Characterization and Catalytic Properties of Sulfated Zirconia

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CHARACTERIZATION AND CATALYTIC PROPERTIES OF SULFATED ZIRCONIA

A Thesis

Presented to

the Faculty of the Department of Chemistry

Western Kentucky University

Bowling Green, Kentucky

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

by

Melody Bi

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CHARACTERIZATION AND CATALYTIC PROPERTIES OF SULFATED ZIRCONIA

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Melody Bi
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Sulfated zirconia has attracted extensive attention due to its superactivity to isomerize alkane and alkenes. Platinum or iron/manganese promoted sulfated zirconia has been shown to increase the reaction rate. These catalysts are normally activated to 650-725°C in air before use. Through on-line analysis of evolved gas species during dynamic heating of the catalysts, some significant information can be obtained concerning the activation mechanism. In the present investigation, combined TG-FTIR, TG-MS and TG-DTA techniques were utilized to measure the weight loss of the samples, analyze the evolved gas species and to monitor the phase transformation temperature of the solid. Four samples [(1%) 5% Pt/\text{SO}_4^{2-}/\text{ZrO}_2, 2% Fe/0.5% Mn (iron(III)nitrate, maganese(II) nitrate treated/iron(III) sulfate, maganese(II) sulfate treated)/\text{SO}_4^{2-}/\text{ZrO}_2] were studied by thermal analysis. Also, the catalytic activity of 0.4% Pt/\text{SO}_4^{2-}/\text{ZrO}_2 was evaluated the isomerization and oligomerization of 1-hexene. It was found that this type of catalyst has high catalytic activity even at ambient and subambient temperatures.
1. INTRODUCTION

Under the pressure of worldwide trend towards more severe environmental legislation the refining industry has started to produce cleaner fuels. In order to maintain a high octane number while avoiding lead additives and aromatic octane boosters because of their toxicity, gasoline is reformulated to include more branched alkanes as well as oxygenates. The specific aim in catalytic reforming is to produce a product whose research octane number lies between 87 and 95. There are four routes by which this aim can be met:

a. increase the concentration of aromatics;

b. increase the concentration of iso-paraffins and decrease their molecular weight;

c. increase the concentration of olefins;

d. decrease the overall molecular weight.

In this regard, superacid catalysts have attracted attention for a number of industrial chemical reactions such as isomerization, oligomerization, cracking and hydrocracking. Intense research interest in terms of preparation and characterization has been focused on these superacid catalysts. Superacids are considered to have an acidity stronger than 100% H$_2$SO$_4$, i.e., exhibiting a Hammett acidity function ($H_0$) greater than -12.$^{1,2}$ They can be prepared using several approaches:$^3$

1. liquid superacids supported on suitable carriers;
Among these, the solid superacid catalysts have attracted industrial as well as academic interest recently, owing to their several advantages over other types of catalysts. First of all, they are easy to separate from the reaction mixtures. Secondly, they may decrease or eliminate corrosion of the reactor and the release of corrosive products from the reactor, thus satisfying both process economics and environmental regulations. Thirdly and the most important, they have high activity at low temperatures, which permits operation where thermodynamic equilibrium compositions contain a high fraction of the desired isoalkane and/or isoalkene components which have high octane ratings. Moreover, these isoalkanes are much less toxic compared with other organic octane boosters. Unlike homogeneous catalysts, which are dispersed at the molecular level, solid heterogeneous catalysts may be fabricated into appropriate shapes with suitable physical properties, with the result that there may be many stages in their manufacture. They are, however, convenient to use on a large scale, and they are used in almost all the major catalytic processes.

The recent breakthrough in the chemistry of catalysis by nonzeolitic solid superacids is related, in particular, to the problem of activation and utilization of paraffins as well as to new applications of superacids for the productions of fine chemicals. In this respect metal oxides (ZrO₂, Fe₂O₃, TiO₂, SnO₂, etc.) modified by sulfate anions have been shown to be the most promising superacidic catalysts for the low-temperature processes.
of isomerization, alkylation, and cracking of paraffins.\textsuperscript{4,5} Brønsted acid sites are assumed to play a decisive role in these reactions. Their strength has often been determined by titration in the presence of Hammett indicators.\textsuperscript{6} The existence of both Brønsted and Lewis acid sites on sulfated catalysts has also been confirmed by IR spectra of adsorbed pyridine.\textsuperscript{7} However, the information about the nature and particular properties of acid centers of different types is rather limited.

Among these solid oxides, zirconium oxide (ZrO\textsubscript{2}) is a very interesting material because of its thermal stability, its mechanical properties and the fact that it is claimed to be the only solid oxide catalyst which has acidic, basic, oxidizing and reducing properties.\textsuperscript{8} Zirconia exhibits three different crystalline isomorphs: monoclinic, stable at temperatures below 1373K; tetragonal, stable between 1373K and 2173K; and cubic, stable above 2173K. Nevertheless, the tetragonal and cubic forms can be generated and maintained as metastable structures at much lower temperatures than those mentioned above.\textsuperscript{9} Tanabe and Hattori’s discovery of the superacidic properties of sulfuric acid treated zirconium oxide (ZrO\textsubscript{2}/SO\textsubscript{4}\textsuperscript{2−}), the acidity of which was estimated to be as high as $H_0 = -14.5$ by the adsorbed Hammett base technique, has given a new impulse to solid superacid catalysis.\textsuperscript{10} It was first reported in 1979 by Hino and coworkers as a catalyst for the room temperature isomerization of n-butane.\textsuperscript{11} Sulfate-promoted zirconia has also been shown to be active for a number of other reactions including cracking, alkylation, and esterification.\textsuperscript{6}

ZrO\textsubscript{2} is a very weak acid material, inactive for the n-butane isomerization reaction. The SO\textsubscript{4}\textsuperscript{2−} addition promotes its acidity, so that SO\textsubscript{4}\textsuperscript{2−}/ZrO\textsubscript{2} is a superacid. It is able to catalyze the isomerization of short linear alkanes at relatively low temperatures (below
150°C). Even though it is accepted that the presence of sulfate species with covalent S=O bonds on the oxide surface is necessary to obtain superacidity, the exact nature of the catalytically active sites remains an open question in the literature. It has been suggested that due to the inductive effect that the S=O groups produces, the Lewis acidity of the Zr cations is markedly increased by electronic deficiency.\textsuperscript{12} However, there are also claims that the catalytic activity derives mainly, or completely, from protonic (Brønsted) acid sites. Some have suggested that the Lewis and Brønsted sites generated from adsorbed water molecules are responsible for the catalytic activity.\textsuperscript{6,13,14} These Brønsted sites are easily interconverted to Lewis sites by evacuation at temperatures above 150°C. Consequently, the preparation and activation conditions of the SO\textsubscript{4}\textsuperscript{2-}/ZrO\textsubscript{2} superacids greatly influence the catalytic properties of the material for the isomerization reaction.\textsuperscript{6,13-15} Also, the addition of the sulfate ion gives zirconia a higher stability, producing an increase in the temperature of the amorphous phase organization as well as in the stability of the t-phase that is produced.\textsuperscript{16,17} Comelli and coworkers concluded that the catalytic activity of SO\textsubscript{4}\textsuperscript{2-}/ZrO\textsubscript{2} for n-butane isomerization is higher in the region where the Lewis acidity is higher. They also indicate the SO\textsubscript{4}\textsuperscript{2-} presence is necessary to generate the strong acid sites, but it is not sufficient to give catalytic activity.\textsuperscript{18}

