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THE UNIVERSITY OF OKLAHOMA
GRADUATE COLLEGE

INVESTIGATIONS OF THE EFFECTS OF IRON, MANGANESE, AND NICKEL
ON THE PROPERTIES OF SULFATED ZIRCONIA CATALYSTS

A DISSERTATION
SUBMITTED TO THE GRADUATE FACULTY
in partial fulfillment of the requirements for the
degree of
DOCTOR OF PHILOSOPHY

By
CHANDJA EMMANUEL SIKABWE
Norman, Oklahoma
1997

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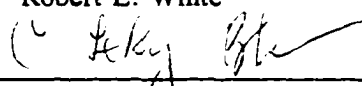
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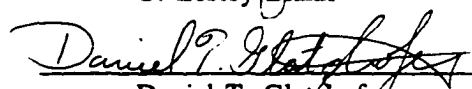
**INVESTIGATIONS OF THE EFFECTS OF IRON, MANGANESE, AND NICKEL
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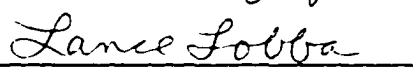
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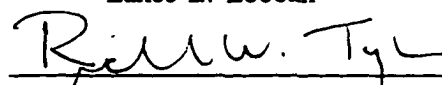
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Dedicated to the memory of my late parents

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INVESTIGATIONS OF THE EFFECTS OF IRON, MANGANESE, AND NICKEL ON THE PROPERTIES OF SULFATED ZIRCONIA CATALYSTS

Chandja Emmanuel Sikabwe

ABSTRACT

Sulfated zirconia, a catalyst with potential to be used for low temperature hydrocarbon isomerization and alkylation reactions was studied. The work described in this dissertation represents a systematic study of the effects of synthesis procedures and metal promoter content on the properties of sulfated zirconia catalysts. Microcatalytic reactor studies revealed that the addition of metal promoters led to higher *n*-butane isomerization rates. The incorporation of nickel into sulfated zirconia catalysts had a similar promoting effect as adding both Fe and Mn. Catalysts containing only Mn were much less active than those containing only Fe or Ni.

Thermogravimetry (TG) was utilized to study catalyst thermal stability and to measure sulfate contents for catalysts with differing compositions. Temperature programmed desorption (TPD) measurements of surface adsorbed species were used to characterize catalyst acidities. Diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS) and variable temperature diffuse reflectance Fourier transform infrared spectroscopy (VT-DRIFTS) were used to characterize adsorbate interactions with catalyst surfaces. Results from TPD studies suggested that metal promoters did not increase the acidity of sulfated zirconia catalysts. Based on TG and VT-DRIFTS studies, a potential structure for sulfated zirconia acid sites was proposed.

Thermogravimetry studies were augmented with chromatographic separation and mass spectrometric analysis of volatiles evolved during 1-butene TPD. Results from these studies suggested that metal promoted catalysts inhibited participation of surface carbenium ions in hydride abstraction reactions, resulting in more abundant unsaturated volatile products compared to the unpromoted catalyst. It was concluded that one role of metal promoters in *n*-butane catalytic isomerization may be to reduce the electrophilic nature of adsorbed carbenium ion intermediates. The magnitude of this effect depends on the type of metal employed as a promoter.

CHAPTER ONE

INTRODUCTION

A new class of solid acid catalysts collectively known as "sulfated metal oxides" has recently been the object of increased interest because of the potential use of these materials in the petroleum industry^[1]. When treated with SO_4^{2-} and after calcination, transition metal oxides such as ZrO_2 , TiO_2 , Fe_2O_3 and SnO_2 exhibit such strong acidity that they have been termed "superacids"^[2]. A superacid is defined as any material with an acidity that is greater than that for 100 % sulfuric acid ($H_o = -12.0$)^[3]. As a result of the increased acidity, these materials show high activity for acid-catalyzed reactions, even at room temperature. Sulfated zirconia ($\text{SO}_4^{2-}/\text{ZrO}_2$) has been found to be the most catalytically active member of the family of sulfated metal oxides. The catalytic behavior of sulfated zirconia for *n*-butane isomerization is enhanced when transition metals (e.g. Fe, Ni) are incorporated in the catalyst at levels as low as 0.1 % by weight^[4]. This finding prompted efforts to determine the nature of metal promoters and whether the incorporation of transition metals increased the acidity of sulfated zirconia^[5-8]. However, despite efforts to characterize these materials, a number of fundamental questions are still

unanswered. For instance, the nature of the catalyst active site is still not clearly established, the role of acid site density and strength in relation to catalytic activity is still a subject of debate, the role played by Lewis and Brönsted acid sites remains controversial, and the nature and role of metal promoters is yet to be explained^[9].

The work described in this dissertation concerns the preparation, testing, and characterization of several sulfated zirconia catalysts. Our main objective in this work was to gain an understanding of the mechanisms of promotion resulting from the addition of transition metals to sulfated zirconia. Before addressing the focus of the present study, it is helpful to discuss what is known about solid acid catalysts in general.

1.1 Industrial Need for Solid Acid Catalysts

A true heterogeneous catalyst is one that accelerates the rate at which a reaction approaches equilibrium without altering the equilibrium. Catalysts provide reaction paths of lower activation energy, permitting rapid conversion of reactants to products.^[10] This is graphically shown in Figure 1.1 for a hypothetical exothermic reaction. The petroleum industry uses acid catalysts for the production of reformulated gasoline. Gasoline blends are characterized by an octane number. An octane rating is a measure of the knocking characteristics produced by gasoline in an automobile engine^[11]. Previously, octane enhancement was accomplished by mixing gasoline with additives such as tetramethyl lead (TML). The elimination of lead additives mandated by the EPA in the late 1970's and demand for cleaner-burning fuels has prompted a search for alternative methods for increasing octane numbers^[12].

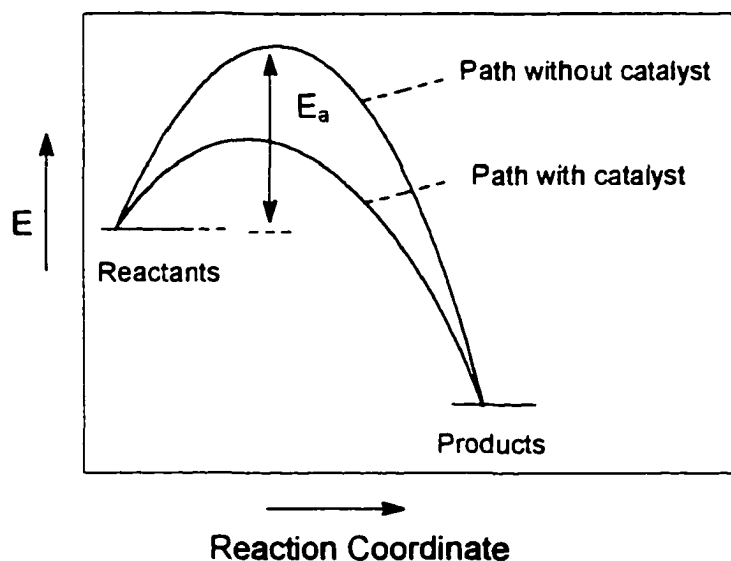


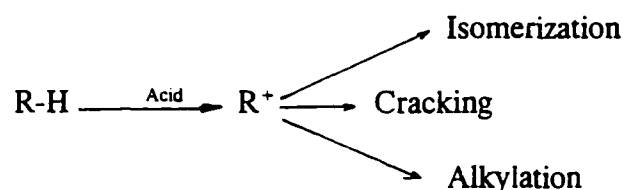
Figure 1.1 Catalyst effect on reaction path

In Table 1.1, octane ratings for a number of branched alkanes are compared to those for the corresponding linear isomers. The data in Table 1.1 reveal that short linear hydrocarbons and branched hydrocarbons are better fuel components than long linear chains. By converting linear hydrocarbons into branched hydrocarbons, gasoline octane can be increased. This transformation can be accomplished by skeletal isomerization or by alkylation. Olah's extensive work on hydrocarbon chemistry, which led to his 1994 Nobel prize, demonstrated beyond question that the formation of carbocations is at the center of hydrocarbon conversion reactions^[2].

Table 1.1 Octane Numbers for Some Hydrocarbons^[2]

Number of Carbons	Octane Number	
	Linear Isomer	Branched Isomer
C ₄	94	100
C ₅	63	116
C ₆	32	95
C ₇	0	116
C ₈	-19	100

Hydrocarbon transformations involve interactions between feed and catalyst to produce carbenium ions, which undergo further reactions:



Unfortunately, R-H bonds are difficult to cleave and very strong acid catalysts are needed to form carbenium ions.

Alternatively, gasoline octane ratings can be increased by adding oxygenates. Methyl-*tert*-butyl ether (MTBE) is an octane-enhancing additive that has received a lot of attention^[13]. In fact, the demand for MTBE is increasing faster than any other

petrochemical product^[14]. In addition to its use in alkylation reactions to produce branched hydrocarbons, isobutane is a precursor for MTBE synthesis. For this reason, isobutane production is critically important to the petroleum industry^[15]. Isobutane can be produced by catalytic cracking or by catalytic isomerization of *n*-butane. At the present time, large-scale isomerization of *n*-butane to isobutane is accomplished by using catalysts consisting of chlorinated alumina with supported platinum or aluminum chloride. Because of health hazards, the use of chlorinated alumina, which requires a continuous feed of a chloride source such as CCl₄ to sustain its activity, is undesirable^[16].

The *n*-butane to isobutane isomerization equilibrium favors isobutane at low temperature. Table 1.2 lists equilibrium concentrations for *n*-butane and isobutane at several temperatures.

Table 1.2 Relative Isomerization Equilibrium Compositions for Butanes

Temperature (°C)	Hydrocarbon Composition (%)	
	Isobutane	<i>n</i> -Butane
-		
-6	85	15
38	75	25
66	65	35
93	57	43

Low temperature *n*-butane isomerization has been accomplished by using liquid superacid catalysts such as fluorosulfuric acid-antimony pentafluoride (the magic acid)^[2,17].

However, liquid superacids, which are efficient and selective at room temperature, are not suited for industrial processes. These acid catalysts pose hazardous environmental problems due to requirements for their disposal and corrosion of equipment^[18]. Because of environmental concerns, the future of industrial isomerization and alkylation of *n*-butane and other linear hydrocarbons will depend on finding catalysts that are less hazardous. Unfortunately, isomerization temperatures required for typical solid acid catalysts are above 200°C. At these temperatures, most catalysts provide low isobutane yields^[19]. However, it has been advocated that increasing the isobutane selectivity by even 1 % over currently attainable levels would correspond to thousands of tons/year enhancement in petrochemical industry production^[20]. Clearly, there is a need to develop environmentally friendly isomerization and alkylation catalysts that can be employed at low temperatures. Solid acid catalysts are potential candidates for these applications.

1.2 Solid Acid Catalysts

A number of solid acid catalysts including : zeolites^[21-25] silica-aluminas^[26-30], and heteropolyacids^[31,32], have been synthesized and characterized. Restricted reaction volumes afforded by zeolites provide size and shape selectivity for catalytic reactions. Unfortunately, many solid acid catalysts (including zeolites) that have been found to be effective for *n*-alkane isomerization, exhibit poor selectivity because they can only be used at high temperatures^[33].

In 1976, Tanabe and Hattori^[34] described procedures for preparation of a family of solid superacids that were made by exposing metal oxides to the vapor of liquid

superacids such as SbF_5 . These catalysts are regarded as liquid superacids supported on metal oxides. Hammett indicator studies showed that these acids had acid strengths of approximately -13.7 on the H_0 scale. Even below room temperature, Tanabe *et al* reportedly observed skeletal isomerization of alkanes over $\text{SbF}_5/\text{SiO}_2\text{-Al}_2\text{O}_3$ catalysts. These materials, however, were found to deactivate very rapidly due to loss of the adsorbed liquid superacid^[19].

In 1962, Holm and Baily^[35] reported that sulfated zirconia containing platinum exhibited higher catalytic activity for *n*-butane isomerization compared to commercial Pt/chlorinated alumina catalysts. However, this material was not studied in detail until 20 years later. In 1976, while studying the effects of anions on metal oxides, Tanabe and Hattori found that TiO_2 became superacidic when calcined with ammonium sulfate^[36]. In 1979, Arata and coworkers^[37] reported that zirconia treated with sulfuric acid exhibited extremely strong acidity and that it was capable of catalyzing the isomerization of *n*-butane to isobutane at room temperature. In 1991, Hsu and coworkers^[38] patented a procedure for making sulfated zirconia catalysts containing Fe and Mn. The rate of *n*-butane isomerization for catalysts containing Fe and Mn was found to be three orders of magnitude higher than similarly treated catalysts that did not contain Fe and Mn. Since then, the promoting effects of transition metals have been confirmed by others^[39,40]. Because sulfated zirconia superacids do not contain halides, they have the advantage of being free from environmental problems. Thus, the industrial use of sulfated zirconia as a replacement for sulfuric acid and catalysts containing aluminum chloride is promising^[41].

1.3 Characterization of Solid Acid Catalysts

The goal of catalyst characterization techniques is to identify catalyst features that determine catalyst performance. This requires measurements of catalytic activity, selectivity, and stability in relation to both bulk and catalyst surface properties. Catalytic activity is a measure of the effectiveness of a catalyst to accelerate a given reaction and is usually expressed in terms of a rate constant, activation energy or preexponential factor, reactant conversion, or space velocity or temperature required for a given reactant conversion^[42]. Catalysts are often compared based on reactant conversion during a given contact time while maintaining feed composition, pressure and temperature constant. Figure 1.2 shows hypothetical plots of conversion versus contact time for two catalysts.

