align*}
\] 

\[5.11\]

5.5 Conclusion

Higher alcohols have higher heating values than that content for lower alcohols and hence their production is of commercial value. While titania is active for 1-butanol formation from ethanol, zirconia is a much better catalyst for this reaction. 1-butanol can be formed by direct condensation of ethanol, a reaction between ethanol and ethylene or by Guerbet chemistry. All three mechanisms are probable and could even simultaneously occur. High temperatures and pressures generally favor 1-butanol formation but there is also a risk that the alcohols formed are dehydrated to olefins in these conditions. Zirconia can not only form 1-butanol but also even higher alcohols. Propanol and butanol do not further react on zirconia to form even higher alcohols. So higher alcohols are formed either by a reaction between ethanol and intermediate alcohols such as propanol and butanol or by hydration of olefins. There is a possibility that olefins are hydrated to alcohols and alcohols are dehydrated to olefins in a dynamic equilibrium in the conditions tested in this chapter. 1-propanol when reacted on zirconia formed propene and oligomerized olefins. 1-butanol formed 2-propanol on zirconia, most probably, by
elimination of $-\text{CH}_2$ groups as ethylene. There is thermodynamic evidence for this mechanism. 2-propanol was virtually unreactive on this catalyst suggesting that a primary hydroxyl group is a requirement for reaction on zirconia.
5.6 References


CHAPTER VI
CONCLUSION

6.1 General Conclusions

The main objective of the work was to analyze the deoxygenation catalysis on titania. This work was initiated by a batch reactor, single model compound study and then a binary model compound study. Acetone conversion to mesitylene is a crucial reaction among the deoxygenation chemistries. Since acetone conversion results in coke formation on strong acid catalysts, another conversion route was necessary to produce fuel range hydrocarbons in an economically-feasible fashion. Also, acetic acid is considered to be the most potent, coke-forming oxygenate and acetic acid can easily be converted to acetone on titania. Hence studying acetone conversion to mesitylene and other hydrocarbon would assist in disposing off both acetone and acetic acid in a technological-viable manner.

The mechanism of mesitylene formation from acetone was studied using promoted and supported titania. Acetone conversion to gasoline and not just mesitylene was studied by a catalytic system combining both titania and a Bronsted/Lewis acid, such as a zeolite. Ethanol can easily be converted to gasoline using H+/ZSM-5 and hence it need not be de-oxygenated on titania. However, during the course of study, it was found that using titania, ethanol can be converted to 1-butanol. While this is not total de-oxygenation, it can be considered partial de-oxygenation as one oxygen is removed as water out of every two ethanol molecules that were converted. The main incentive to
make higher alcohols from ethanol is that higher alcohols have higher heating value than lower ones. Hence higher alcohols can be a better fuel additive than ethanol. These higher alcohols can even be directly used as a fuel. Higher alcohols produce greater yields of gasoline when reacted on H⁺/ZSM-5 catalyst. In the course of study, it was found that zirconia is a much better catalyst for ethanol conversion to butanol. Zirconia produced not only just 1-butanol but even higher alcohols from ethanol. The mechanism for the formation of such alcohols was also investigated.

The model compound study on titania showed that acetone can be converted to mesitylene, acetic acid to acetone, ethanol to 1,1-diethoxyethane, acetaldehyde to degradation products and methyl acetate to acetic acid. There were some other compounds formed as well. The binary compound study revealed reactions between the oxygenates and possibly their reaction intermediates. The binary pair reactions were not merely the sum of individual reactions. Hence it is important to include oxygenate interactions in any such model compound studies. Acetone condensation to mesitylene reaction is highly favored at high temperatures and pressures. This reaction follows a first order reversible kinetics. The dual acid-base catalyst nature of titania was crucial in catalyzing this reaction. MgO and zirconia also catalyze this reaction but with lesser success. Zeolite H⁺/ZSM-5 produces aromatics but also high amount of coke when used alone for reacting acetone. However, adding titania to it substantially reduces coke formation. Ball milled titania and H⁺/ZSM-5 showed lower acetone conversion and high non-aromatic hydrocarbon formation. This result is attributed to the partial destruction of zeolite structure which was confirmed by XRD and pore volume studies. Ethanol was initially reacted on a highly acid form of titania called titanic acid to form 1-butanol. While high catalyst concentration and long reaction time resulted in high ethanol
conversion, rigorous conditions also meant that the butanol formed could react further to form olefins. Among the catalysts tested, it was found that zirconia gave highest yields of 1-butanol. Also, zirconia formed even higher alcohols than titania at various conditions. Higher pressure and temperatures, generally favored the reaction. 1-propanol, 2-propanol and 1-butanol were reacted on zirconia in separate experiments to understand better the mechanism of higher alcohol formation. These alcohols did not form higher alcohols; suggesting a different mechanism for higher alcohol formation. However, the results showed that primary alcohols are very reactive on zirconia but secondary alcohols are apparently much less reactive. This result may be used to infer something about the reaction mechanism. If the mechanism were protonation to form carbenium ions, then one might expect that the secondary alcohol to be more reactive than the primary one, which is contrary to what was observed. Accordingly, we conclude that the primary route to alcohol conversion does not use carbenium ion intermediates. This observation does not rule out completely the participation of carbenium ions in a secondary pathway. The higher alcohol formation was envisaged as a reaction between ethanol and an intermediate alcohol or by hydration of oligomerized olefins.