In fact, the SO\textsubscript{4}\textsuperscript{2-} addition should be done to the amorphous Zr(OH)\textsubscript{4}. In this case, after calcination, the tetragonal structure is always obtained. The catalytic activity is independent of the precursor salt and of the Zr(OH)\textsubscript{4} preparation method.\textsuperscript{19} It has been reported that the transition of hydrous zirconia from the amorphous state to a crystalline state was affected by the adsorption of sulfate anions on the surface of zirconia.\textsuperscript{20,21} Scurrell suggested that the presence of sulfate anions somehow inhibits the
recrystallization of ZrO$_2$\textsuperscript{22} and the sulfated zirconia catalysts retain a much greater fraction of the initial surface area than the unsulfated catalysts. Chokkaram and coworkers found that the tetragonal to monoclinic phase transformation of zirconia is triggered by oxygen, on the cooling rather than on the heating cycle.\textsuperscript{23} They also indicated that the sulfate is adsorbed at the sites that adsorb oxygen and thereby inhibits the tetragonal to monoclinic phase transformation.\textsuperscript{24}

Sulfated zirconia catalysts have been tested for various reactions, based upon their strong acidity. When the reaction is carried out in the presence of hydrogen, the addition of a metallic phase to SO$_4^{2-}$/ZrO$_2$, e.g., Pt, will theoretically enable:

a. the reaction to take place via a bifunctional mechanism, a chemical path with less stringent acid strength requirements;

b. activated hydrogen to be produced over the metal, a species known to inhibit the formation of cake precursors which deactivate the catalyst.

The presence of noble metal crystallites in sulfated zirconia superacid catalysts is believed to greatly enhance the activity/stability,\textsuperscript{25,26} although this is subject to debate. Platinum is one of the noble metals widely utilized for this purpose. However, the state of platinum in this type of platinum impregnated zirconia catalysts is still a matter of controversy. Commonly, these catalysts are activated at temperatures in the region of 600-725°C in air prior to use as catalysts for various reactions. Several opposing views have been postulated for the role of platinum. Wender and coworkers suggested a bifunctional role for platinum.\textsuperscript{26} However, Ebitani and coworkers suggested that the promoting effect of hydrogen was due to the generation of the strong protonic acid sites, via., hydrogen dissociation, followed by spillover and proton formation.\textsuperscript{27,28} Recently,
Ebitani and coworkers showed that Pt/SO_{4}^{2-}/ZrO_{2} catalyst pretreated with hydrogen at 350°C scarcely chemisorbed CO molecules and that in the presence of sulfate ions platinum remained essentially in an oxidized state after reduction in hydrogen at 400°C. Ebitani and coworkers have also suggested that the unique properties of the Pt/SO_{4}^{2-}/ZrO_{2} catalyst could arise from the fact that a large fraction of the platinum remains in the form of PtO and PtS, and the metallic fraction is low. Sayari and coworkers, however, reported that metallic platinum was present after activation of this catalyst at 600°C in air. XRD data confirm that metallic Pt is present following the heating of a Pt/SO_{4}^{2-}/ZrO_{2} sample at 725°C. Therefore, it was suggested that the evolution of SO_{2} in air from the Pt/SO_{4}^{2-}/ZrO_{2} generated some reducing species, which in turn converted ionic platinum to its metallic state. It is also reported the effect of sulfur species on the state of Pt was two-fold:

a. they decreased the interactions between platinum oxide and the support, thus leading to large particles which easily decompose into large metallic Pt particles that resist reoxidation in air;

b. sulfur dioxide produced by decomposition of sulfate ion plays the role of a reducing agent.

Platinum supported on SO_{4}^{2-}/ZrO_{2} has the same activity as SO_{4}^{2-}/ZrO_{2}, but the stability is increased. The hydroisomerization and hydrocracking of n-hexadecane were studied using a sulfate zirconia catalyst containing 0.5 wt % Pt. The conversions were made using both batch microautoclaves and continuous trickle bed reactors. Various process conditions were studied in both reactors using a reaction temperature of 150°C. Hexadecane conversions varied from 5 to 96 wt %, depending on the process conditions.
At lower conversions (<5 wt %), isomerization products accounted for most of the total conversion, while at higher conversions (>80%), cracking products accounted for most of the total conversion.

Water or carbonaceous deposits, which decrease the Lewis acidity, were found to produce catalyst deactivation. Keogh and coworkers reported that the activity measurements, defined by hexadecane conversions, showed that at a ratio of approximately 0.5 mol H\textsubscript{2}O absorbed per sulfate molecule, the water was functioning as a complete poison.\textsuperscript{35} A carbonaceous deposit that is produced by polymerization on the active Lewis sites can also cause catalyst deactivation. The catalytic activity is recovered by burning off this deposit.

Recently, another class of solid superacid catalysts has spurred research interests. Sulfated zirconia oxide containing Fe and Mn have been shown to be active for the skeletal isomerization of n-butane at room temperature, even at very low n-butane partial pressures.\textsuperscript{36-39} Kinetic results indicated that this class of catalysts was about three orders of magnitude more active than a sulfated ZrO\textsubscript{2}.\textsuperscript{37,38} Fe and Mn promoted zirconia has been referred to as the most strongly acidic nonhalide solid acid.\textsuperscript{40} Lin and coworkers, using a series of adsorbates based on substituted benzene, demonstrated that there were much stronger acid sites in Fe/Mn/\textsubscript{2}SO\textsubscript{4}/ZrO\textsubscript{2} catalysts than are found in the sulfated ZrO\textsubscript{2} catalyst.\textsuperscript{38} However, deactivation is rapid compared with platinum promoted sulfated zirconia.\textsuperscript{36} Jatia and coworkers recently published results for the isomerization of n-butane to iso-butane at room temperature which were in good agreement with those of Hsu and coworkers.\textsuperscript{38-40}
The activation of these catalysts involves complex chemical changes. Chemical processes at the surface or in the solid state are often characterized by a distribution of activation energies, and it then becomes possible to characterize successive stages by studying the process at successively increasing temperatures. Thermal analysis methods may be used with two different objectives. On the one hand, the reaction temperature profile may be used qualitatively to fingerprint a given system. On the other hand, thermal programming methods can often yield a great deal of valuable information about the nature of chemical processes occurring with a catalyst, and thus be of great value for catalyst characterization.

In the present investigation, various combinations of instrumentation were utilized to investigate the activation mechanism of the catalysts. The combination of a thermogravimetric analyzer (TG) interfaced with a Fourier transform infrared spectrometer (FTIR), or a mass spectrometer (MS) are available. Thermogravimetric analysis involves heating a sample over a set temperature range and measuring the mass loss. FTIR spectroscopy involves exposing a sample to infrared radiation. The absorption of specific wavelengths of radiation by a molecule results in rotational and vibrational movement of the molecule. These absorptions produce peaks on an intensity versus wavelength scale, which are characteristic of the particular vibrations and rotations. A mass spectrometer measures the ions produced in its ionizing chamber and subsequently separated according to their mass-to-charge ratio by the ion accelerator/separation component of the system. Both FTIR and mass spectrometry were used to identify the evolved gas species during dynamic heating which covers the activation temperature range of the catalyst samples. They provide information complementing one another. Mass spectrometry has a lower
detection limit for HCl; it can also identify gas species such as oxygen, nitrogen, etc., which cannot be identified by FTIR. On the other hand, FTIR can help to identify different species which have the same molecular weight. Therefore, a combined TG-MS and TG-FTIR can investigate the weight loss and monitor the chemical compounds that evolve under controlled heating in different environments. Also, a simultaneous TG-DTA is used to investigate the phase transformation of the solid. These thermal analyses techniques can help us get some insight into the chemical changes during catalyst activation.