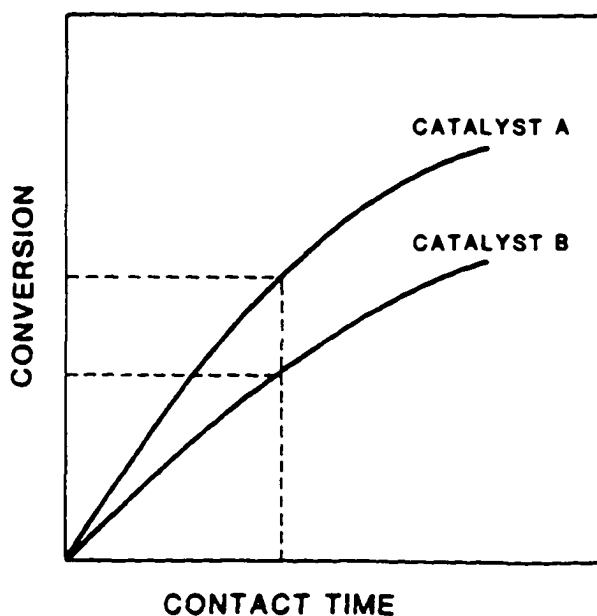


Figure 1.2 Reactant conversion versus contact time plots

Figure 1.2 shows that catalyst **A** is more active than catalyst **B** because **A** exhibits a higher conversion than **B** for the indicated contact time. Catalytic activity studies are typically conducted with microcatalytic reactors in which small amounts of catalyst are placed in contact with gas phase reactants. Reactor conditions can be easily changed to investigate catalytic processes.

Ideally, catalytic activity would be maintained indefinitely. Unfortunately, catalytic activity usually decreases with time on stream. Catalyst deactivation may occur in a matter of minutes or years. Deactivation can be caused by several factors, which are either mechanical or chemical in nature. Catalyst poisoning, for instance, is a chemical effect that is often accelerated by increasing reactor temperatures^[43]. A poison can be any agent that reacts permanently with catalyst active sites leading to loss of activity. The term coking is used to describe surface phenomena that leave carbonaceous residues on catalysts^[44]. The tendency of a catalyst to form coke is related to its acidity. Therefore, coking is an important deactivation mechanism for acid catalyzed reactions^[45].

The most important bulk properties of a catalyst are those that concern its composition and structure. Studies of catalyst bulk properties should provide information regarding not only the chemical composition of the principal and minor catalyst components but also the structures of units that make up the catalyst. Particle properties such as mechanical strength, particle size distribution, pore size, and surface area contribute to catalyst performance. The particle mechanical strength usually determines the lifetime of catalysts whereas particle size and pore size determine the number of active sites exposed to reactants. In zeolites, for instance, as much as 95 %

of the total catalyst surface area may be found inside pores.

Catalyst activity may also depend on the presence of modifiers, promoters, and inhibitors. A promoter is a substance that produces an increase in activity, selectivity or catalyst stability^[17]. By itself, a promoter usually has no activity for catalytic reactions. Promoters can be divided into two classes. Textural promoters help in stabilizing catalyst surface structures but are not involved in catalytic reactions. Structural promoters cause a chemical effect by altering the catalyst electronic character^[46]. For a given reaction, the promoter mechanism of action may vary with the promoter utilized. For instance, the addition of rhenium to platinum catalysts used in catalytic reforming results in a decrease in hydrocarbon hydrogenation. It is believed that rhenium electronically affects sites that are involved in hydrogenolysis and also inhibits coking^[42]. This is an example of a promoter that modifies catalyst adsorption properties. The promoter may also modify catalyst acidity properties. For instance, Chu *et al*^[47] have demonstrated that Fe generates Brönsted acid sites when it is incorporated into zeolite structures.

Heterogeneous catalysis involves reactions between species that are adsorbed on catalyst surfaces. The catalyst surface provides an energetically favorable pathway for catalyzed reactions. Therefore, elucidating catalytic reaction mechanisms requires an understanding of catalyst surface properties that are responsible for catalytic activity^[48]. Acidity is probably the most often studied catalyst surface property^[49-51]. Acid site types, strengths, and distributions have been measured and related to catalytic activities. In some instances, metal promoters have been found to increase the acid strength of a

catalyst^[50]. In such instances, an understanding of how promoters affect acidity can be useful for accelerating a specific reaction when several competing reactions may occur. Clearly, establishing relationships between factors that govern catalyst performance and catalyst composition and structure is extremely important for development of improved catalysts.

1.4 Research Focus

Catalysts derived from sulfated zirconia have potential for environmentally acceptable industrial applications. However, many questions regarding these catalysts remain unanswered. The observation that higher activities for *n*-butane isomerization can be obtained with metal promoted sulfated zirconia catalysts compared to unpromoted catalysts has led several investigators to search for an explanation for this phenomenon. The work described in this dissertation was performed in an attempt to answer some of the questions that are still subject of debate regarding these catalysts. In particular, emphasis was placed on elucidating the roles of transition metal promoters on sulfated zirconia catalyst activity.

This dissertation is divided into six chapters. A general introduction to solid acid catalysis is given in this chapter. In Chapter Two, the instrumentation used for catalyst characterizations is described. After initial studies, it became necessary to construct a unique interface between a thermogravimetric analyzer and a mass spectrometer, which is also described in Chapter Two. Studies of how catalyst preparation conditions affect catalyst activities are described in Chapter Three. Chapter Four is devoted to a

discussion of a proposed sulfated zirconia structure that is consistent with experimental results derived from characterization studies. Catalyst acidity measurements for promoted and unpromoted catalysts are described in Chapter Five. Finally, Chapter Six describes results from studies of the effects of metal promoters on the reactivities of surface adsorbed carbenium ions derived from 1-butene.

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CHAPTER TWO

INSTRUMENTATION AND PROCEDURES

This chapter describes the instrumental techniques and methods utilized to characterize sulfated zirconia catalysts in the present work. Characterization of the catalysts involved reactor studies, infrared measurements, thermal methods, chromatography, and mass spectrometric measurements. Catalyst preparation techniques are discussed in Chapter Three.

2.1 Microcatalytic Reactor

Catalytic activity measurements are used to assess the degree to which changes in catalyst properties affect reaction rates^[1,2]. A microcatalytic reactor was used to measure rates of *n*-butane isomerization over sulfated zirconia catalysts. Figure 2.1 is a block diagram of the flow control apparatus and the microcatalytic reactor. Reproducible activity measurements required precise control of reactant flow rates. The function of the flow control apparatus was to precisely regulate the flows of various gases during catalytic reactions. The apparatus comprised three Brooks 5850E mass flow controllers. One flow controller was used to regulate the flow of air during catalyst

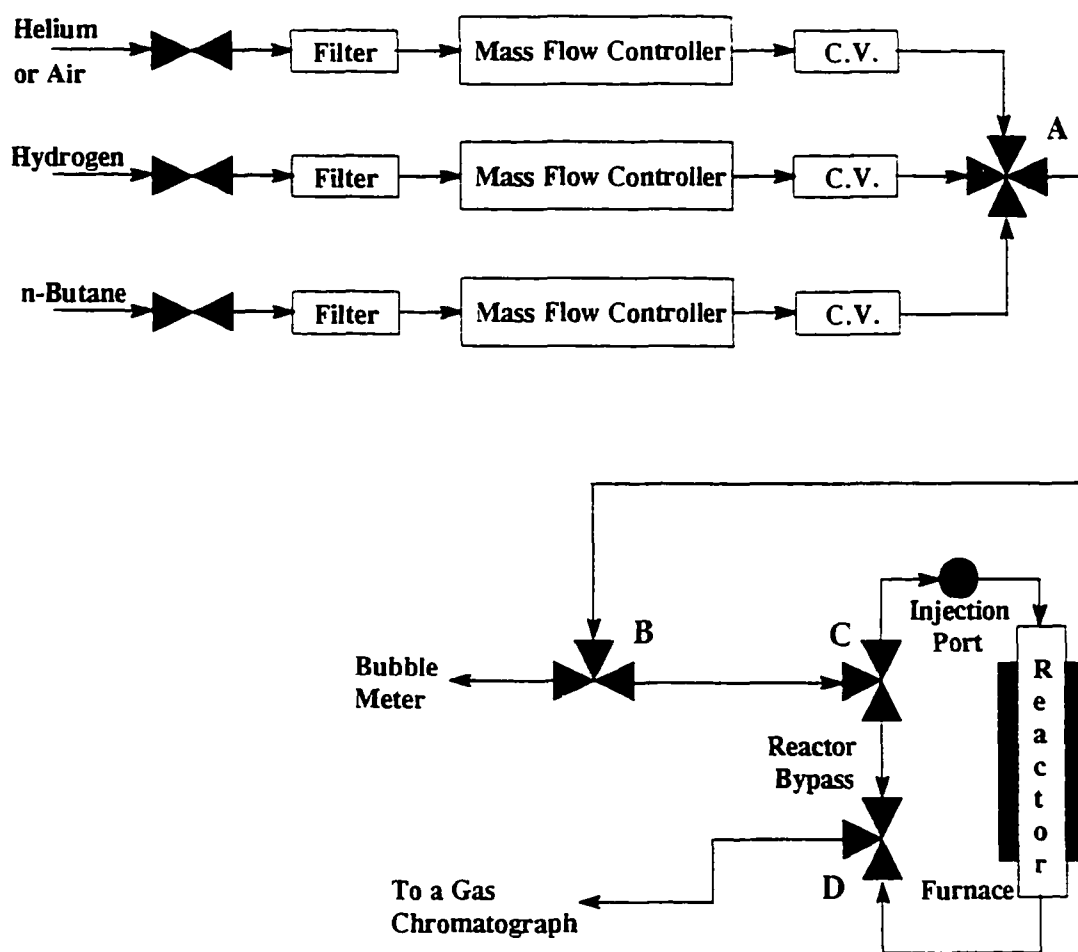


Figure 2.1 Diagram of the microcatalytic reactor flow system

sample pretreatment and to regulate the flow of helium during catalytic reactions. Two other flow controllers were used for hydrogen and *n*-butane. A fourth flow controller (not shown) was used to regulate the gas chromatographic carrier gas for reaction product analyses. Molecular sieve traps and 7 micron Swagelok filters were placed between the pressurized gas cylinders and the flow controllers to prevent water and other contaminants from entering the reaction stream. Swagelok check valves (denoted by C.V. in Figure 2.1) were placed at the exits of the mass flow controllers to prevent gas back flow. Flow rates of individual gases were measured with a bubble meter after diverting flow from the reactor by switching valve B. After the desired reaction mixture composition was established, thorough mixing of reactant gases was accomplished by allowing the gases to flow through a 1 m long, 1/4 inch diameter copper tube that was used to connect the flow controller system to the reactor.

Before starting catalytic reactions, the gas mixture was diverted to a reactor bypass loop by using bidirectional valve C. The purpose of the reactor bypass loop was to facilitate analysis of reactant mixtures by gas chromatography to assure that the desired reactant compositions were attained prior to reactor studies. Valve C was then switched to pass the reactant mixture into the reactor where catalytic reactions took place. An injection port connected in series with the reactor provided the capability of adding pulses of additional reactants when desired. To ensure that the reactant mixture was maintained at a constant temperature, heating tape was wrapped around the tubes leading to and exiting from the reactor. Figure 2.2 shows a diagram of the reactor. The reactor was a 1/4 inch o.d. x 16 inch long quartz tube attached to the rest of the system

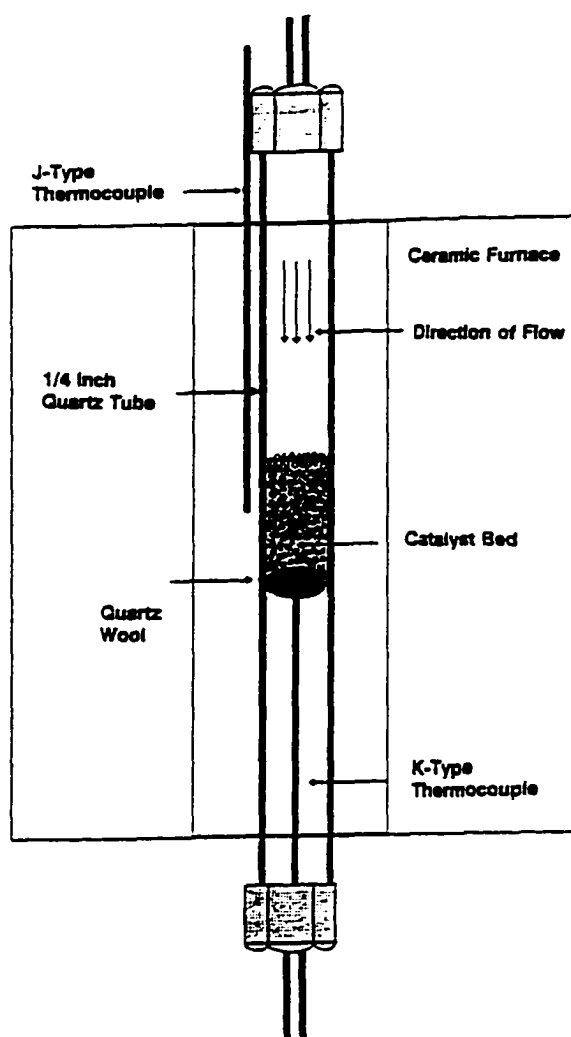


Figure 2.2 Microcatalytic reactor

by 1/4 inch Swagelok fittings at each end. The catalyst sample was packed as a plug in the middle of the quartz tube and held in place by silanized quartz wool. The reactor was heated by a cylindrical 600 watt Omega Engineering, Inc. (Stamford, CA) ceramic furnace. The reactor was insulated by covering the furnace with glass wool and wrapping it with sheet metal. The furnace temperature was maintained by an Omega CN3002 programmable temperature controller and a J-type thermocouple. Catalyst temperatures were measured with a K-type thermocouple inserted at the bottom of the reactor as indicated in Figure 2.2.