A process flow sheet for conversion of syngas to hydrocarbon is shown in fig 5.1. The technologies shown in the green box with dotted line are those which were developed in this project. Syngas can be first converted to a mixture of ethanol and oxygenates using Rh/Mo based catalytic systems. The ensuing liquid product line is separated into ethanol and other oxygenates. Ethanol can be converted into gasoline on H⁺/ZSM-5 catalyst or can be routed to a zirconia catalyst to upgrade into higher alcohols. Higher alcohols can be used as fuels themselves, or as fuel additives. Alternatively, they can be routed to the H⁺/ZSM-5 catalyst to be converted to gasoline with better yields than
with ethanol. The oxygenates coming from the first separator are fed into a reactor with titania catalyst. Here they are deoxygenated into gasoline range hydrocarbon. This hydrocarbon can be blend with gasoline or used as a fuel.

6.2 Engineering Significance

A cost analysis was performed to understand the commercial value of converting the oxygenates to hydrocarbon instead of separating them and selling as individual products. The cost of syngas is estimated to be $0.15/kg. By a material balance using the data that we have reported here and provided to us by researchers at PNNL, we estimate that 1 kg of syngas can produce 80 g of ethanol, 90 g of acetic acid, 60 g of acetaldehyde, 80 g of methyl acetate and 60 g of acetone and the rest water. The total amount of organic compounds is equal to 370 g. This 370 g of organic compounds cost $0.15/kg to manufacture taking into account only the raw material cost. Ethanol cost is $0.58/kg, acetic acid is that of $0.40/kg, acetaldehyde is at $0.82/kg, methyl acetate is $0.15/kg and acetone at $0.45/kg. On an average the market value of the stream would be $0.22/kg (table 6.1). This would yield $0.07/kg profit not counting the production costs of the oxygenates and separation costs. While the production cost is just operating a packed bed reactor and could safely be assumed to be less than the profit margin of $0.06/kg; distillation on the other hand is an expensive operation. Particularly on this case the oxygenates are mixed with water with the possibility of forming azeotropes. If extractive distillation is employed, the cost would further increase. Hence distillation and separation of the oxygenates is definitely not a good pathway. Next, the value of the product is calculated if the oxygenates are converted to hydrocarbon. The numerical values are taken from the acetone conversion to hydrocarbon on TiO$_2$/H$^+$-ZSM-5. In this case
conversion of acetone was 90% and hydrocarbon yield was 80.1%. The value of the hydrocarbon was estimated by two methods to confirm accuracy (table 6.2). In method I, the value of the hydrocarbon is estimated based on an approximate gasoline cost of $3.00/gal. In method II, the product values are estimated separately for 4 classes of compounds. They are: mesitylene ($2.60/kg), BTX (based on toluene price of $0.82/kg), Ethyl benzene ($1.00/kg) and ‘other hydrocarbon’ (based on hexane price of $0.98/kg). The method I yielded a product value of $0.23 and method II yielded a product value of $0.22. These values are very close and hence the hydrocarbon value can safely be assumed to be $0.22-0.23 on the basis of 1 kg of syngas feed at $0.15 (table 6.2). The gross profit would be $0.7 – 0.8/kg. This profit margin is very close to that of mixed oxygenate stream ($0.7/kg) without converting to hydrocarbon. However, as stated previously, the cost of separating the oxygenates from each other and from water is very expensive. On the other hand, if they are converted to hydrocarbon, the hydrocarbon phase can be separated from aqueous phase by decantation. The aqueous phase containing the unreacted oxygenates and water can be recycled back to the reactor.
6.3 Future work needed

It was shown in this work that binary pair of oxygenates had a different reaction products to single compound studies. Hence a more detailed interaction study needs to be made with several oxygenated reacted simultaneously at various reaction conditions. Mixed oxygenate streams need to be reacted on modified titania (promoted and supported) catalysts to optimize both the conditions and the catalyst for deoxygenation. In this project, the crucial reaction of acetone conversion to gasoline was studied. Similar analysis need to be made for methyl acetate, acetaldehyde and acetic acid on titania. Acetic acid can be converted to acetone on titania and acetone can be converted to
hydrocarbon on the same catalyst. Hence a one-step conversion of acetic acid to hydrocarbon through acetone intermediate can be studied on a titania based catalytic system. Ethanol was converted to 1-butanol and some other higher alcohols in this study. This should be probed further to see if very high yield of higher alcohols exclusively can be obtained by modifying the catalyst. Lastly, the deoxygenation catalysis in this project was confined to the oxygenated byproducts formed in syngas to alcohol reactions. This study can be extended to the oxygenates formed in pyrolysis of biomass.