In considering the worth of a catalyst, four factors are normally identified as being the most important. These are: 1) activity, 2) selectivity, 3) life and 4) cost. The object of catalyst testing in the laboratory is to define one or more of the first three of these criteria. Usually one of these factors will be dominant in determining the potential of a catalyst for a particular application. The testing of a catalyst for activity may imply a range of experiments varying widely in the degree of sophistication of both the experimental equipment employed and the interpretation of information obtained. While there is the intuitive notion of activity as some function of the overall conversion rate, a number of possibilities exist which include the following:

1. conversion achieved at a given reaction temperature;
2. the temperature required to achieve a given degree of conversion;
3. the overall reaction rate at given conditions, and;
4. kinetic parameters derived from experimental studies of the system.

Various experiments have been carried out to define the catalytic activity of sulfated zirconia; however, most of them were conducted using 1-butene, which is a gas
at room temperature. In the present case, 1-hexene, whose boiling point is 46.3°C, was used for the isomerization reaction at room temperature. A series of runs were conducted to study the following effects:

1. effect of stirring;
2. effect of moisture influence;
3. optimum feed-to-catalyst ratio;
4. effect of temperature influence and activation energy;
5. selection of isomer products.

A gas chromatograph was utilized to identify the products. Gas chromatography involves injecting a sample into a heated separation column and measuring the retention times of the species as they separate. Comparing the retention times and percentages of the species to those for standards run under the same conditions allows for species analysis. The purpose of the GC analysis is the quantitative determination of the amounts of the several hexene isomers associated with each sample.
II. EXPERIMENTAL

Zirconia was prepared by rapid precipitation from a 0.3 M solution prepared from anhydrous ZrCl$_4$ with an excess amount of NH$_4$OH to produce a final pH of 10.5. The resulting precipitate was washed thoroughly with deionized water until a negative test was obtained for the presence of chloride ions in the wash. The dried hydroxide gel was sulfated by immersing the powder in 0.5 M H$_2$SO$_4$ and stirring for 2 hours. The precipitate was collected by filtration without further washing, and dried. Pt/SO$_4^{2-}$/ZrO$_2$ was obtained by impregnating sulfated zirconia powders with an aqueous solution of H$_2$PtCl$_6$. The Fe/Mn promoted sulfated zirconia were prepared by dissolving appropriate amounts of Fe(III) and Mn(II) nitrate/sulfate salts in the amount of water needed to prepare a catalyst containing the desired amount of Fe and Mn using an incipient wetness impregnation technique. All catalysts, after impregnation, were dried at 120°C overnight and stored in a desiccator until used for thermal analysis. The samples, thus prepared, used in the present analysis include 1% platinum promoted sulfated zirconia (1% Pt/So$_4^{2-}$/ZrO$_2$), 5% platinum promoted sulfated zirconia (5% Pt/So$_4^{2-}$/ZrO$_2$), iron and manganese nitrate salt treated sulfated zirconia (2% Fe/0.5% Mn (nitrate)/So$_4^{2-}$/ZrO$_2$) and iron and manganese sulfate salt treated sulfated zirconia (2% Fe/0.5% Mn (sulfate)/So$_4^{2-}$/ZrO$_2$).

The samples were analyzed with a DuPont TG 2950 instrument which was coupled to a VG ThermoLab Mass Spectrometer (Figure 1). The TG 2950 measures the amount and rate of weight change in a material, either as a function of increasing temperature, or
Figure 1. Simultaneous TG/MS analytical system.
isothermally as a function of time, in a controlled atmosphere. It can be used to characterize any material that exhibits a weight change and to detect phase changes due to decomposition, oxidation, or dehydration. The mass spectrometer allows the determination of multiple gas components in the mass range of 1-300 amu. It has a specially designed flexible capillary tube with a fused silica liner, which is heated to 170°C to avoid condensation of evolved gases. It requires 60 milliseconds for gas transfer from the TGA to the MS. The mass spectrometer has a Nier type enclosed ion source, a triple mass filter, and two detectors (a Faraday cup and a secondary emission multiplier). The TG-MS system has an operating temperature range to 900°C. Data from the mass spectrometer were acquired using a log histogram mode scan (LHG) in which the intensities of all peaks in a specified mass range were monitored and stored repeatedly during the temperature program. A data conversion program was used to display the intensities of the desired ions as a function of temperature. The runs were conducted separately in a purge gas of helium or air at a flow rate of 50 mL/min. Heating rates were 20°C/min.

The samples were also analyzed using a DuPont TG 951 instrument which was coupled to a Perkin Elmer 1650 FTIR spectrometer (Figure 2). The TG 951 is coupled to an FTIR using an insulated teflon tube heated to a temperature of 150°C by a powerstat variable autotransformer. The gas cell (25 cm x 10 cm) with KBr windows used with the FTIR is heated using a Barnant thermocouple controller to prevent condensation within the tubing or gas cell. FTIR scans were obtained 9 times for 53.0 sec. so that the change in the concentration of a species in the gas stream can be followed and displayed using either time or temperature scales. The Pt-SO$_4^{2-}$-ZrO$_2$ samples were also analyzed in a TA
Figure 2. Simultaneous TG/FTIR analytical system.
SDT 2960 instrument, which is an analysis module that is capable of performing both thermogravimetric analysis (TGA) and differential thermal analysis (DTA) at the same time in a temperature range from room temperature to 1500°C in a controlled atmosphere. While the physical measurement of weight loss is obtained by TGA, in the meantime, the thermal events occurring in the samples are recorded by DTA. A positive peak represents an exothermic event while a negative peak represents an endothermic event on a DTA curve. Platinum crucibles were used as sample holders, and Al₂O₃ was used as the reference material.

The 0.4% Pt promoted sulfated zirconia was used to isomerize 1-hexene in the liquid state. The 1-hexene has a boiling point of 46.3°C and a density of 0.6371 g/ml. The 1-hexene used here was a 99+% pure [Aldrich] sample and used without further purification. Since the catalysts are extremely sensitive to moisture, which deactivates the catalysts, two series of runs were conducted and compared, one series using 1-hexene treated with calcined molecular sieves. The molecular sieves were calcined to 500°C in a muffle furnace for an hour before they were put in the 1-hexene reagent bottle. After addition of the molecular sieves, the 1-hexene reagent was dried overnight before use. Except for one run conducted at 0°C, all runs were conducted at room temperature. The 1-hexene isomerization was performed at atmospheric pressure using a 8 mL glass vial as a reactor. A series of runs with and without stirring and at different feed-to-catalysts ratio were carried out. A Shimadzu QP-5000 GC/MS was used to analyze the isomer products. The GC has a 60 m long 0.32 mm diameter column packed with 1.00 μm thick layer of polydimethylsiloxane. Its standard configuration features a direct capillary column interface to the GC/MS and an electronimpact-type ion source. A sample injected via the
GC sample injection port is separated in the capillary column, and passes through the transfer interface to be introduced into the ion source box. Here, the sample is ionized, and the ions are focused by a lens stack into a quadrupole filter. The ions are detected by an electron multiplier.

The following steps were carried out as the experimental procedures.

1. Preheat the muffle furnace to 650°C with adequate air flow. Put the inactivated catalyst in a porcelain crucible, and heat at 650°C for two hours. The weight loss during the activation is around one half of the original weight.

2. It takes around 15 minutes for the activated catalyst to cool down to near room temperature. Measurement of the weight of catalyst is conducted in the reactor to minimize air exposure.

3. As soon as the catalyst cools, measure the amount of the catalyst needed to make a desired ratio with 2 mL 1-hexene (the density of 1-hexene is 0.6371 g/mL). Dump the 1-hexene into the reactor to mix with catalyst. Start timing at the same time.

4. A 10 µl sample is collected at certain time intervals. This sample then is diluted with 1.0 ml methanol and 10 µl cyclohexane is added to the sample as the internal standard.