Catalytic reaction product analyses were accomplished by using a Hewlett Packard 5890 gas chromatograph equipped with a flame ionization detector and a Chrompack 50 m KCl/Al₂O₃ capillary column. This column was selected because it readily separates C₁-C₅ hydrocarbon isomers. A 6-port injection valve (Valco, Inc) fitted with a 50 microliter sample loop was used to introduce reaction products into the gas chromatograph. Helium at a flow rate of 100 mL/min was used as the carrier gas. The gas chromatograph was operated in a split mode such that 6 ml/min were permitted to flow through the column. The GC oven was maintained at 80°C during *n*-butane conversion studies.

2.2 Variable Temperature Diffuse Reflectance Fourier

Transform Infrared Spectroscopy

A relationship between highly scattering solid material absorber concentration and diffusely reflected radiation intensity was discovered by Kubelka and Munk^[3]. For an

"infinitely thick" sample, the Kubelka-Munk (KM) equation for dilute absorbers can be written as :

$$f(R_{\infty}) = (1-R_{\infty})^2/2R_{\infty} = k/s = 2.303aC/s \quad [\text{Eq 2.4}]$$

where R_{∞} is the absolute reflectance of the sample, k is the absorption coefficient, s is the scattering coefficient, a is the absorptivity, and C is the concentration of the absorber.

In our studies, diffuse reflectance Fourier transform infrared spectra (DRIFTS) were acquired between 50 and 600°C. These spectra were converted to apparent absorbance format ($\log [1/R_{\infty}]$)^[4] before display. Apparent absorbance was chosen instead of the Kubelka-Munk format because spectra acquired at high temperature exhibited temperature-dependent baseline artifacts that severely distorted Kubelka-Munk spectra^[5]. Apparent absorbance is much less sensitive to spectral baseline offsets than the Kubelka-Munk format. Unfortunately, because apparent absorbance was employed, it was not possible to obtain quantitative information regarding catalyst surface adsorbed species because apparent absorbance is not a linear function of concentration. Instead, semi-quantitative measurements are reported here.

The apparatus used for infrared measurements was an FTIR spectrophotometer with a variable temperature diffuse reflectance attachment. Figure 2.3 shows the layout of the VT-DRIFTS apparatus. The spectrophotometer was a Mattson Instruments (Madison, WI) Sirius 100 equipped with a water-cooled Globar infrared source and a

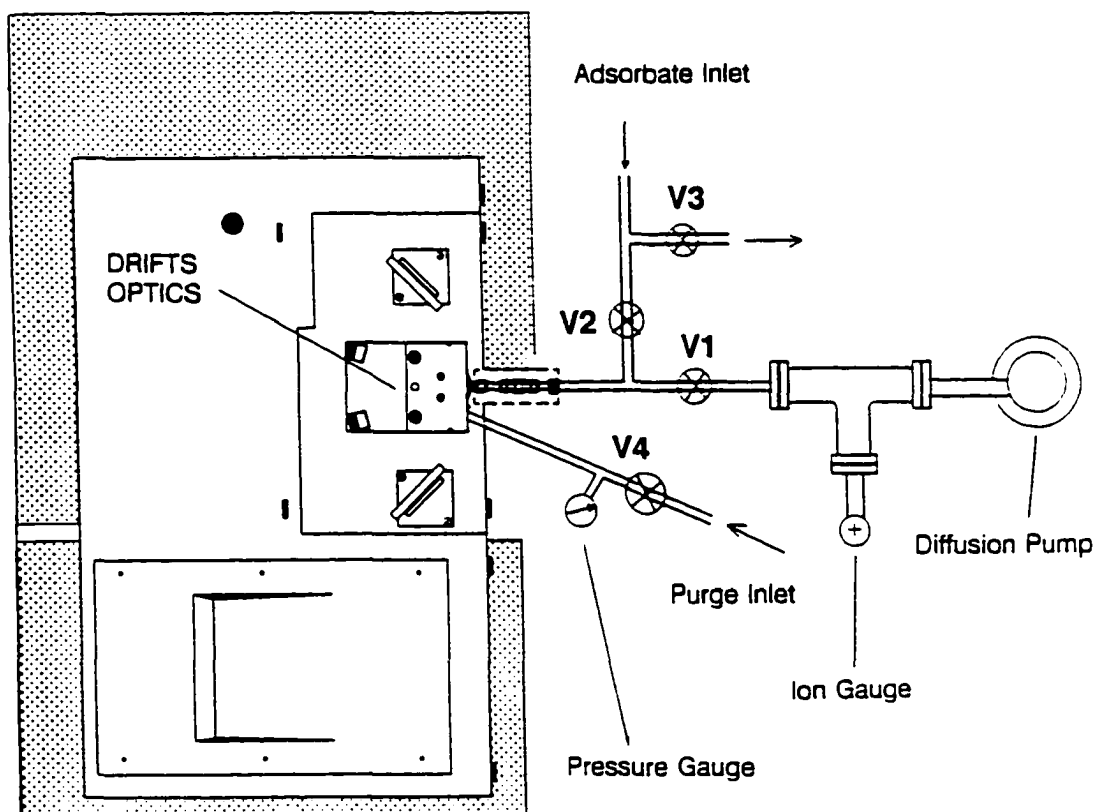
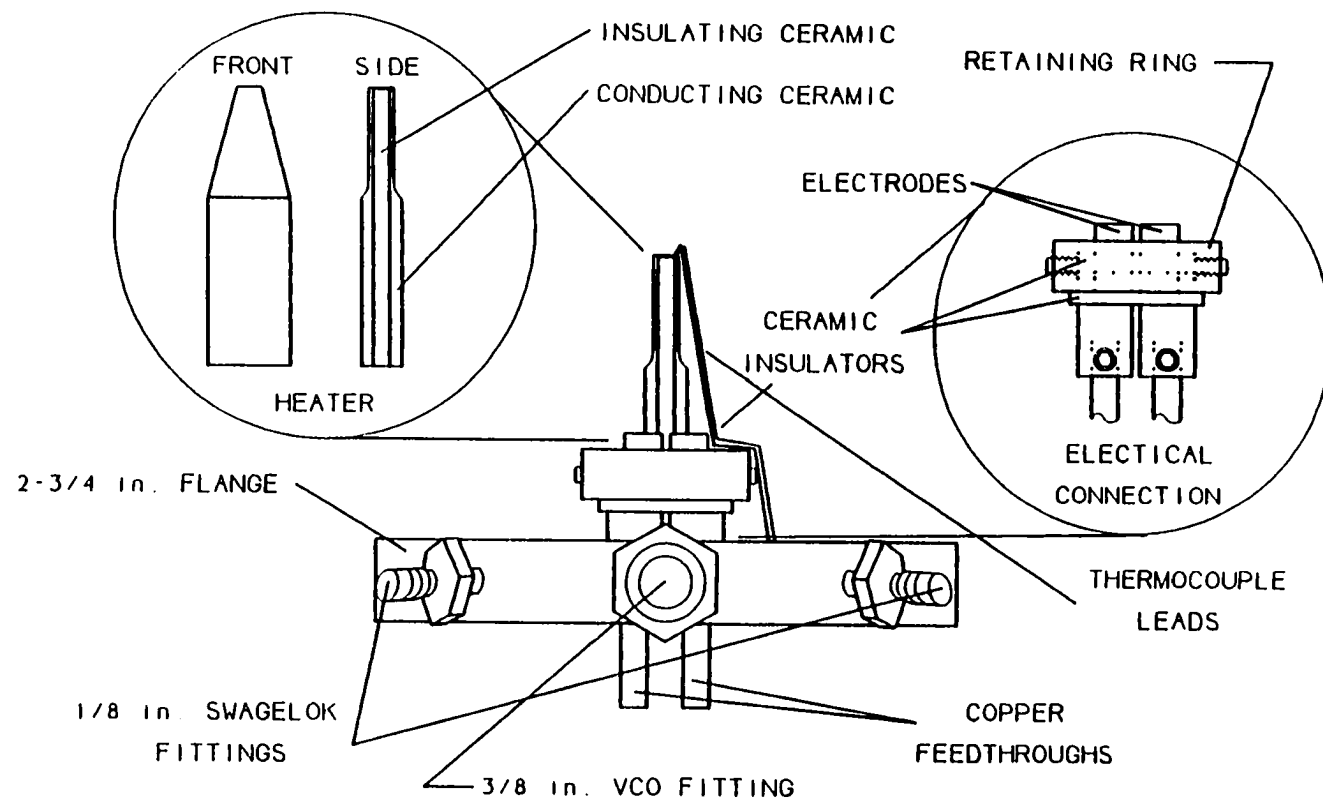


Figure 2.3 VT-DRIFTS and vacuum system layout

liquid nitrogen-cooled mercury-cadmium-telluride (MCT) photoconducting detector. A Harrick Scientific, Inc. (Ossining, NY) "praying mantis" diffuse reflectance accessory and a modified Harrick Scientific environmental chamber were used for diffuse reflectance measurements. A vacuum system was attached to the environmental chamber via the central port of the mounting flange. An Edwards High Vacuum Inc. (Grand Island, NY) E2 rough vacuum pump was used in series with a high vacuum diffusion pump to provide background pressures as low as 10^{-6} Torr. The environmental chamber mounting flange had two other ports (Figure 2.4). One of these ports was used as an inlet for helium purge to the chamber during VT-DRIFTS measurements. The other port was used to pass the fast response thermocouple into the environmental chamber. The thermocouple wires were hermetically sealed by using Master Bond Inc. (Hackensack, NJ) EP34CA high-temperature epoxy adhesive.

The original Harrick sample holder was replaced by a ceramic heater^[6] that was custom fabricated by Hitachi Research Laboratory (Hitachi-shi, Japan). Figure 2.4 shows the ceramic sample holder/heater and flange mount. A small indentation at the top of the ceramic heater served as the sample holder and was capable of holding about 15 mg of catalyst powder. Two copper feedthroughs were used to supply power to the ceramic heater and also served as mounting supports. The sample holder/heater was located at the focus of the FTIR infrared beam and diffusely reflected radiation was collected by the praying mantis accessory mirrors and focused onto the detector via the spectrophotometer optics. Catalyst sample temperatures were measured and maintained by using a 818p Eurotherm Controls, Inc. (Reston, VA) temperature controller. An

Figure 2.4 Diagram of the ceramic sample holder/heater



Omega Engineering Inc. CHAL-O1O fast response chromel-alumel thermocouple was imbedded in powdered catalysts to measure sample temperatures. A HVC-DRP stainless steel cover (Figure 2.5) was attached to the mounting flange by three bolts and a Viton o-ring. The stainless steel cover and the mounting flange constituted the sample environmental chamber.

During VT-DRIFTS measurements, the Eurotherm temperature controller was programmed to heat catalyst samples at rates of 10°C/minute and infrared spectra were measured at one minute intervals. Synchronization of the heating ramp and DRIFTS data acquisition was made possible by manually starting the temperature controller and the FTIR data acquisition system at the same time. High temperature FTIR measurements were prone to artifacts due to sample emission reflected back to the interferometer^[7]. These artifacts were eliminated by blocking one-half of the collimated beam exiting the interferometer. All reference spectra were acquired by using silver powder as a non-absorbing background. Sample and reference single beam spectra were measured over the same temperature range to minimize effects due to sample holder thermal expansion and blackbody radiation that would otherwise result in spectral artifacts.

The VT-DRIFTS apparatus shown in Figure 2.3 was designed to provide the capability of introducing volatile probe molecules to catalyst samples. This was achieved by connecting the environmental chamber to the vacuum line with a 1/2 inch Swagelok union tee. One branch of this tee was attached to a 1/4 inch stainless steel tube that was connected to the source of the volatile adsorbate. Three on/off valves were employed to isolate one line when the other two were used. For instance, by closing the valve

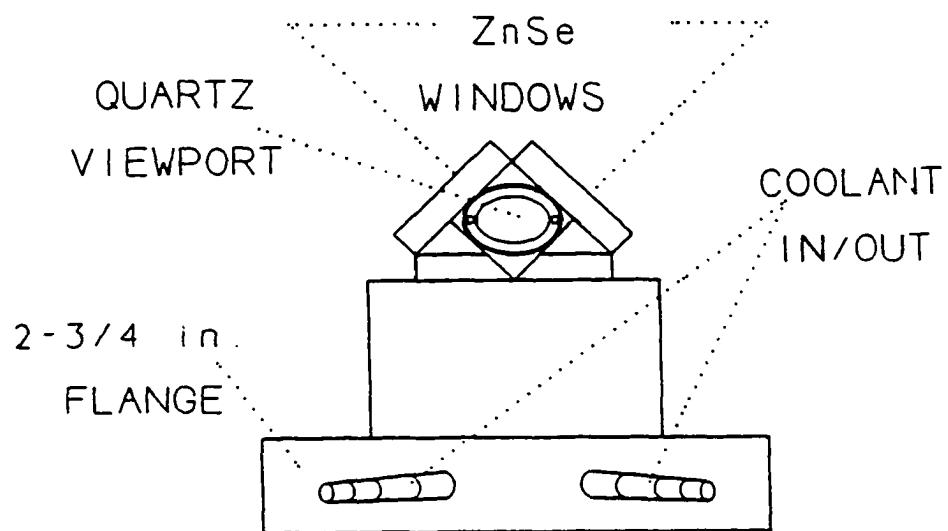


Figure 2.5 VT-DRIFTS environmental chamber cover

denoted V1 in Figure 2.3, it was possible to prevent volatile adsorbate loss to vacuum when adsorbate admission to the environmental chamber was desired. The room temperature vapor pressure of organic amines was sufficient to enable them to be introduced to catalyst samples. The HVC-DRP stainless steel cover and all system lines were heated to prevent volatile organics from adsorbing on metal surfaces. A variac was used to control the heaters and maintain a 120°C constant temperature. The environmental chamber was evacuated by using an Edwards High Vacuum rough pump. Adsorbates bound to catalyst surfaces were not removed by this procedure. During VT-DRIFTS measurements, the environmental chamber was continuously purged with helium at a rate of 10 mL/min. Helium purge gas was passed through an Alltech (Deerfield, IL) gas purifier to remove contaminants.