Table 6.1  Estimation of the oxygenate product value from syngas

<table>
<thead>
<tr>
<th>Basis</th>
<th>1 kg synthesis gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>cost</td>
<td>$0.15</td>
</tr>
<tr>
<td>Products</td>
<td>g value/kg syngas</td>
</tr>
<tr>
<td>EtOH</td>
<td>80 $0.58 $0.05</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>90 $0.40 $0.04</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>60 $0.82 $0.05</td>
</tr>
<tr>
<td>Methyl acetate</td>
<td>80 $0.82 $0.07</td>
</tr>
<tr>
<td>Acetone</td>
<td>60 $0.45 $0.03</td>
</tr>
<tr>
<td>Total</td>
<td>370 $0.22</td>
</tr>
<tr>
<td>Profit</td>
<td></td>
</tr>
</tbody>
</table>

Table 6.2  Estimation of hydrocarbon product value from oxygenates

<table>
<thead>
<tr>
<th>Method I</th>
<th>Method II</th>
</tr>
</thead>
<tbody>
<tr>
<td>Based on Gasoline cost</td>
<td>Based on direct petrochemicals value</td>
</tr>
<tr>
<td>FW acetone</td>
<td>g-mol formed</td>
</tr>
<tr>
<td>Basis</td>
<td>0.37 kg acetone</td>
</tr>
<tr>
<td>Conversion</td>
<td>90.00%</td>
</tr>
<tr>
<td>Moles of Acetone</td>
<td>6.37931 g-mol</td>
</tr>
<tr>
<td>Yield of HC</td>
<td>0.801</td>
</tr>
<tr>
<td>g mol of acetone yielding HC</td>
<td>5.109828 g-mol</td>
</tr>
<tr>
<td>g mol of HC</td>
<td>1.703276</td>
</tr>
<tr>
<td>g mol of HC</td>
<td>204.3931</td>
</tr>
<tr>
<td>g mol of HC</td>
<td>3.00 gal</td>
</tr>
<tr>
<td>g mol of HC</td>
<td>6.0 lb/gal</td>
</tr>
<tr>
<td>g mol of HC</td>
<td>0.450205 lb</td>
</tr>
<tr>
<td>g mol of HC</td>
<td>$0.23 value of products</td>
</tr>
</tbody>
</table>
APPENDIX A

REACTOR SET UP
A.1 Batch Reactor System

The batch reactor made of Hastelloy C with a capacity of 450 cc was purchased from Parr Instruments company (figure A.1). The reactor stirrer is fitted with catalyst basket to place the catalyst pellets inside. The reactor stirrer is also fitted with coolant water connection to keep it from overheating the motor. The reactor is fitted with a temperature controller and a pressure transducer. The reactor has purge gas inlets and outlets to purge it with inert gas before a reaction. It also has a liquid connection arrangement using a septum where a liquid bottle was connected via a needle and vacuum was applied to the system to suck the liquid in. The reactor can be heated to a temperature of about 370°C and can be pressurized to 3000 PSI. The reactor has a pressure rupture disc for safety.

A.2 Flow reactor system

The reactor itself is a ¼” stainless steel tube with thermocouple at the centre to note the temperature (figure A.2). The reactor is heated with an electric oven. The reactor is connected to the gas cylinder via mass flow controller and valve system. Up stream of the reactor is fitted with a pressure transducer for online monitoring of pressure as well as a analog pressure meter. The reactor gas line is connected to a liquid pump with a 1/16” stainless steel tube to a T-junction. The reactor is fitted with a pressure relief valve for safety. Down stream of the reactor is fitted with a condenser and a collection vessel, both of which are maintained at -5°C using a mixture of ethylene glycol and water. Finally a back pressure regulator is connected for maintaining the pressure. The reactor can be heated to 600°C and pressurized to 1500 PSI.
Figure A.1  Schematic of batch reactor system used in this project

Figure A.2  Schematic of flow reactor system used in this project
APPENDIX B

CALIBRATIONS
All product analysis was performed using Gas chromatography (GC). Mass spectrometer (MS) was used for product detection. Flame ionization detector (FID) was used for most product detection and quantification. Thermal conductivity detector (TCD) was used to detect and quantify CO₂. GS-GASPRO (Agilent) column was used for all gas analysis. Liquid analysis was performed by HP-5MS (Agilent) column for the research presented in chapters 2 & 3 and DB-WAX column (Agilent) was used in the analysis for the research presented in chapter 4. An internal standard (IS) was used in all liquid analysis. 1-propanol was used in acetone condensation reactions and tetrahydro furan (THF) was used in ethanol conversion reactions as an IS. For calibration, a standard solution with analyte was made and 5% IS was added to it. It was run in the GC and the area ratio of analyte was calculated. This was performed for various concentrations of analyte keeping the IS concentration constant. The weight ratios of analyte and IS were calculated and plotted against their respective area ratios. Then an equation (usually linear) was fit to this data. This gives the calibration curve. An example calibration curve for 1-butanol is shown in fig B.1.

Figure B.1 Sample Calibration curve for 1-butanol