5. Inject the sample into GC-MS for analysis.

Two GC/MS temperature programs were used to analyze the products. In program (a), the initial temperature was set at 45°C and then isotherm for 12 minutes. This program is efficient to identify the isomer products. In program (b), after initially
isotherm at 45°C for 12 minutes, raise the temperature to 180°C at a heating rate of
10°C/min and isotherm for 5 minutes. Then raise the temperature again from 180°C to
260°C at the same heating rate then isotherm for 5 min. Program (b) is designed to
identify oligomer products which have higher boiling points. Also, for both programs,
the injector temperature was 230°C. The split ratio was 100.00. Runs were conducted
at constant flow rate of 233.80 mL/min.

Limitations of this GC-MS is that the 1-hexene isomers are not completely
separable. *cis*-3-Hexene and *trans*-2-hexene have essentially identical retention times on
all reported stationary phases. These two isomers were treated as if they were a single
species, *trans*-2-hexene. In addition, while 1-hexene appears first (around 7.1 min) and
is well separated under our conditions, and *cis*-2-hexene appears last (around 8.1 min) and
is also well-separated, the *trans*-3-hexene (around 7.6 min) peak appears very close to
the leading edge of the *trans*-2-hexene (around 7.8 min) peak, so the peak deconvolution
technique is needed for precise calculation.
III. RESULTS AND DISCUSSION

A. Thermal Analysis of Catalysts Samples

When 5% Pt/\(\text{SO}_4^2-\)/ZrO\(_2\) samples were heated in air, two major weight loss regions were seen on the TG curve (Figure 3). The first major weight loss region is between room temperature and 620°C. The weight loss is about 20% of the original sample weight. According to the MS data, as shown in Figure 4, the first major weight loss corresponds to the loss of water (mass 18), some hydrogen chloride (mass 36) and some chlorine (mass 70). The HCl evolution starts around 250°C and levels off around 800°C. The identification of HCl is based upon the mass-to-charge ratio of 36, as well as the mass ratio of the Cl isotopes. The theoretical data in the NIST library in the MS system shows HCl has 4 major isotope peaks:

\[
\begin{array}{cccc}
\text{mass:} & 36 & 38 & 35 & 37 \\
\text{abundance:} & 999 & 324 & 170 & 54
\end{array}
\]

The above data indicate the theoretical data for the mass ratio of HCl (mass 36/mass 38) should be 999/324, which is around 3:1. In the present case, the ratio of peak area integration of HCl (mass 36/mass 38) is 1.31E-8/3.88E-9 (Figure 5), that is, 3.4:1, which is in reasonable agreement with the chlorine isotope distribution. The identification of HCl is also evidenced by FTIR data (Figures 6, 7, 8). For chlorine, the theoretical ratio for the isotopes, Cl\(_2\) (mass 70): Cl\(_2\) (mass 72): Cl\(_2\) (mass 74) should be 100:32.4:10.5. However, the integration of Cl\(_2\) peak area of the Cl\(_2\) MS profile shows a ratio of Cl\(_2\)
Figure 3. TG curve for 99% Fe/FeS/FeSO₄/Fe₂O₃ heated in air.

Weight (%)
Figure 4. Mass profile for 5% Pt/\text{SO}_4/\text{ZrO}_2 heated in air.
Figure 5. Isotopic mass profiles for HCl and Cl₂ from 5% Pt/SO₄²⁻/ZrO₂ heated in air.
Figure 6. Identification of HCl in the FTIR spectra for 5% Pt/SiO₂-ZrO₂, heated in air.
Figure 7. 3D FTIR spectra of evolved gas species of 5% Pt/SO$_4$$^2-/ZrO$_2$ heated in air.
Figure 8. FTIR profile for the evolution of HCl, H$_2$O and SO$_2$ from the heating of 5% Pt/SO$_4$/$\text{ZrO}_2$ in air.
(mass 70): \( \text{Cl}_2 \) (mass 72) as \(1.25\times10^{-8}/4.71\times10^{-9} \), that is 100:37.7, while \( \text{Cl}_2 \) (mass 74) can barely be identified. These results are not in as good agreement with the theoretical data as was the case for HCl. The reason is when only a trace amount of chlorine is released from the sample, the magnitude of noise is comparable to the \( \text{Cl}_2 \) profile. In that case, the integration cannot give the real isotope mass ratios. But still, the trend does agree with the isotope peaks:

\[
\text{Cl}_2 \text{ (mass 70)} > \text{Cl}_2 \text{ (mass 72)} > \text{Cl}_2 \text{ (mass 74)}
\]

Water evolved from the very beginning of the heating process. It shows a major peak from room temperature to around 120°C and a second peak, which is somewhat overlapped with the first one around 500°C. The feature of the water profile indicates that most of the water is present in the sulfated zirconia sample as adsorbate on the surface, whereas some water exists in the deeper pores within the solid. Also, a tighter bond is suggested for water with sulfated zirconia.

The evolution of carbon dioxide showed up at different time period in the MS profile for different samples (Figures 4 and 9). The case is the same for other zirconia samples. However, according to the preparation process, there is no carbon compound involved except that the zirconia sample is washed by ethanol to remove most of the water before it is dried and sulfated. Therefore, we suggest some of the carbon dioxide is from decomposition of trace amounts of ethanol. On the other hand, zirconium is a transition metal, which has empty \(d\) orbital and can act as a Lewis acid, while carbon dioxide has lone pair electrons and can be a Lewis base. Therefore, zirconia can easily coordinate with carbon dioxide in the air during sample preparation, giving rise to the release of different amounts of carbon dioxide during various temperature regions. The
Figure 9. Mass profile for 1% Pt/\(\text{SO}_4^{2-}/\text{ZrO}_2\) heated in air.
variation of weight loss in this temperature region depends upon the drying conditions of the catalyst sample as well as the amount of sulfuric acid and platinic acid adsorbed on the sample.

The second weight loss region is from 620°C to a temperature of 900°C (Figure 3), the temperature limit of the TG-MS system. The weight loss is over 7% of the original weight. According to the MS data (Figure 4), this weight loss corresponds to the evolution of sulfur oxides, hydrogen chloride and chlorine.

Sulfur oxides result from the decomposition of the sulfate ion from around 650°C. Referring to the NIST library in the MS system, the mass spectrum of sulfur dioxide should include the following major fragments:

mass: 64 48 32 16 66 50 65 24 34 49
abundance: 999 493 104 52 49 23 9 8 4 4

The data indicate the mass ratio of sulfur dioxide to sulfur monoxide is:

\[ \text{SO}_2 \text{ (mass 64)}/\text{SO} \text{ (mass 48)} = \frac{999}{493} = 2.0:1. \]

The integration of the peak areas of sulfur dioxide and sulfur monoxide in one sample shows that:

\[ \text{SO}_2 \text{ (mass 64)}/\text{SO} \text{ (mass 48)} = \frac{2.54}{1.79} = 1.4:1. \]

The SO component of the second ratio is larger than the theoretical value, indicating that some sulfur monoxide is a primary product of the decomposition of sulfur dioxide. In other words, the sulfur monoxide peak did not result entirely from the fragmentation of sulfur dioxide. There are peak maxima for sulfur oxides around 700°C, corresponding to the peak maximum on the DTG curve. However, the peak profiles of sulfur oxides show a continuum beyond 900°C since the profiles of SO₂ and SO did not return to the base
line level, as supported by TG data which shows that the TG curve does not level off at this point. The results indicate that there could be different types of bonding between the sulfate ion and zirconia. The evolution profile of HCl also shows three peak maxima which indicate several forms of bonding between Cl and zirconia.

The evolution of water, hydrogen chloride and sulfur dioxide was also identified by their characteristic FTIR peaks (Figures 6, 7, 8). The FTIR profile shows good agreement with MS data. In the case of 1% Pt/\(\text{SO}_4^{2-}/\text{ZrO}_2\), the results were similar to that of 5% Pt/\(\text{SO}_4^{2-}/\text{ZrO}_2\), except that, since less platinic acid was used to treat the sample, the amounts of HCl and Cl\(_2\) evolution are much less (Figure 9). The Cl\(_2\) peak is barely observable in the MS data.