The Sirius 100 FTIR was operated via an IBM compatible computer. Typically, DRIFTS spectra were acquired over a 4000-800 cm^{-1} range at 8 cm^{-1} resolution. The Mattson Instruments (Madison, WI) "FIRST" Macros software enabled the computer to collect, process, and store spectra. A program called "SAMCOL", written by R.L. White (Norman, OK), was used to acquire and store multiple spectra while the catalyst sample was heated. Structure specific bands were profiled and plotted by using Trimetric (Seattle, WA) "AXUM" software.

2.3 Thermogravimetry-Mass Spectrometry

Thermogravimetry (TG) coupled with mass spectrometry (TG-MS) was used for thermal studies of catalysts and for analyses of species evolved during temperature

programmed desorption of probe molecules adsorbed on catalyst surfaces. Thermogravimetry is a thermal analysis method in which sample mass changes are measured as a function of temperature. TG alone does not provide information concerning the identities of products evolved from catalysts. However, TG-MS can provide structural information regarding specific volatile species^[8].

A DuPont (Wilmington, DE) 951 thermogravimetric analyzer was used to measure sample mass changes that occurred as a function of temperature. Figure 2.6 shows a schematic of the TG analyzer. The analyzer was composed of an aluminum housing that contained an electromagnetic balance meter movement assembly. On one side of the aluminum housing was fitted a quartz furnace tube enclosed in a 500 W furnace. A glass chamber that housed tare weights was attached to the other side of the aluminum housing. The furnace could be operated from ambient temperature to 1200°C and the balance could accommodate sample sizes in the range of 0.020 to 400 mg. Measurements made with an empty sample pan revealed that the instrument peak-to-peak noise for mass measurements was about 0.0025 mg. Catalyst samples were loaded on platinum sample pans suspended on a horizontal quartz rod that was connected to the balance meter movement. Sample temperatures were monitored by a thermocouple placed near the sample pan. A 50 mL/min helium purge was used to remove volatiles from heated samples. Originally, the purge gas was introduced into the sample chamber through an inlet in the aluminum balance chamber. A new design allowed the purge gas to be introduced axially through the tare weight chamber. Helium purge gas flow rates were controlled by using an Edwards High Vacuum (Grand Islands, NY) type 825 mass

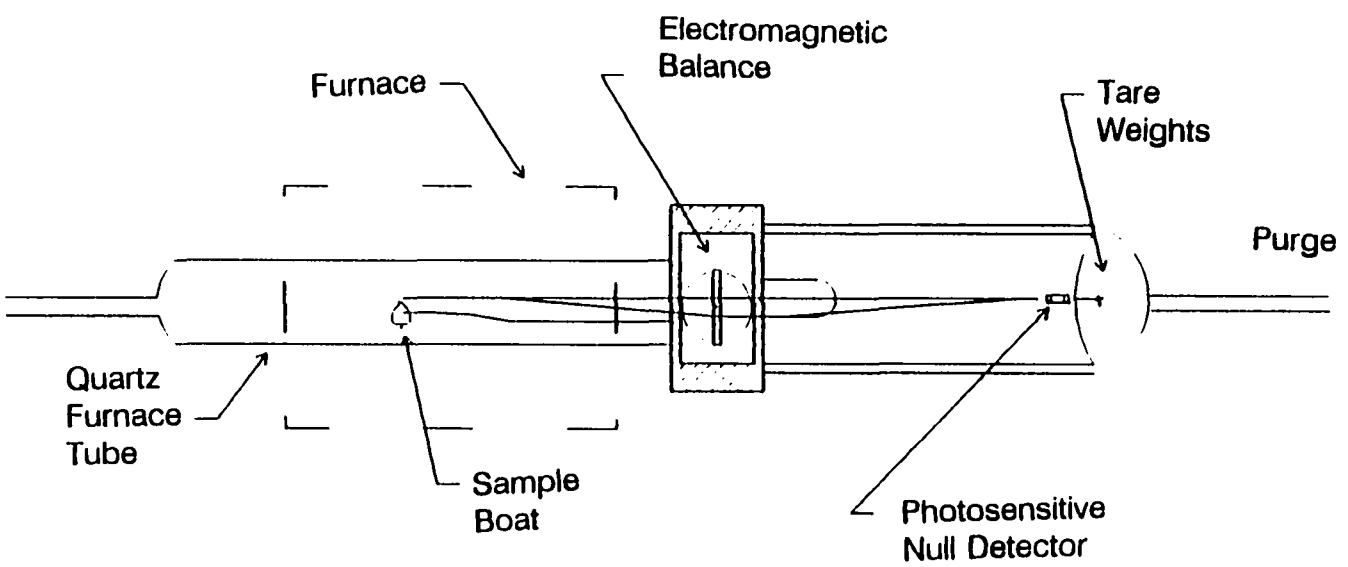


Figure 2.6 Thermogravimetric balance

flow controller in combination with a Model 1605 digital display controller unit. Volatile products were analyzed by using a Hewlett Packard (Palo Alto, CA) 5985 quadrupole mass spectrometer. The spectrometer was equipped with an electron impact/chemical ionization ion source, a quadrupole mass filter, and a Galileo channeltron electron multiplier detector. Sample ionization was accomplished by operating the ion source in the electron impact mode at 70 eV. Two Edwards High Vacuum, Inc. E2M8 rough pumps and two Edwards Diffvak diffusion pumps were used to maintain a background pressure of about 10^{-7} Torr in the ion source chamber. One of the diffusion pumps was a model 160 with a pumping capacity of 805 liters/second. The other diffusion pump was a model 63 with a pumping capacity of 150 liters/second.

The mass spectrometer was calibrated every morning by introducing perfluoro-tert-butylamine (PFTBA) calibrant through a direct insertion probe (DIP). The PFTBA ion source pressure was adjusted to 5×10^{-6} Torr and satisfactory performance of the mass spectrometer was assessed in terms of the peak shapes, widths, and relative abundances of selected ion signals. Table 2.1 lists the relative abundances of some PFTBA ions used for calibration. When necessary, ion source voltages were adjusted until the relative ion abundances listed in Table 2.1 were achieved before catalyst studies were initiated.

Table 2.1 PFTBA Selected Ion Relative Abundances

m/z	69	131	219	502
Relative Abundance (%)	100	48	51	2.6

Figure 2.7 shows a diagram of the TG-MS apparatus layout. Introduction of evolved products into the mass spectrometer was facilitated by connecting the TG quartz tube to the mass spectrometer ion source via a Scientific Glass Engineering, Inc (Austin, TX) MCVT-150 splitter valve. Figure 2.8 shows a diagram of the interface. A Swagelok 1/4 inch to 1/16 inch reducing union was used to connect the quartz furnace tube and the splitter valve. The function of the splitter valve was to isolate the MS ion source during TG sample changing and to adjust the TG effluent flow rate into the MS ion source.

To avoid volatile product condensation during transport from the TG to the mass spectrometer, the interface was enclosed in an aluminum oven heated by two 1 inch x 10 inch 100 watt strip heaters. Unless otherwise stated, the interface was maintained at 200°C by using an Omega Engineering, Inc. CN-76000 temperature controller. The interior of the aluminum oven was insulated with glass fiber and a model 85000C fan (Pamotor, CA) was used to attain uniform heating.

The thermogravimetric analyzer was controlled by an IBM personal computer equipped with a Dupont (Willmington, DE) "Analyst 2000" operating system. The data system controlled heating programs and displayed sample mass changes and temperatures in real time. Samples were typically heated at a rate of 10°C/min. At the end of each measurement, information regarding elapsed time, sample temperature and instantaneous mass were saved in a TG data file.

Mass spectrometric data collection was facilitated by using a Teknivent (St. Louis, MO) Vector One data acquisition system installed on an IBM compatible personal

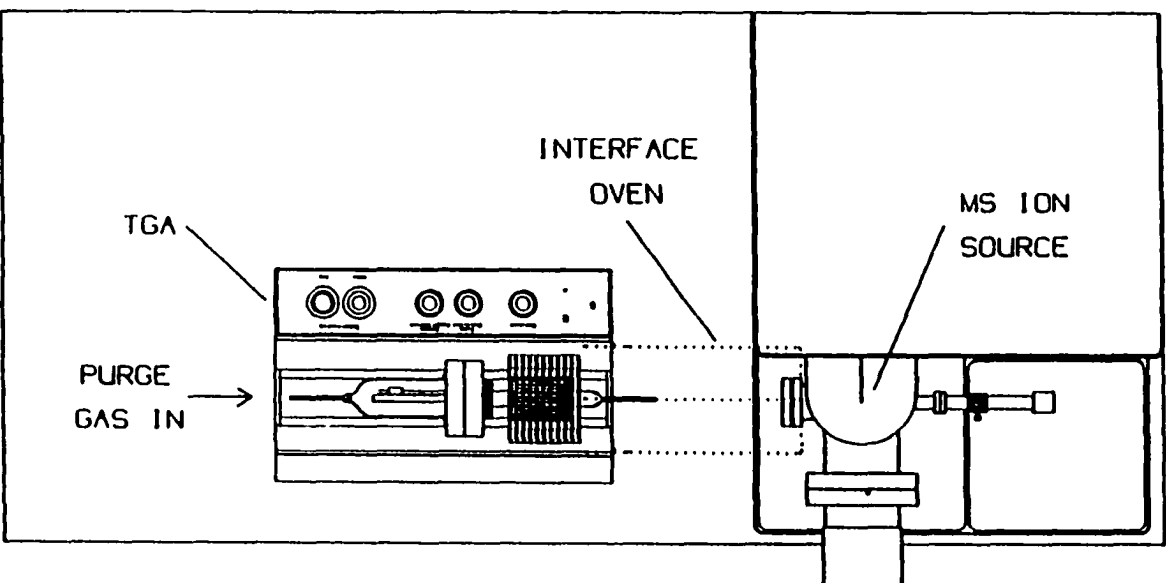


Figure 2.7 TG-MS Layout

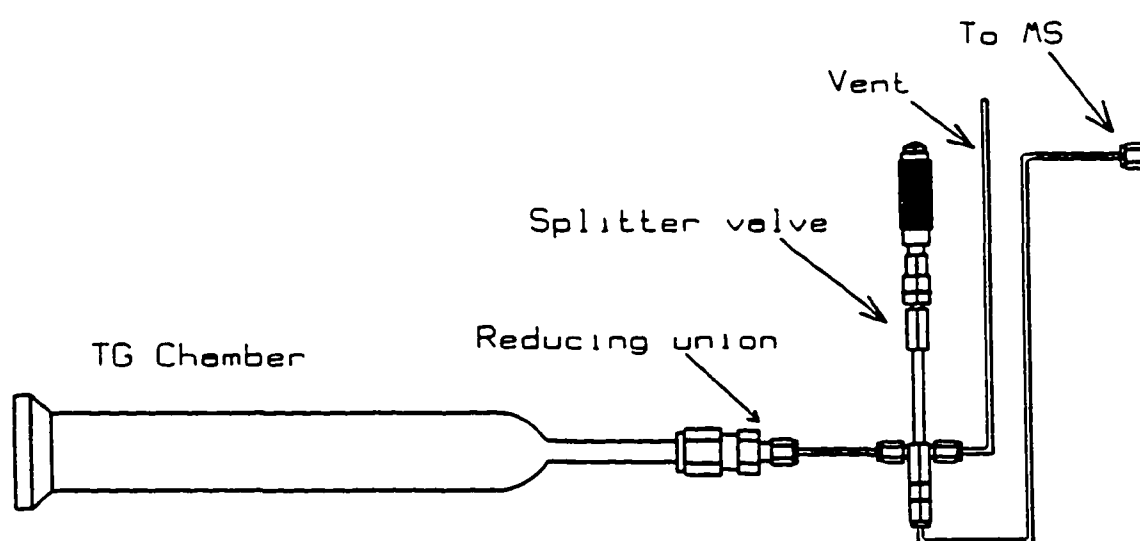


Figure 2.8 TG-MS Interface

computer. The software permitted acquisition and display of mass spectral data in real time. Mass spectra were typically obtained by scanning from m/z 10 to m/z 250 at 10.131 seconds/stored data file. Elapsed time, scan number, and ion abundances were automatically stored in a data file during measurements. No means of combining TG and MS data acquisition was available. Instead, each data system was manually started at the same time so that correlation between detected volatile species and TG mass loss information could be achieved by comparing elapsed times. Ion abundances versus temperature profiles for specific fragment ions were generated after converting scan numbers to corresponding TG sample temperatures. Mass spectral searches employed a 38,000 spectra NBS library.

2.4 Thermogravimetry-Chromatography/Mass Spectrometry

Thermogravimetry is an important analytical tool for materials characterization. TG mass loss information is often augmented by attaching evolved gas analyzers to the thermobalance purge exit. Mass spectrometry^[9-13] and infrared spectrophotometry^[14-16] are commonly employed TG evolved gas analyzers. Although these analyzers provide structural information regarding volatiles generated during TG analysis, species-specific evolution profiles can only be obtained when mass spectral or infrared spectroscopic features can be correlated with individual substances in TG evolved gas mixtures. To facilitate species-specific analysis when unique spectroscopic features are unavailable, gas chromatographic separations^[17-19] and tandem mass spectrometry^[20] have been employed with TG. Gas chromatographic separations have typically been used to separate TG

effluent components that were cryogenically trapped during TG analysis. Species-specific evolution profiles are difficult to obtain by this method because it is difficult to repetitively trap and separate volatiles during a single TG analysis. Species-specific evolution profiles are readily obtained by rapid scanning tandem mass spectrometry. However, simultaneous measurements of evolution profiles for many volatile products is difficult to achieve by this technique.

In the present work, TG effluent usually contained mixtures. Most often effluent mixtures consisted of hydrocarbon homologs and isomers that could not be identified by mass spectrometry alone. It was therefore necessary to modify our TG-MS interface by adding gas chromatographic separation prior to mass analysis. In designing the TG-GC/MS interface, our purpose was to achieve chromatographic separations of TG evolved gas mixtures repetitively while volatile products were removed from catalyst surfaces. Figure 2.9(a) shows a typical TG weight loss curve obtained by TG-MS. Mass spectra obtained at two points during the course of the experiment are shown in Figure 2.9(b,c). The mass spectra are different, confirming that the volatile products evolved from the sample were different at the indicated temperatures. Unfortunately, these mass spectra cannot be assigned to specific products but rather represent mixtures. TG effluent trapping followed by GC/MS analysis could have been used to separate mixture components. However, this would not have permitted measurements of species-specific temperature profiles. Only real time separation and analysis can provide such information.

McClennen *et al*^[18] recently described TG-GC/MS and TG-GC/IR systems that

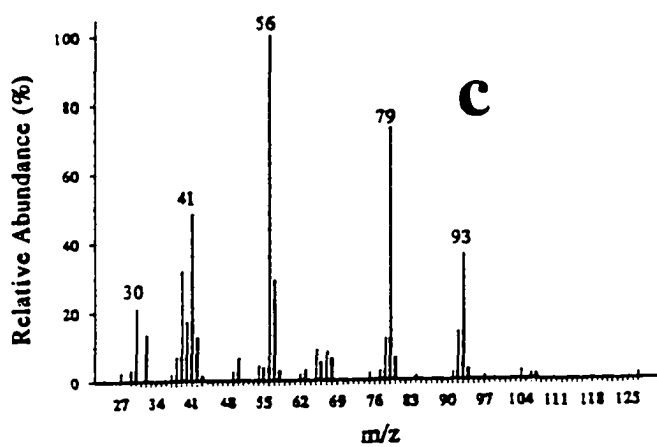
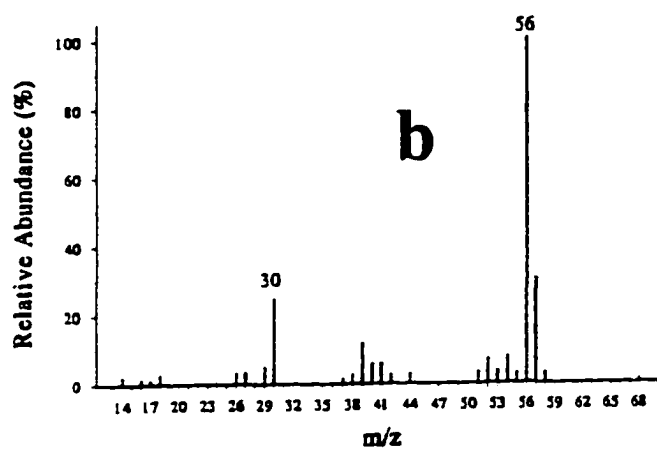
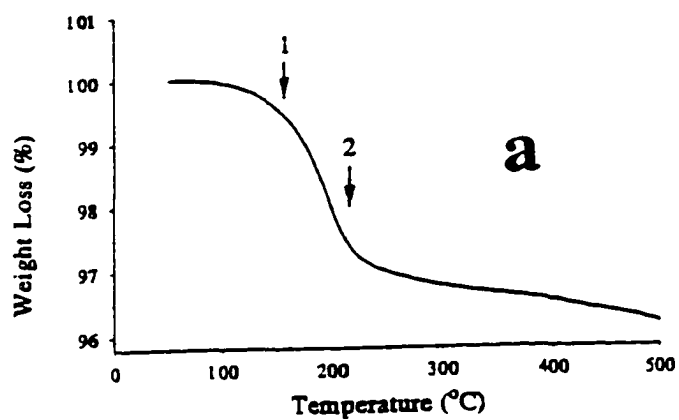


Figure 2.9 TG-MS results: (a) TG weight loss curve, (b) mass spectrum obtained at point #1, (c) mass spectrum obtained at point #2

incorporated automated vapor sampling and short chromatographic columns and provided both satisfactory gas chromatographic separations and species-specific evolution profiles. Isothermal chromatographic separations could be repeated at one minute intervals during TG analysis by using their system. Although the TG-GC/MS apparatus described by McClennen *et al* represents a significant advance in the state-of-the-art of evolved gas analysis, it is limited to isothermal chromatographic separations and column flow rates are not easily varied. We designed a new TG-CC/MS interface that provides rapid temperature programmed gas chromatographic analysis and permits repetitive effluent separations during a single TG analysis^[21].

A diagram of the interface and the gas chromatograph is shown in Figure 2.10. The interface was contained within a 30 cm x 25 cm x 15 cm aluminum oven. An opening was made on one side of the oven to accommodate the mass spectrometer inlet flange. On the opposite side, a 1/2 inch diameter hole permitted the end of the TG quartz tube to enter the interface oven. Glass fiber was used to insulate the oven interior. To minimize cold spots and avoid effluent condensation during transfer of TG effluent to the mass spectrometer, all transfer lines and valves were placed inside the interface oven and maintained at elevated temperature. The interface oven was heated by two 3 inch x 10 inch 500 watt strip heaters and the temperature was adjusted and maintained by an Omega (Stamford, CT) CN 76000 temperature controller. A Valco Instruments (Houston, TX) 4C8T eight port injection valve, equipped with two 100 microliter stainless steel sample loops, was held in place through a 3/4 inch diameter opening drilled in the top of the oven. The TG quartz furnace tube extended into the

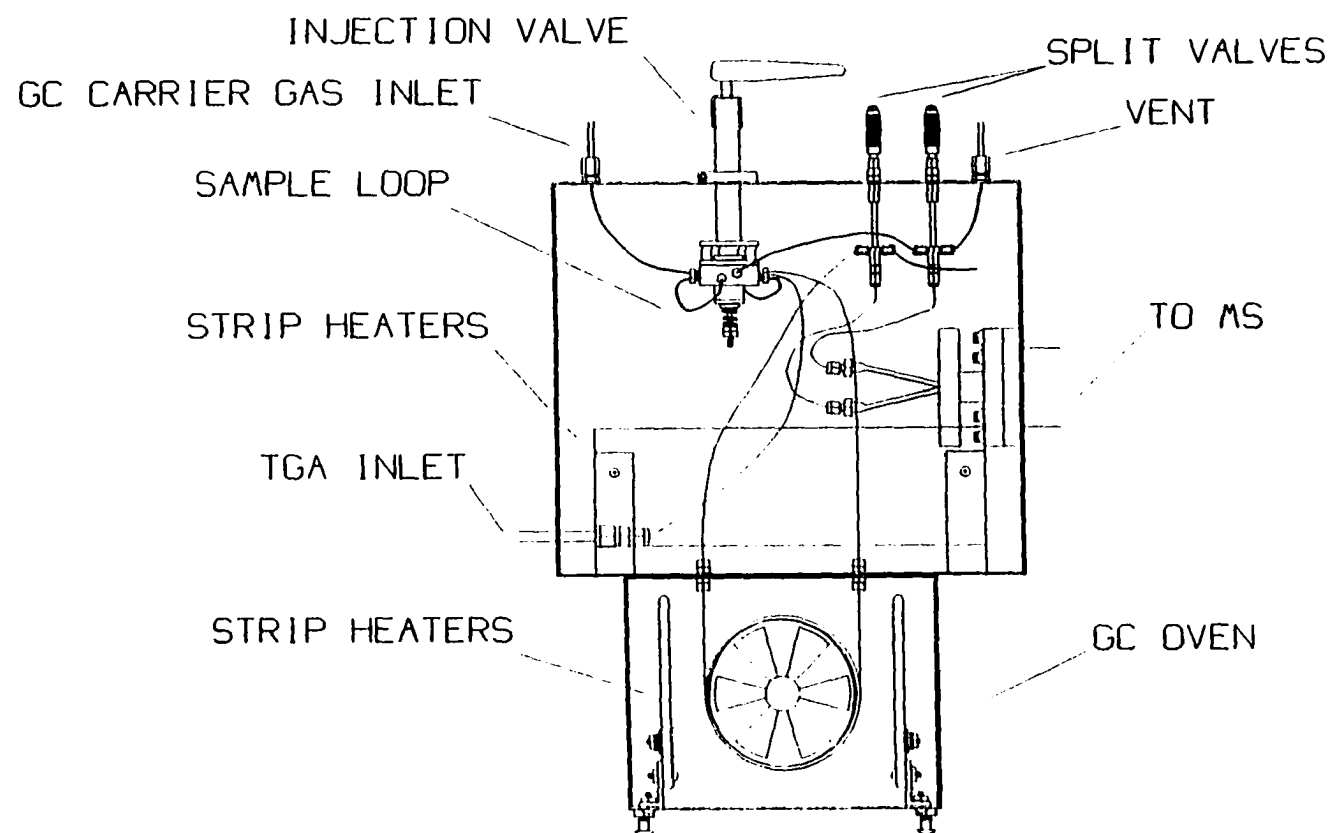


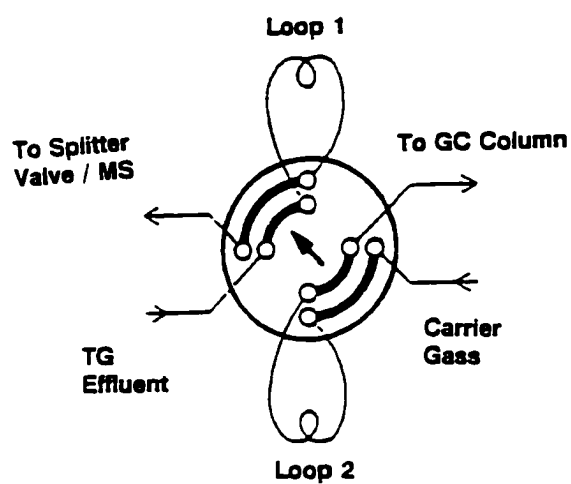
Figure 2.10 TG-GC/MS Interface

interface oven and was connected to the injection valve by a 1/16 inch o.d. stainless steel tube via a Swagelok reducing union. Two holes were drilled in the top of the oven and were used to attach two Swagelok bulkhead unions, one of which served as the GC carrier gas inlet and the other was used as a vent for TG effluent. Two SGE (Austin, TX) MCVT-1-50 effluent splitter valves were attached to two additional openings. One splitter valve was connected to the TG effluent exit port of the injection valve and the other was connected to the GC column exit. Short pieces of 0.332 mm o.d. uncoated fused silica tubing were used to connect the splitter valves to the mass spectrometer entrance flange.

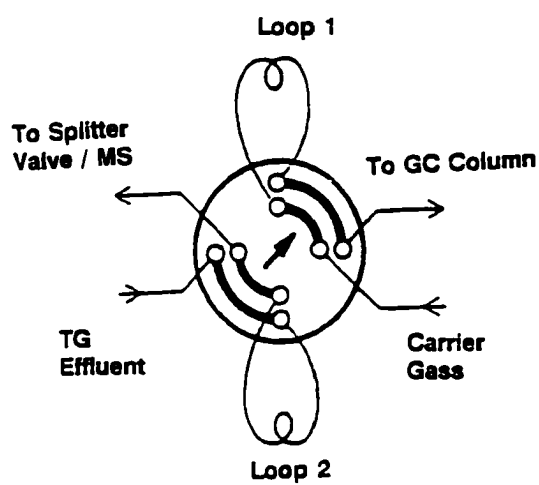
The gas chromatographic oven was a 20 cm x 16 cm x 15 cm aluminum box attached to the bottom of the interface oven by 2 Swagelok bulkhead unions through which the GC column was passed. The GC oven was heated by two strip heaters and temperature was adjusted and maintained by using an Omega CN3202 temperature controller. A 10 m x 0.314 mm DB-5 capillary gas chromatography column with 0.25 μm stationary phase film thickness was installed in the GC oven. One end of the GC capillary column was connected to the injection valve and the other end was connected to the mass spectrometer through the SGE effluent splitter valve in the interface oven. For TG-GC/MS analyses, TG sample heating rates were 10°C/min, the TG helium purge gas flow rate was 25 mL/min, and the GC column flow rate was 2 mL/min. The TG-GC/MS system was designed so that the GC could be bypassed to also permit TG-MS analyses. During analyses, the TG effluent entering the eight port valve passed through a 100 μL stainless steel sample loop and subsequently passed through a 1/16 inch o.d.

stainless steel tube to a splitter valve and then to an exit at the top of the interface oven. For TG-MS analyses, the splitter valve was opened until the ion source pressure was approximately 2×10^{-5} Torr and mass spectra were acquired by using the procedures described in the previous section. For TG-GC/MS analyses, the effluent splitter valve attached to the GC column was opened until the column flow rate measured at the exit on top of the interface oven was reduced to nearly zero. This established a near direct couple interface between the capillary gas chromatograph column and the mass spectrometer ion source. TG effluent was injected into the gas chromatograph column by manually rotating the eight port injection valve, which switched the 100 μ L sample loop containing TG effluent to the gas chromatograph carrier gas stream. At the same time, the 100 μ L sample loop that had been in line with the gas chromatograph column was switched to the TG effluent stream. Figure 2.11 is a diagram of the injection valve showing its two positions.