When the samples were heated in helium using the same heating program, the evolution profiles were similar to those when the samples were treated in air. However, in the inert gas environment, oxygen species can be detected by the mass spectrometer. For 5% Pt/\(\text{SO}_4^{2-}/\text{ZrO}_2\) sample, the MS data show that the evolution of oxygen coincides with the evolution of sulfur oxides (Figure 10). The integration shows the following mass ratio:

\[
\text{SO}_2 \text{ (mass 64)/SO (mass 48)/O}_2 \text{ (mass 32) = 2.77E-8/2.76E-8/1.63E-8}
\]

This suggests that SO\(_3\) might form prior to the evolution of SO\(_2\) and SO. Then, when SO\(_3\) decomposes, it gives off SO, SO\(_2\) and oxygen. However, SO\(_3\) was not identified by mass spectrometry, which could reflect the decomposition of SO\(_3\) in the chamber before it reached the MS detection.

Thus, in air or inert gas environments, the heating events can be described as occurring in two temperature regions:
Figure 10. Mass profile for 5% Pt/SO$_4^2$-ZrO$_2$ heated in helium.
Region I (<620°C)

$$\text{SO}_4^{2-} \bullet \text{ZrO(OH)}_2 \bullet \text{H}_2\text{PtCl}_6 \rightarrow 2\text{HCl} + \text{Pt-}\text{SO}_4^{2-} \bullet \text{ZrO}_2 + \text{H}_2\text{O} + +2\text{Cl}_2$$  \hspace{1cm} (1)

Region II (>620°C)

$$\text{SO}_4^{2-} \bullet \text{ZrO}_2 \rightarrow \text{ZrO}_2 + \text{SO}_3(\text{O}_x)$$ \hspace{1cm} (2)

$$\text{SO}_3 \rightarrow \text{SO}_2(\text{SO}) + \text{O}_x$$ \hspace{1cm} (3)

When the 1% Pt/\text{SO}_4^{2-}/\text{ZrO}_2 samples were heated in \text{H}_2/\text{N}_2 mixture, two major
weight loss regions were observed on the TG curve (Figure 11). However, the two
regions were not as clear-cut as for air and inert gas environments. MS data obtained are
shown in Figure 12. According to the MS data, the first weight loss was primarily due
to the loss of water (mass 18) and hydrogen chloride (mass 36). Chlorine was not
identified, probably because it combined with hydrogen to form hydrogen chloride (mass
36). In this case, the hydrogen chloride magnitude in the MS profile is greater than was
seen in the runs under air or inert gas environment. The second weight loss is due to the
evolution of sulfur in both oxidized (\text{SO}_x) and reduced (\text{H}_2\text{S}) forms. For the same
sample, the \text{H}_2\text{S} peak appears immediately right after the evolution of sulfur oxides.
Also, the water profile shows another peak maximum around 600°C coinciding with the
\text{H}_2\text{S} peak maximum. Therefore, we can infer that the second water peak corresponds to
the water formed from reduction of sulfur oxides by hydrogen. Thus, in a flow of
hydrogen, we must modify the reactions that occur:

Region(II)

$$\text{SO}_4^{2-} \bullet \text{ZrO}_2 \rightarrow \text{ZrO}_2 + \text{SO}_x$$ \hspace{1cm} (4)

$$(x +1)\text{H}_2 + \text{SO}_x \rightarrow \text{H}_2\text{S} + x\text{H}_2\text{O}$$ \hspace{1cm} (5)

$$\text{O}_2 + 2\text{H}_2 \rightarrow 2\text{H}_2\text{O}$$ \hspace{1cm} (6)
Figure 11. TG curve for 1% Pt/SO$_4^{2-}$/ZrO$_2$ heated in hydrogen/nitrogen mixture.
Figure 12. Mass profile for 1% Pt/So$_4$/$ZrO_2$ heated in hydrogen/nitrogen mixture.
At this point, a question is raised. Does platinic acid treated sulfated zirconia completely decompose to give off hydrogen chloride and chlorine during heating in the inert gas? Or is there still chlorine left with the complex? One way to answer this question is to first heat the sample in the inert gas. Through on-line analysis, monitor the HCl profile until it levels off around 900°C, then cool down the residue, switch the gas to hydrogen, and reheat it to 800°C. The result is that no more hydrogen chloride is released during the second heating period.

The catalysts samples of 2% Fe/0.5% Mn (nitrate salt/sulfate salt)/SO$_4^{2-}$/ZrO$_2$ were analyzed by TG-MS and TG-FTIR under the environments of air and helium. On both TG curves, there are two major weight loss regions (Figures 13, 14). The first weight loss of about 20% is between 25°C and 440°C. The second weight loss of about 8% is between 600°C and beyond 850°C. According to the MS data (Figures 15) for both gas environments, the first major weight loss corresponds to the loss of water, carbon dioxide and nitrogen oxides. The mechanism of the evolution of water and carbon dioxide is similar to that for the platinum promoted sulfated zirconia samples. However, the mechanism of nitrogen oxides had been a puzzle. According to mass data, their evolution started around 150°C and reach maxima around 320°C. The peaks level off around 400°C. The identification of nitrogen dioxide was based upon the mass-to-charge ratio (46) as well as the ratio of abundance for different major fragments.

Referring to the NIST library, the cracking pattern for NO$_2$ in the mass spectrometer chamber is as follows:

<table>
<thead>
<tr>
<th>mass</th>
<th>30</th>
<th>46</th>
<th>16</th>
<th>14</th>
<th>47</th>
</tr>
</thead>
<tbody>
<tr>
<td>abundances</td>
<td>999</td>
<td>370</td>
<td>223</td>
<td>96</td>
<td>1</td>
</tr>
</tbody>
</table>
Figure 13. TG curve for 2% Fe/0.5% Mn (nitrate salt)/SO₄²⁻/ZrO₂ heated in helium.
Figure 14. TGA curve for 2% Fe/0.5% Mn (sulfate salt)/SO$_2$ doped in helium.
Figure 15. Mass profile for 2% Fe/0.5% Mn (nitrate salt)/SO$_4^{2-}$/ZrO$_2$ heated in helium.
The data show that the mass ratio of nitrogen monoxide to nitrogen dioxide is:

$$\frac{\text{NO (mass 30)}}{\text{NO}_2 \text{ (mass 46)}} = \frac{999}{370} = 2.70:1.$$ 

Integration of peak areas in the MS spectra shows that the mass ratio of nitrogen monoxide to nitrogen dioxide in helium (Figure 15) is:

$$\frac{\text{NO (mass 30)}}{\text{NO}_2 \text{ (mass 46)}} = \frac{1.69E-8}{2.87E-9} = 5.89:1.$$ 

Compared with the theoretical data, the ratio is larger than expected indicating that either there is another source of NO or the amount of NO$_2$ was somehow reduced during the analysis. One reasonable explanation is that due to the existence of water, NO$_2$ can easily combine with it to form HNO$_3$, thus decreasing the amount of NO$_2$ in the mass spectrometer chamber for analysis. That is:

$$3\text{NO}_2 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3 + \text{NO} \quad (7)$$