The TG-MS and TG-GC/MS apparatus described here were used to study temperature programmed desorption (TPD) of species adsorbed on catalyst surfaces. Figure 2.12 shows a schematic diagram of the vacuum/inlet system used for TPD experiments. The purge inlet on the TG balance housing was modified to permit introduction of volatile probe molecules to TG samples. A 6 inch long, 1/4 inch o.d. stainless steel tube was attached to the TG inlet by a Whitey (Highland Heights, OH) ball valve (V3). The purpose of the ball valve was to isolate the TG from the adsorbate source during analyses. The other end of the stainless steel tube was connected to a Swagelok union tee. One branch of the tee was connected to an Edwards High Vacuum



a



b

Figure 2.11 Two-position sample injector flow paths

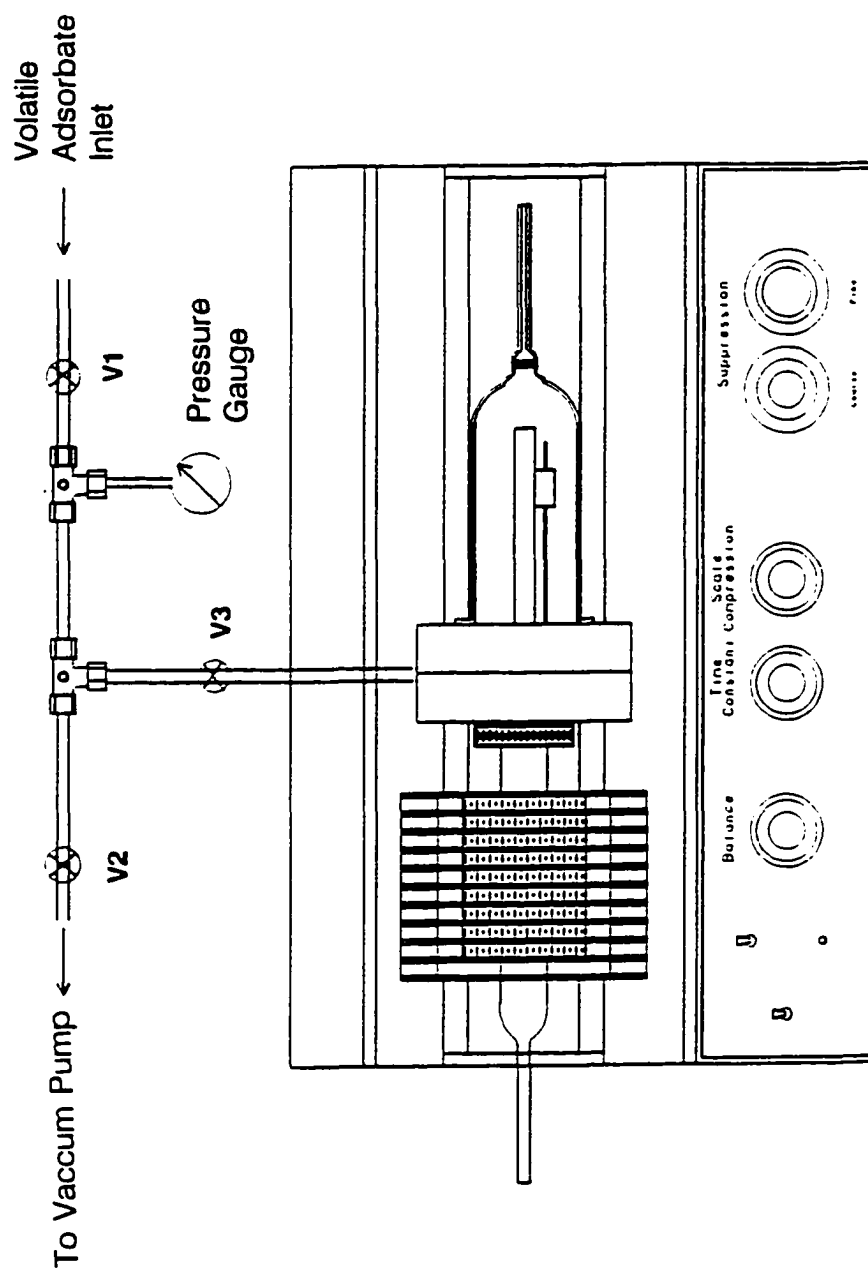


Figure 2.12 TPD adsorbate inlet system

EM2 pump and the other arm was connected to the adsorbate source. The pump facilitated chamber evacuation to near 10^{-1} Torr. An Edwards High Vacuum pressure gauge was used to monitor the adsorbate pressure inside the sample chamber during adsorbate loading. The adsorbate source was a pressurized lecture bottle for NH_3 and CO or a 3 inch long, 1/4 inch o.d. glass tube for liquid adsorbates. Lecture bottles were connected to the vacuum system by a 1/8 inch o.d. copper tube. The glass tube containing liquid adsorbates was held in place by an Ultratorr fitting. The ball valves denoted by V2 and V3 in Figure 2.12 permitted the TG sample chamber to be evacuated during catalyst sample pretreatment. During adsorbate introduction, ball valves V1 and V3 were opened and the vacuum line was shut off by closing ball valve V2.

2.5 Pyrolysis-Gas Chromatography/Mass Spectrometry

Pyrolysis was used to rapidly remove adsorbates at selected temperatures. The pyrolysis-GC/MS apparatus used for studies described here comprised a microfurnace pyrolyzer^[22] and a Hewlett Packard 5988 GC/MS. Figure 2.13 shows the components of the microfurnace pyrolyzer. The furnace was a 1.5 inch long, 1/4 inch o.d. stainless steel tube. A 40 mm x 2 mm quartz tube flared at its top, in which sample desorptions and reactions took place, was inserted inside the stainless steel tube. Cotronics (Brooklyn, NY) ceramic tape was wrapped around the stainless steel tube. Furnace heating was facilitated by passing current through a coil of 1 mm diameter nichrome heater wire tightly wound around the ceramic tape. A variac was used to control the

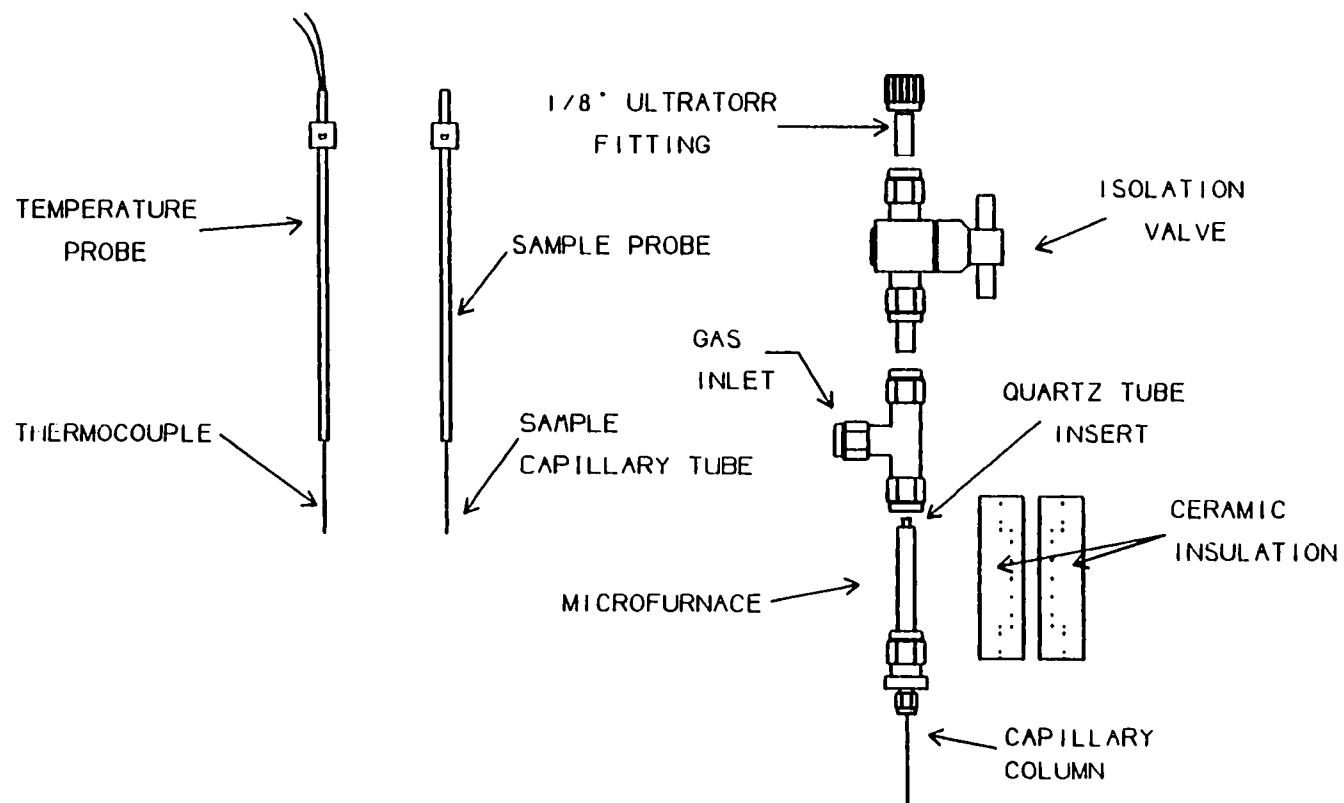


Figure 2.13 Microfurnace pyrolyzer

current through the nichrome wire. The stainless steel tube wrapped with nichrome wire was insulated by inserting it into a 3 inch x 1.5 inch x 1.5 inch ceramic block. A Swagelok 1/4 to 1/16 inch reducing union was welded to the bottom of the furnace tube and was used to attach a gas chromatographic column. A 50 m x 0.32 mm i.d. fused silica bonded-phase column with a 0.52 μm crosslinked methyl silicone gum stationary phase was inserted into the reducing union through a graphite ferrule until it was just inside the quartz tube. The top of the stainless steel microfurnace tube was attached to a stainless steel union tee via a Swagelok fitting. Helium GC carrier gas was introduced through this tee and the other end of the tee was attached to a Whitey Co. isolation ball valve. A Cajon Co. (Macedonia, OH) 1/8 inch Ultratorr fitting was attached to the isolation ball valve and served as the sample introduction port. The microfurnace assembly was mounted vertically on top of a Hewlett Packard 5890A gas chromatograph and the stainless steel reducing union was inserted into the GC through a hole provided for an injection port. The entire assembly was held in place by stainless steel brackets clamped around the ceramic insulation block that were attached to the gas chromatograph by screws. The GC column exit was inserted into the ion source of an HP 5988 quadrupole mass spectrometer through a heated interface.

The pyrolysis sample probe was a 6 inch long, 1/8 inch o.d. ceramic tube sealed on one end and partially filled with ceramic cement. A catalyst sample to which adsorbates had been added was loaded into a glass capillary tube sealed on one end. The open end was then heat drawn by using a Bunsen burner. A pinhole was made in the drawn end so that reaction products could escape when the tube was heated and catalyst

powder was tapped into the drawn end of the tube. The sealed end of the capillary tube was then inserted into the ceramic tube. Teflon tape was wrapped around the capillary tube to achieve a tight fit. Before sample introduction, the furnace temperature was measured by inserting an 8 inch long, 1/8 inch o.d. Omega Engineering, Inc. thermocouple through the Ultratorr fitting and into the microfurnace. Microfurnace temperatures were displayed by a Model 115KC digital thermometer connected to the thermocouple. By moving the thermocouple up and down inside the microfurnace, the furnace location corresponding to the maximum temperature was determined and an aluminum collar fitted around the thermocouple probe was tightened to mark this position. This distance (about 14-15 cm) was transferred to the sample probe by tightening an aluminum collar on the sample probe at the same distance from the sample tip. Before sample introduction, the sample probe was inserted into the Ultratorr fitting and isolation ball valve. The microfurnace assembly was then evacuated and subsequently purged with helium to remove air. Sample injection was made by slightly loosening the Ultratorr fitting and rapidly pushing the probe into the microfurnace until the metal collar was stopped by the top of the Ultratorr fitting. Volatile products were then transferred to the capillary GC column. Chromatographic separations were accomplished with a helium carrier gas flow rate of 1.2 mL/min. and a 10°C/min. column heating rate from 30 to 150°C was employed for GC separations. Mass spectra were acquired at a rate of 2.30 seconds/data file from m/z 10 to m/z 200.

2.6 Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) is useful for studying the thermodynamics of thermal processes^[23]. DSC was employed to study sulfated zirconia crystallization processes. A Dupont (Wilmington, DE) 910 differential scanning calorimeter equipped with a TA Instruments (Wilmington, DE) low pressure DSC cell was utilized for measurements. DSC samples were heated from ambient temperature to 700°C and helium flow through the cell during measurements was maintained at a rate of 25 mL/min. Catalyst samples were encapsulated in aluminum sample pans and typical sample sizes ranged between 0.5 and 10 mg. The DSC instrument was calibrated daily by using a 10 mg indium standard. The 156.6°C indium melting point was used to calibrate the DSC temperature. The DSC module was controlled by the same data acquisition system that was used to operate the DuPont TG analyzer.

2.7 Data Reduction

Several computer programs written by R.L. White (Norman, OK) were used for data reduction and file conversions. The "IRFIT" program was a curvefitting algorithm that was used to deconvolve overlapping infrared absorbance bands so that functional group specific temperature profiles could be obtained. After curvefitting, individual band intensities were plotted as a function of temperature. The "IR-AXUM" program converted deconvolved infrared band information to ASCII files that could be plotted by using the "AXUM"TM software. The "TMSFIT", "TMSMAKE" and "TMSLIST"

programs were used to analyze TG-MS data, to reconstruct TG-MS ion signal temperature profiles from mass spectral data, and to generate a list of ion signal peak temperatures and integrated ion signal areas, respectively. The "MS-AXUM" program was used to convert TG-MS data files to ASCII format so that plots could be made by using the "AXUMTM" software.

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CHAPTER THREE

CATALYST SYNTHESIS AND ACTIVITY MEASUREMENTS

In this chapter, methods used to prepare sulfated zirconia catalyst samples are described along with *n*-butane isomerization catalyst activity measurements obtained by using a microcatalytic reactor.

3.1 Catalyst Preparation Methods

Figure 3.1 summarizes the different routes that have been successful for preparing sulfated metal oxides. Most methods involve the use of metal hydroxides^[1,2]. However, it is possible to synthesize catalysts directly from oxides. Sulfur dioxide and hydrogen sulfide have been used to make sulfated metal oxides but the synthetic procedure must include calcination in oxygen. Alternatively, sulfuric acid, sulfur trioxide, and ammonium sulfate can be used in non-oxidative atmospheres. The sulfated metal oxide preparation method can determine catalyst surface areas and activities. For instance, catalysts prepared from metal hydroxides have been found to have greater surface areas than catalysts derived from metal oxides.