This reaction is evidenced by the water profile in the MS spectra. There is a decrease in the amount of water during the evolution of nitrogen oxides (Figure 15). In the FTIR analysis in the helium environment, only a trace amount of nitrogen monoxide, if any, was identified, while nitrogen dioxide was clearly shown in the spectra (Figure 16). In air, NO oxidizes spontaneously to NO$_2$, but at low NO concentration this reaction is extremely slow. Nitrogen dioxide has its strongest band right in the middle of the main water vapor band, which complicates atmospheric measurements of the molecule. However, in the present case, the decomposition of nitrate ion gives off a large amount of nitrogen oxides, which obviously appear with the water peak. The discrepancy between the MS results and the FTIR results was caused by the different process in identifying gas species in the gas chamber. The normal case for the decomposition of iron(III) nitrate and manganese(III) nitrate is to produce nitrogen dioxide and the metal
Figure 16. 3D FTIR for 2% Fe/0.5% Mn (nitrate salt)/SO$_4^{2-}$/ZrO$_2$ heated in helium.
oxide. In the mass chamber, NO was obtained in large amount because of the fragments of \( \text{NO}_2 \), while in the FTIR chamber, when \( \text{NO}_2 \) was produced; it combines with water to form nitric acid very quickly through the latter process as is shown on FTIR spectra. The amount of NO is much less compared with the process in the mass chamber. However, this is reasonable when checking the stoichiometry of the reaction equation (7). Therefore, the heating events for this sample below 620°C can be described as follows:

\[
\text{Region I (<620°C)} \\
\text{ZrO}(\text{OH})_2 \cdot \text{Fe(NO}_3)_3 / \text{Mn(NO}_3)_2 \rightarrow \text{ZrO}_2 \cdot \text{Fe}_2 \text{O}_3 / \text{MnO} + 5\text{NO}_2 + \text{H}_2 \text{O} + \frac{1}{2}\text{O}_2 \quad (8)
\]

The second major weight loss around 600°C to beyond 850°C can be attributed to the decomposition of sulfate ion. The mechanism of the evolution of sulfur oxides is similar to that for platinum sulfated zirconia samples.

As for the Fe/Mn sulfate salt treated sulfated zirconia, the result is similar to that of the platinum sulfated zirconia samples (Figure 17). It was shown that the existence of different metals or metal oxides does not affect the decomposition temperature of the sulfate ion. Also, the results obtained when the pretreating gas is air are similar to those of the runs in helium, which indicate that oxygen does not have any significant effect on the activation process (Figure 18).

The platinum sulfated zirconia samples were also analyzed in SDT in an air environment to monitor the thermal events of the samples during dynamic heating. We can see clearly the endothermic peak on the DTA curve corresponding to the evolution of gas species (water, carbon dioxide, hydrogen chloride and chlorine) (Figure 19). There is a distinct exothermic peak on the DTA curve occurring at 648°C, which corresponds to the transformation of the solid from the high surface area to a low surface area form. Depending on heating rates and time, the peaks may also correspond to the conversion
Figure 17. Mass profile for 2% Fe/0.5% Mn (sulfate salt)/SO$_4^{2-}$/ZrO$_2$ heated in helium.
Figure 18. Mass profile for 2% Fe/0.5% Mn (nitrate salt)/SO$_2^2$ZrO$_2$ heated in air.
Figure 19. TG and DTA curves for 1% Pt/SO$_2$/$\text{ZrO}_2$ heated in air.
from an amorphous state to a crystalline state. As a matter of fact, this exothermic event overlaps with an endothermic event which corresponds to the decomposition of the sulfate ion. Therefore, when heating the sample in air or an inert gas, the exothermic event is the result of the exothermic and an endothermic event, so that the shape of the trace will depend upon the heat balance for these two events. For zirconia alone, this exotherm occurs at 450°C under the same heating condition, while in the presence of sulfate ion, the phase transformation process is retarded to a much higher temperature. It was found for sulfated zirconia samples, this exotherm occurs at 622°C under the same heating conditions, which indicates that the existence of metals on the sulfated zirconia does not have a significant effect on this exothermic event. When anions other than sulfate ion were used to treat zirconia, this exotherm occurs at 533°C for molybdate-zirconia, 527°C for dichromate-zirconia and 465°C for tungstate-zirconia (Figure 20). It was found that the sulfate ion is so far the most efficient species to retard phase transformation of the catalyst, thus permitting a high surface area to be maintained through a higher temperature range.

B. 1-Hexene Isomerization upon Platinum Promoted Sulfated Zirconia

1. Qualitative Test (Run No. 1)

A sample of 0.4% Pt/SO₄²⁻/ZrO₂ was used to catalyze the 1-hexene isomerization reaction. The first successful run was carried out by using a catalyst activated at 650°C in air in a muffle furnace for 2 hours. The mass ratio of feed (1-hexene) to catalyst was 3.0:1.0. The catalyst charge was 0.5833 g, measured on a balance, while 2.00 mL 1-hexene was measured by a pipet. The mass of 1-hexene is calculated as follows:
Figure 20. DTA curves for dichromate zirconia, molybdate zirconia and tungstate zirconia.
Mass of 1-hexene (g) = D_{1-hexene} \times V_{1-hexene} = 0.6371 \text{ g/mL} \times 2.00 \text{ mL} = 1.27 \text{ (g)}

No stirring was used for this run.

As soon as 1-hexene is mixed with catalyst, the reaction mixture releases heat, which can be felt if holding the reactor. Samples were collected at certain time intervals up to 5 hours. However, it turned out, according to the analysis data on GC, the reaction proceeded so fast that 100% conversion of 1-hexene was reached in only three hours. The GC temperature program was set at 45\(^\circ\)C for 12 minutes and then raised to 180\(^\circ\)C at 10\(^\circ\)C/min and held for 10 min (program a). The products which showed up in the GC/MS analysis include \textit{trans}-3-hexene, \textit{trans}-2-hexene, \textit{cis}-2-hexene and dimers. Since \textit{cis}-3-hexene has a retention time nearly identical with that of \textit{trans}-2-hexene, it is included as a minor component of the \textit{trans}-2-hexene peak (Figure 21). However, when the temperature program is modified to raise the temperature to 240\(^\circ\)C (program b), trimers appear at around 35 min (Figure 22). As discussed in the experimental chapter, the identification of the products is based upon the comparison between the retention time of product peaks and the retention time of the standard peaks under the same GC temperature program. The purpose of the GC analysis is the quantitative determination of the amounts of the several hexene isomers associated with each sample. Therefore, the GC technique is very important. Every step was made as systematically as possible, to assure optimum repeatability. Also, GC/MS runs were normally conducted two times for the first sample, to verify that each peak occurs in the same place in each run. This step is especially important for temperature-programmed runs; residues from a previous analysis might be obtained. However, if a peak appears in two different runs, we could tell it is real. The dimers were identified relative to the retention time of dodecane
Figure 21. Isomer products from 1-hexene isomerization reaction analyzed by GC program (a).
Figure 22. Dimer and trimer products from 1-hexene isomerization reaction analyzed by GC program (b).
standard, which is around 28 min for this GC temperature program. However, since the dimer products are branched isomers of \textit{C}_{12} \text{alkene} or \textit{C}_{12} \text{alkane}, they have lower boiling points than \textit{n}-dodecane, and therefore they show up as a group of peaks ahead of the \textit{n}-dodecane standard peak.

The conversion is calculated based upon the concentration of 1-hexene. In the present case, 10.00 \mu l cyclohexane is added as an internal standard for each sample so that the concentration of 1-hexene can be calculated according to the peak area ratio. Three 1-hexene standards with cyclohexane were analyzed in the GC/MS first and the mean percentage (89.68\%) of 1-hexene (\textit{A}_{1-hexene}) to cyclohexane peak area (\textit{A}_{cyclohexane}) was taken as 100\% 1-hexene concentration. Therefore, the conversion is calculated as:

\[
\text{Conversion \%} = 100 \times \frac{\text{\textit{A}_{1-hexene}}}{0.8968 \text{\textit{A}_{cyclohexane}}}
\]

Also, the amounts of different isomers are calculated based upon the peak area as well as the justified standard peak area:

\[
\text{Selectivity \%} = 100 \times \frac{\text{\textit{A}_{isomer}}}{0.8968 \text{\textit{A}_{cyclohexane}}}
\]

The peaks of reagent 1-hexene and its isomers, the dimer and trimer products are well defined on the GC/MS chromatogram. The interesting point is that except for the isomer products of \textit{C}_6, \textit{C}_{12} and \textit{C}_{18} no other \textit{C}_n \text{products} in between were identified, indicating that the catalysts are good for isomerization and oligomerization reactions.