Methods used for preparing sulfated zirconia can be categorized as one or two

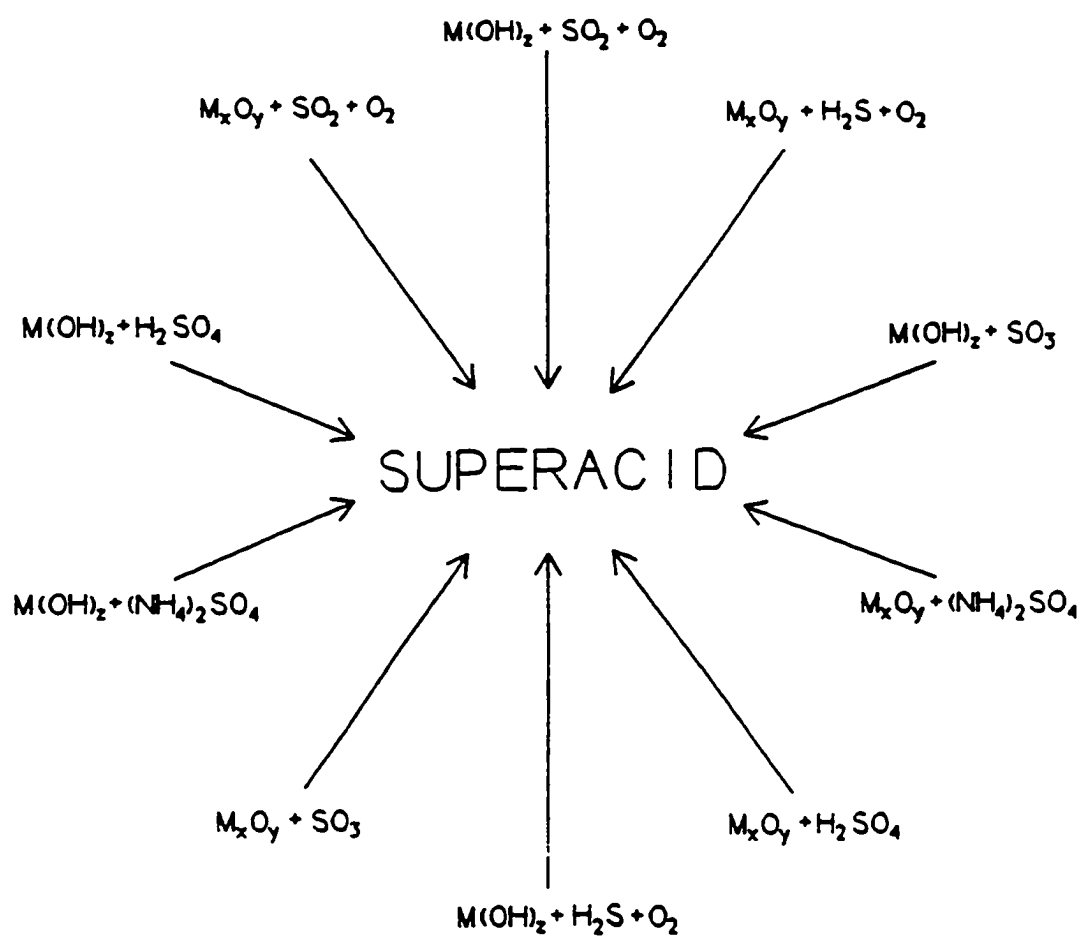


Figure 3.1 Sulfated metal oxide preparation methods

step methods^[3]. An example of the one-step method is the thermal decomposition of $\text{Zr}(\text{SO}_4)_2$ ^[4]. This method, although simple, has the disadvantage that it does not allow adequate control of final sulfate content. A "sol-gel" method is another one-step method that has been employed to prepare sulfated metal oxides^[5]. The sol-gel method for sulfated zirconia synthesis uses zirconium n-propoxide mixed with n-propanol to which nitric acid and sulfuric acid are added. The mixture is then stirred until a gel is formed. The "alcogel" is aged for 2 hours at room temperature and then the alcohol is removed supercritically by using CO_2 . Subsequent calcination removes organic impurities and yields sulfated zirconia catalyst. During zirconia crystallization, sulfate ions initially trapped in the bulk of the alcogel are expelled to the surface and transformed into catalytically active species.

The two-step method illustrated in Figure 3.2 is the most frequently used method for sulfated zirconia preparation^[6-10]. In the first step, zirconium hydroxide is precipitated from a zirconium salt solution. ZrOCl_2 , $\text{ZrO}(\text{NO}_3)_2$, ZrCl_4 and $\text{Zr}(\text{OC}_3\text{H}_7)_4$ are commonly used as zirconium salt solution sources. Aqueous ammonia and urea have been employed to precipitate zirconium ions as $\text{Zr}(\text{OH})_4$. Davis *et al*^[7] reported that the zirconium salt utilized to prepare $\text{Zr}(\text{OH})_4$ had a significant impact on the crystal phase obtained during calcination. Tetragonal zirconia was obtained regardless of the preparation procedure when $\text{Zr}(\text{OH})_4$ was prepared from ZrOCl_2 whereas other zirconium sources produced both the tetragonal and monoclinic forms. Sulfate is added to the zirconium hydroxide in the second step. Initially, sulfuric acid was used as the sulfating agent, but ammonium sulfate has been found to work equally well^[11]. If transition metal

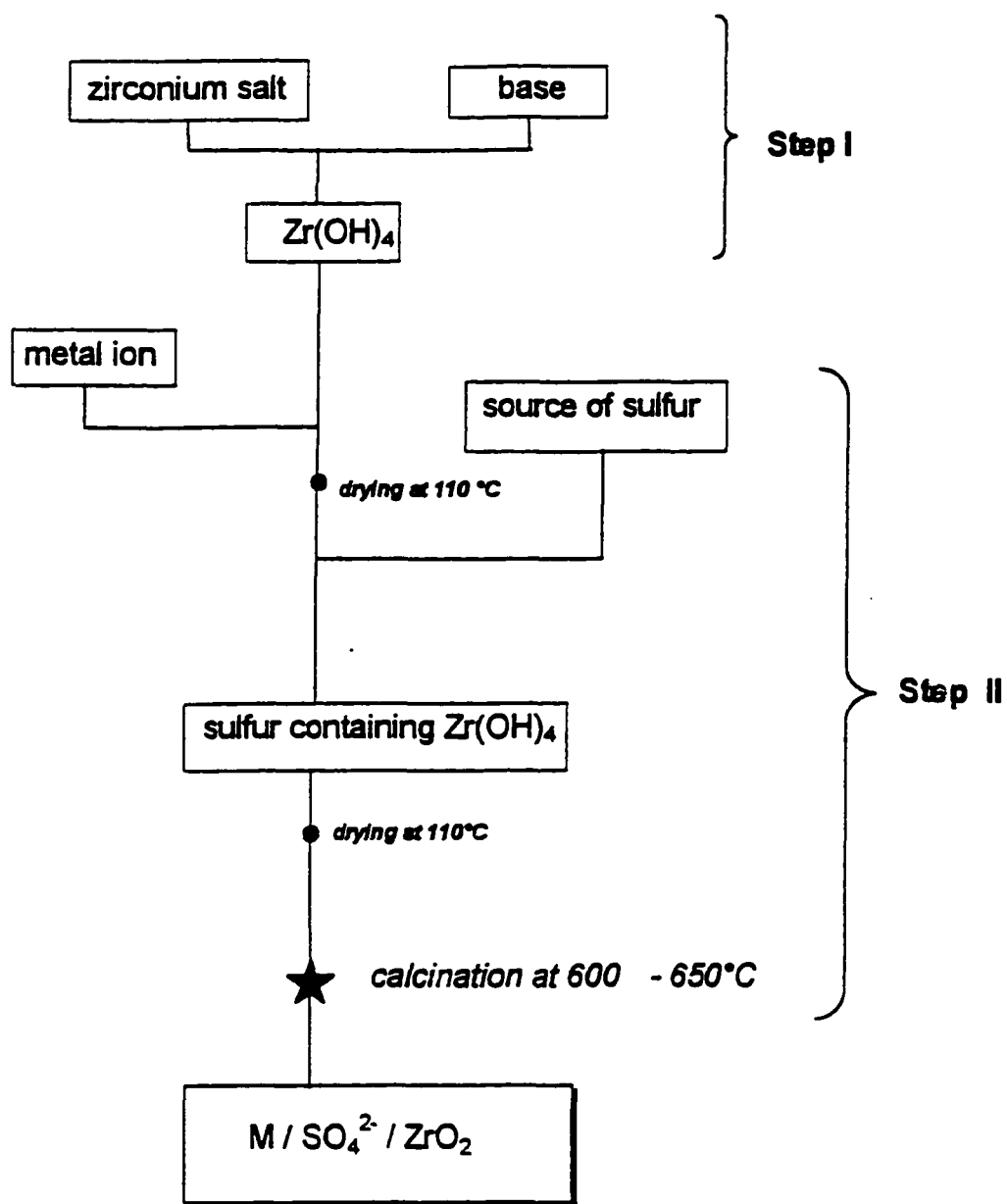


Figure 3.2 Sulfated zirconia preparation methods

promoters are to be included in the catalyst, they can be added as nitrate salt solutions to sulfate containing $\text{Zr}(\text{OH})_4$. Calcination of the resulting mixture yields the catalyst. Calcination conditions can be adjusted to change the final sulfate content of the catalyst.

Materials and Stock Solutions. All chemicals were reagent grade and were obtained from Aldrich (Milwaukee, WI). Zirconium hydroxide was precipitated from a 0.5 M solution of zirconium tetrachloride by dropwise addition of NH_4OH solution. The precipitate was washed and then dried at 110°C . The dried $\text{Zr}(\text{OH})_4$ was stored and used for preparing all sulfated zirconia catalysts described in this work. Ammonium sulfate was used as the sulfating agent. A solution of ammonium sulfate was prepared by dissolving $(\text{NH}_4)_2\text{SO}_4$ in distilled water to make a 1.0 M stock solution. Solutions of iron nitrate, nickel nitrate and manganese nitrate were prepared by dissolving the solids in distilled water to make 0.1 M solutions of Ni^{2+} and Fe^{3+} and a 0.05 M solution of Mn^{2+} .

Catalyst Preparation. To ascertain the effects of synthesis conditions on catalyst properties, sulfated zirconias were made in a variety of ways. Two sulfate addition methods were tested. The "soak" method consisted of immersing one gram of $\text{Zr}(\text{OH})_4$ in approximately 7.5 ml of ammonium sulfate solution, as described by Hino and coworkers^[2]. After 2 hours, the solid was separated from excess sulfate solution by decantation. An incipient wetness method was also used to add sulfate to $\text{Zr}(\text{OH})_4$. This procedure involved adding 0.9 ml of $(\text{NH}_4)_2\text{SO}_4$ solution to one gram of $\text{Zr}(\text{OH})_4$. The resulting paste was thoroughly mixed and dried at 110°C . This procedure yielded 8 %

sulfate by weight prior to calcination.

To make metal promoted catalysts, zirconium hydroxide was impregnated with transition metals by using the incipient wetness method. As indicated in Figure 3.2, sulfation of metal promoted catalysts was performed after the metals had been added. The volumes of metal ion solutions required to make catalysts with desired metal contents were pipetted into a beaker containing zirconium hydroxide. The mixture was stirred and then dried at 110°C for an hour. Sulfation was achieved as previously described for unpromoted catalyst synthesis.

Calcination. Properties of sulfated zirconia catalysts are very sensitive to calcination conditions^[9,12]. To investigate the effects of temperature during calcination, studies were conducted in which the thermal properties of catalyst precursors (i.e. $\text{Zr}(\text{OH})_4$, $(\text{NH}_4)_2\text{SO}_4$, and $\text{Fe}(\text{NO}_3)_3$) were examined. Differential scanning calorimetry (DSC) was employed to study the crystallization behavior of neat zirconium hydroxide and the effects of added ammonium sulfate and metal promoters on crystallization. Thermogravimetry coupled with mass spectrometry (TG-MS) was utilized to assess the thermal stability of sulfated zirconia sulfate groups after calcination and to determine the amounts of sulfate present in catalyst samples calcined at different temperatures. Catalyst stability was determined by measuring the temperature at which the catalyst started to decompose. Sulfate content was determined by measuring the weight loss due to the removal of sulfate as the catalyst decomposed.

Heating $\text{Zr}(\text{OH})_4$ results in the formation of zirconium oxide^[13] (ZrO_2). This

transformation was studied by using TG-MS and DSC. Figure 3.3 shows TG-MS results obtained by heating Zr(OH)_4 at 10°C/min . The TG curve indicates that weight loss began below 100°C . Mass spectrometric analysis revealed that the weight loss was primarily due to water evolution, which is represented by the m/z 18 (H_2O^+) ion signal temperature profile in Figure 3.3. About 16 % of the sample weight loss corresponded to water. The TG curve in Figure 3.3 exhibits a change in slope near 300°C that cannot be attributed to water evolution. This was probably due to impurities as indicated by the presence of unidentified ions of m/z 30, 46, and 64 observed in TG-MS mass spectra obtained near 300°C .

DSC results for Zr(OH)_4 obtained by using the same temperature program as that used for TG-MS analysis are shown in Figure 3.4. Positive peaks indicate exothermic processes whereas negative peaks represent endothermic processes. Two endothermic peaks were detected below 200°C . The first peak occurred at 135°C and was likely due to removal of adsorbed water. In fact, when samples were dried at 110°C prior to DSC measurements, this peak was absent. The second endothermic peak occurred at 195°C and was assigned to Zr(OH)_4 dehydroxylation, which produced amorphous ZrO_2 . Two exothermic peaks are also present in Figure 3.4. The first peak occurs at 328°C and was likely due to the impurities as previously detected by TG-MS. The large exothermic peak at 440°C was caused by crystallization of the amorphous oxide^[13].