The reaction parameters for all runs are listed in Table 1.

2. Effect of Stirring (Run Nos. 2 and 3)

Since the reaction is between a solid and a liquid phase, the effect of stirring is important for study. Two parallel runs were conducted, both using a feed to catalyst mass ratio of 4.0:1.0. One run made use of continuous stirring while the other run was only
Table 1. Reaction Parameters of 1-Hexene Isomerization Study

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Catalyst Charge (g)</th>
<th>Feed/Cat. Ratio</th>
<th>Stirring</th>
<th>Run T (min)</th>
<th>Conver. Rate_{min} (mmol/g-cat/min)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.6007</td>
<td>2.1:1</td>
<td>none</td>
<td>180</td>
<td>----</td>
<td>Qualitative test</td>
</tr>
<tr>
<td>2</td>
<td>0.4665</td>
<td>2.7:1</td>
<td>none</td>
<td>550</td>
<td>0.72</td>
<td>Stirring effect</td>
</tr>
<tr>
<td>3</td>
<td>0.4440</td>
<td>2.9:1</td>
<td>72.1(rpm)</td>
<td>550</td>
<td>0.95</td>
<td>Stirring effect</td>
</tr>
<tr>
<td>4</td>
<td>0.3115</td>
<td>4.1:1</td>
<td>54.1(rpm)</td>
<td>180</td>
<td>1.07</td>
<td>Reaction order</td>
</tr>
<tr>
<td>5</td>
<td>0.3182</td>
<td>4.0:1</td>
<td>66.4(rpm)</td>
<td>180</td>
<td>1.10</td>
<td>Reaction order</td>
</tr>
<tr>
<td>6</td>
<td>0.4489</td>
<td>3.0:1</td>
<td>73.0(rpm)</td>
<td>120</td>
<td>0.72</td>
<td>Reaction order</td>
</tr>
<tr>
<td>7</td>
<td>0.5000</td>
<td>2.5:1</td>
<td>none</td>
<td>120</td>
<td>0.45</td>
<td>Optimum ratio</td>
</tr>
<tr>
<td>8</td>
<td>0.3297</td>
<td>4.0:1</td>
<td>none</td>
<td>120</td>
<td>0.73</td>
<td>Optimum ratio</td>
</tr>
<tr>
<td>9</td>
<td>0.2555</td>
<td>5.0:1</td>
<td>none</td>
<td>120</td>
<td>0.76</td>
<td>Optimum ratio</td>
</tr>
<tr>
<td>10</td>
<td>0.2168</td>
<td>6.0:1</td>
<td>none</td>
<td>120</td>
<td>0.90</td>
<td>Optimum ratio</td>
</tr>
<tr>
<td>11</td>
<td>0.2553</td>
<td>5.0:1</td>
<td>none</td>
<td>180</td>
<td>0.97</td>
<td>Moisture effect</td>
</tr>
<tr>
<td>12</td>
<td>0.3136</td>
<td>4.0:1</td>
<td>none</td>
<td>180</td>
<td>0.85</td>
<td>Moisture effect</td>
</tr>
<tr>
<td>13</td>
<td>0.6046</td>
<td>2.0:1</td>
<td>none</td>
<td>180</td>
<td>0.52</td>
<td>Moisture effect</td>
</tr>
<tr>
<td>14</td>
<td>0.3674</td>
<td>3.5:1</td>
<td>none</td>
<td>180</td>
<td>0.83</td>
<td>0°C</td>
</tr>
</tbody>
</table>
shaken every half hour. The 1-hexene conversion results show stirring accelerates the reaction rate (Figure 23). This result indicates that the reaction is diffusion controlled, as we expect for reactions between a solid and liquid. The larger the contact area between 1-hexene and catalyst, the faster the reaction rate.

Also, from the second run, a semiquantitative number can be calculated to show a minimum rate of conversion, assuming the rate in the first few minutes is greater than the 0-30 min. average. We call this number the conversion rate number, which is calculated according to the following expression:

\[(\text{conv.\%}_1\text{-hexene/time min}) \times (1274 \text{ mg/100\%}) \times (1 \text{ mmol/84.16 mg}) \times (1/ \text{ mass}_{\text{cat g}})\]

with a unit of "mmol per gram catalyst per minute". Thus for the reaction of 1,274 mg of 1-hexene the conversion rate number for each run was calculated and is listed in Table 1. Obviously, this number is higher for runs with stirring.

3. **Reaction Order (Run Nos. 4 and 5)**

The reaction rate is studied based upon 1-hexene conversion. Several stirring rates were used until the point was reached where a further increase in stirring rate does not influence the reaction rate, i.e., the effect of diffusion is removed. Only under this condition can we study the order of the reaction. When plotting log[1-hexene] versus time, we could see the shape of the curve, which is roughly straight as expected for 1st order reactions. For a linear curve, the square of regression coefficient \(R^2\) is 0.835. This is understandable when isomerization and oligomerization take place at the same time, the reaction order can be a complex (Figure 24).
Figure 23. Study of stirring effects on 1-hexene isomerization reaction.
Figure 24. Study of reaction order of 1-hexene isomerization reaction.
4. **Optimum Feed-to-Catalyst Ratio (Run Nos. 7 - 13)**

The feed-to-catalyst ratio has also been studied in order to find an optimum which is efficient for the reaction and is also economical. Two sets of runs were conducted without stirring but with constant shaking of the reactor. Closed systems were used to avoid any evaporation of 1-hexene which could lead to errors in the feed-to-catalyst ratio. The runs were set at different feed-to-catalyst weight ratios of 2.5:1.0, 4.0:1.0, 5.0:1.0 and 6.0:1.0. The result of 1-hexene conversion shows that for all mass ratio reactions 1-hexene has high conversion within the first ten minutes. This conversion reaches around 40% for all the runs in the first set (Figure 25). According to this series of experiments, the ratio of 4.0:1.0 seems to be the optimum. However, the conversion rates for the other runs are quite close. However, in the series runs 11, 12, 13, the results show the highest conversion for a feed-to-catalyst ratio of 2.0:1.0 (Figure 25), which indicates the conversion to be directly proportional to the amount of catalysts added. This result is reasonable for heterogeneously catalyzed reactions. The discrepancy of the results obtained by these two series of runs may arise because, since stirring was not used during the reaction, there was some variability in mixing. More constant shaking of the reactor was applied in the second series of runs; therefore, the conversions are higher and the results are more reliable. It can be concluded that even though there is an increase in the conversion rate with increase in the catalyst charge, it could be more economical to use the feed-to-catalyst ratio 5.0:1.0.

5. **Effect of Moisture (Run Nos. 7-10 and Nos. 11-13)**

Comparing the runs with same feed-to-catalyst ratio as shown in Figure 25, the second series runs have higher 1-hexene conversions. The main difference between the
Figure 25. Study of optimum feed-to-catalyst ratio and effect of moisture on the reaction.
two run series is that in the second set of runs, the 1-hexene reagent was treated by calcined (500°C) molecular sieves before use. This result suggests that drying of the reagent plays a role in the reaction. It was found by other workers\textsuperscript{35} that water is a poison to the sulfated zirconia catalysts. In the present study, it was also manifested that trace amounts of moisture retard the reaction rate.

6. **Effect of Temperature**

All the above discussed runs were conducted at room temperature. Since we obtained a high conversion and fast reaction rate, it would be interesting to investigate the reaction at a lower temperature. We conducted the reaction at 0°C with a feed-to-catalyst ratio of 3:1. The results show a slower conversion than at room temperature, but still as high over 80% at 40 minutes (Figure 25, line A), which indicates that the catalyst has a very high activity.

7. **Selectivity of Isomer and Oligomer Products**

The selectivity of the products was also studied by plotting the concentration of cis-2-hexene, trans-2-hexene and 3-hexene against time (Figure 26). The results are consistent for each run with different feed-to-catalyst ratio. Oligomers account for the greater part of the products. However, it is difficult to determine the accurate amount of oligomers based on GC analysis. We can generally estimate the part of 1-hexene conversion, after deducting the amount of isomers, as oligomers. Therefore, selecting one run with feed-to-catalyst ratio of 5.0:1.0, we obtain the following data (Table 2).
Figure 26. Selectivity of isomer products of 1-hexene isomerization reaction.
Table 2. Selectivity of Isomers and Oligomers (%)

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Conversion</th>
<th>Cis-2-</th>
<th>Trans-3-</th>
<th>Trans-2-</th>
<th>Oligomer</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>65.3</td>
<td>1.8</td>
<td>0.8</td>
<td>2.9</td>
<td>59.8</td>
</tr>
<tr>
<td>40</td>
<td>70.4</td>
<td>3.3</td>
<td>3.6</td>
<td>5.1</td>
<td>58.4</td>
</tr>
<tr>
<td>80</td>
<td>79.4</td>
<td>4.9</td>
<td>2.4</td>
<td>1.0</td>
<td>63.1</td>
</tr>
<tr>
<td>130</td>
<td>63.6</td>
<td>13.8</td>
<td>7.3</td>
<td>25.7</td>
<td>16.8</td>
</tr>
<tr>
<td>180</td>
<td>79.5</td>
<td>10.8</td>
<td>6.5</td>
<td>22.7</td>
<td>39.4</td>
</tr>
</tbody>
</table>

We can see that isomerization increases as the reaction proceeds, while the percentage of oligomers in the products decreases. But still, oligomers are the major products in the reaction. We can also see that trans-2-hexene has highest selectivity, cis-2-hexene the second, while trans-(cis-)3-hexene has the lowest selectivity among isomers.

8. Mechanism of the Reaction

The reaction can be concluded to proceed as shown in Figures 27 and 28. Since the reaction is acid catalyzed, the isomerization is initiated when 1-hexene first abstracts a proton from the surface of the catalyst, forming a carbonation. When this carbonium ion loses a proton, it most probably form 2-hexene. There are two geometric isomers for 2-hexene, trans-2-hexene and cis-2-hexene. When 2-hexene abstracts a proton, a 3-hexyl carbonation may be formed and consequently 3-hexene can be formed according to the same mechanism as the formation of 2-hexene. There are two geometric isomers for 3-hexene, trans-3-hexene and cis-3-hexene. Dimers are formed when a hexyl carbonation combines with another hexene molecule to form a C_{12} carbonation. This C_{12} carbonation can lose a proton to form C_{12} alkene or it can abstract a hydride to form C_{12} alkane. The C_{12} products have a lot of isomers, which gives rise to the groups of peaks appearing in the chromatogram.
Figure 27. Mechanism of isomer products formation upon acid catalyst.
Figure 28. Mechanism of dimer products formation upon acid catalyst.
According to the thermodynamic data, the equilibrium among the linear hexenes is:

\[
\begin{align*}
1\text{-hexene} & \quad 1.64 \pm 0.09\% \\
\text{trans-2-hexene} & \quad 52.3 \pm 0.3\% \\
\text{cis-2-hexene} & \quad 15.5 \pm 0.2\% \\
\text{trans-3-hexene} & \quad 30.4 \pm 0.2\%
\end{align*}
\]

The percentage equilibrium gives the sequence that \(\text{trans-2-hexene} > \text{trans-3-hexene} > \text{cis-2-hexene}\). However, in the case of 1-hexene, kinetic effects also play a role in determining the percentage of the products. Thermodynamic data gives a similar free energy of formation of \(\text{cis-2-hexene} (\Delta G_f^0 = 71.30 \text{ KJ/mol})\) and \(\text{trans-2-hexene} (\Delta G_f^0 = 71.46 \text{ KJ/mol})\), \(^{43,45}\) kinetically \(\text{trans-2-hexene}\) is favored over \(\text{cis-2-hexene}\), since when methyl group and propyl groups are at the same side of a double bond, there is a significant nonbonding repulsion which gives rise to the higher selectivity for \(\text{trans-2-hexene}\).
IV. SUMMARY AND CONCLUSIONS

Thermal analysis of metal promoted sulfated zirconia by means of coupled TG-MS and TG-FTIR has provided information about evolved gas species during dynamic heating. For 1% Pt or 5% Pt promoted sulfated zirconia, the mechanism of the chemical changes during the heating process is similar. When the catalyst samples were heated in air or in an inert gas, online analysis by TG-MS shows different gas species evolved during different temperature regions. HCl and Cl₂ were identified by the mass spectrometer according to their atomic mass and isotope mass ratios at a temperature range starting around 250°C to around 750°C. The evolution of HCl was also evidenced by online analysis of TG-FTIR using the same temperature programs. There are three peak maxima of HCl and Cl₂ on the mass profile, indicating different forms of bonding between Cl and zirconia. The SO₂ and SO evolution in air was also identified in the temperature range around 650°C to beyond 900°C by mass spectrometer while O₂ was identified as well in an inert gas environment. Also, the evolution of SO₂ was evidenced by FTIR. The peak profiles of sulfur oxides show a continuum beyond 900°C since the profiles of SO₂ and SO did not return back to the base line level--also evidenced by TG data which shows that the TG curve does not level off at this point. The results indicate that there could be different types of bonding between the sulfate ion and zirconia. In the H₂/N₂ environment, the evolved species included H₂S and water, which are the reduction products of sulfur oxides in the temperature range from 450°C to 600°C.
Samples of 2% Fe/0.5% Mn (nitrate salt/sulfate salt)/SO$_4^{2-}$/ZrO$_2$ were analyzed by TG-MS and TG-FTIR under the environments of air and helium. The evolved gas species include water, sulfur oxides for iron(III) sulfate/manganese(II) sulfate samples and nitrogen oxides for iron(III) nitrate/manganese(II) nitrate samples. There is a large amount of NO identified by the mass spectrometer, while in FTIR spectra the NO signal is so small that it almost cannot be identified. The discrepancy between the mass and FTIR results was caused by the different processes of identifying gas species in the gas chamber. According to DTA data, sulfate ion was found so far to be the most efficient species to retard the phase transformation process of zirconia.

Sample of 0.4% Pt/SO$_4^{2-}$/ZrO$_2$ was found to have high catalytic activity to isomerize and oligomerize 1-hexene in the liquid state. When the feed of 1-hexene to catalyst ratio ranges from 6.0:1.0 to 2.0:1.0, the conversion reaches as high as 50% at least within the first 30 minutes at room temperature. The average value of conversion rate number for all the runs is 0.81 mmol/g$_{cat}$/min within the first 30 minutes of the reaction. The reaction proceeds by acid catalysis so the carbenium ion is the intermediate for both isomerization and oligomerization. The reaction is diffusion controlled. It was also found that moisture functions as a poison to the catalyst. Oligomers are found to be the major products in the reaction at short times. Trans-2-hexene has the highest selectivity, cis-2-hexene the second while trans-(cis)-3-hexene has the lowest selectivity among the isomers.
V. BIBLIOGRAPHY


32. Srinivasan, R.; Davis, B. H. unpublished data.