To study the thermal behavior of zirconium hydroxide in the presence of metal promoters, precursor mixtures prepared by adding enough Fe (as iron nitrate) to solid hydroxide to yield samples with 0.2, 0.5, 1.0, and 2.0 %Fe by weight were analyzed.

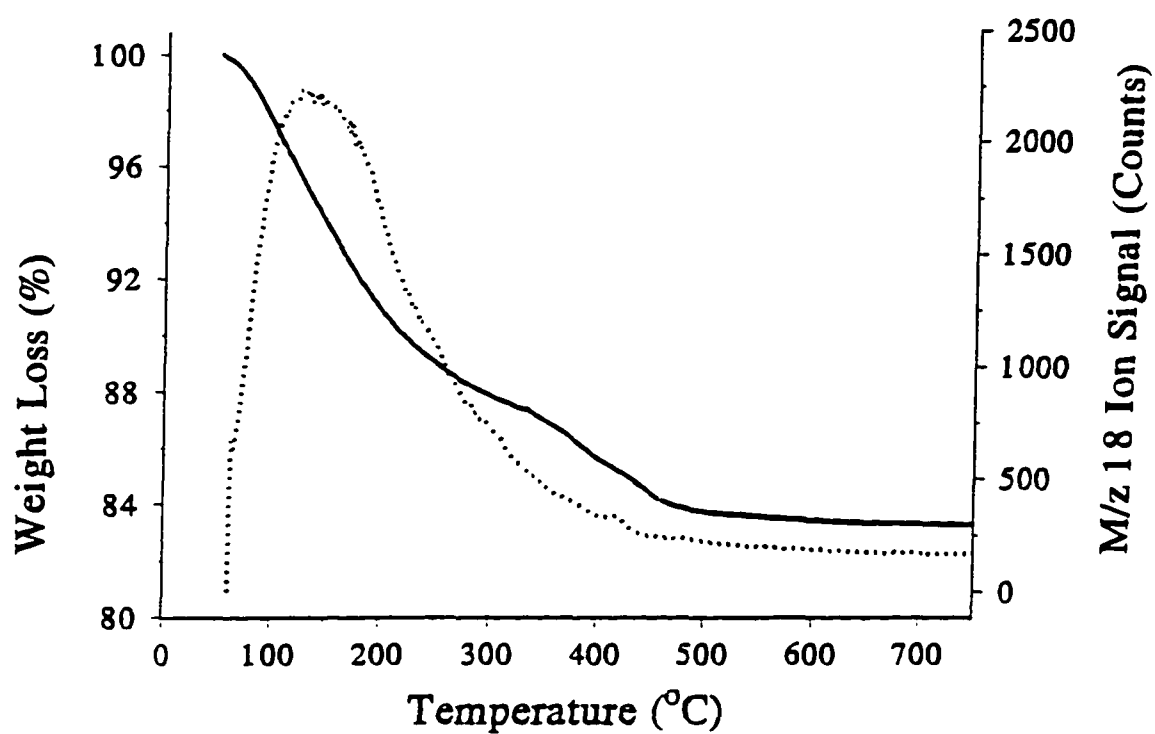


Figure 3.3 Zr(OH)_4 TG-MS results. Solid line represents weight loss curve and dotted line represents m/z 18 ion signal

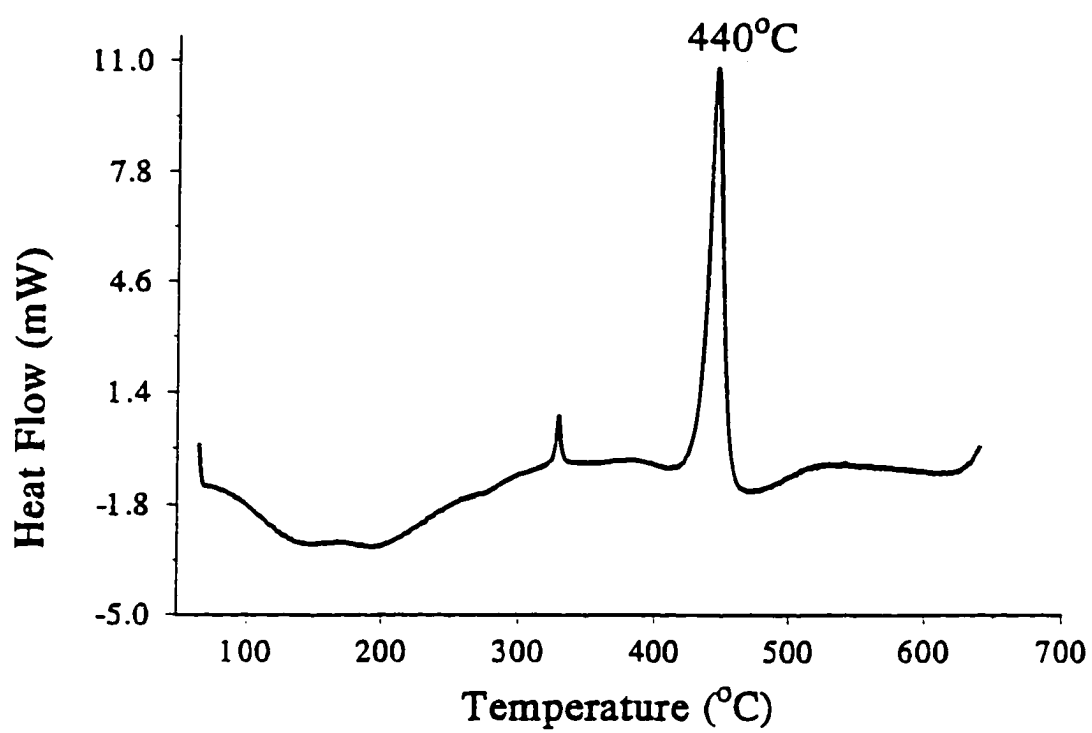


Figure 3.4 DSC curve for Zr(OH)_4 crystallization

These samples were subjected to the same DSC analysis conditions that were used for neat zirconium hydroxide studies. DSC results for these samples are shown in Figure 3.5 and indicate that the exothermic crystallization peak shifted to higher temperatures when the amount of Fe was increased. The exothermic DSC peaks shown in Figure 3.5 are shorter and broader when Fe is present. Table 3.1 summarizes the DSC crystallization results.

Table 3.1 Effects of Fe on $\text{Zr}(\text{OH})_4$ Crystallization

% Fe	Crystallization Temperature ($^{\circ}\text{C}$)	$\Delta\text{H}(\text{J/g})$
0.0	440	138
0.2	446	128
0.5	450	126
1.0	468	120
2.0	482	(-) ^a

^avalue could not be calculated due to baseline irregularity.

The data in Table 3.1 also indicate that the enthalpy change associated with zirconia crystallization decreased with increasing Fe content. A change in ΔH of phase transition normally suggests a distortion of the phase^[14]. The DSC crystallization peak temperatures for the five samples listed in Table 3.1 are plotted as a function of Fe content in Figure 3.6. A linear relationship between the amount of Fe present and sample crystallization temperature is evident. DSC measurements were also conducted

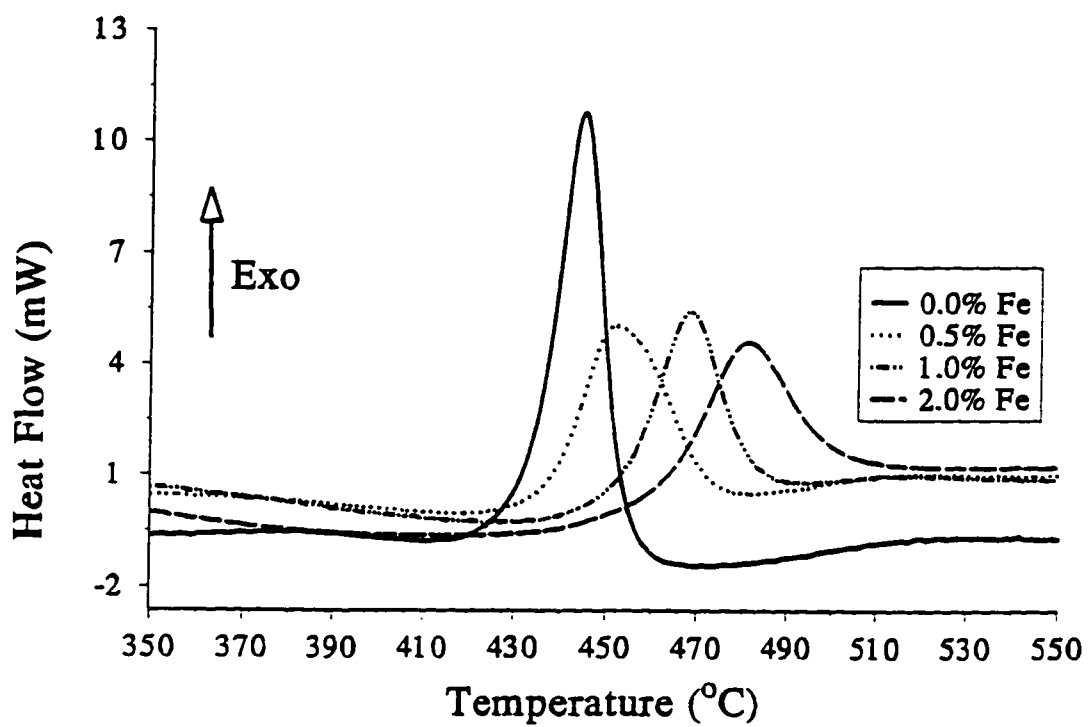


Figure 3.5 DSC curves for $\text{Zr(OH)}_4/\text{Fe}$ crystallizations

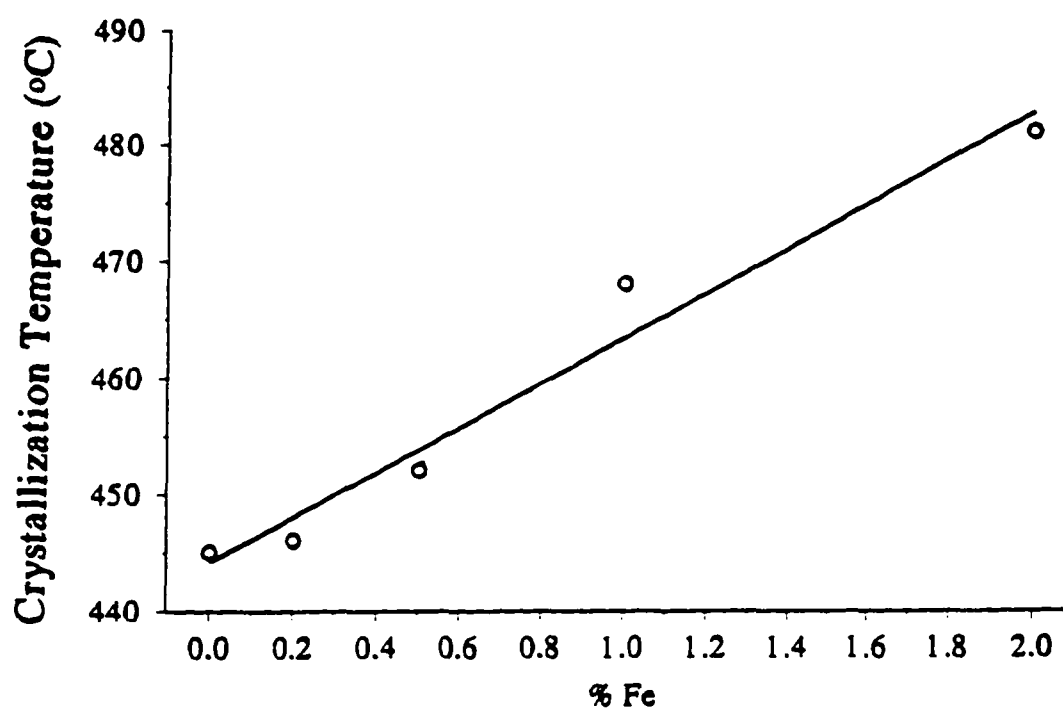


Figure 3.6 Effects of Fe content on Zr(OH)_4 crystallization temperature

for a sample consisting of Zr(OH)_4 , 1.5 % Fe, and 8 % sulfate that was subjected to the same heating program as the samples listed in Table 3.1. As shown in Figure 3.7, the endothermic DSC peak attributed to dehydroxylation was found at 230°C and the exothermic crystallization peak occurred at 540°C. DSC results indicated that the incorporation of sulfate and metal promoters into zirconium hydroxide samples increased the zirconium oxide crystallization temperature by at least 100°C. Therefore, to assure complete crystallization, calcination of metal promoted sulfated zirconias at temperatures above 550°C was required.

Figure 3.8 depicts a diagram of the quartz tube furnace that was used to calcine catalyst samples. Solid mixtures consisting of dried zirconium hydroxide containing ammonium sulfate with and without transition metal promoters were placed in small ceramic boats. The ceramic boats were placed inside the quartz tube furnace. Sample heating was accomplished by passing current through a nichrome wire wound around the quartz tube. The current through the nichrome wire was controlled with a variac. A thermocouple was placed inside the quartz tube above the ceramic boat containing the sample to measure calcination temperatures. Air at a flow rate of 10 MI/min was introduced into the quartz tube during calcination.

The effects of calcination duration were examined by calcining unpromoted sulfated zirconia (SZ) at 500°C for different lengths of time. The thermal properties of samples calcined at 500°C were then characterized by using TG-MS. Typical results are presented in Figure 3.9 for a SZ sample calcined at 500°C for 4 hours. Figure 3.9(a) shows TG weight loss curves for analyses conducted in helium and air. The catalyst

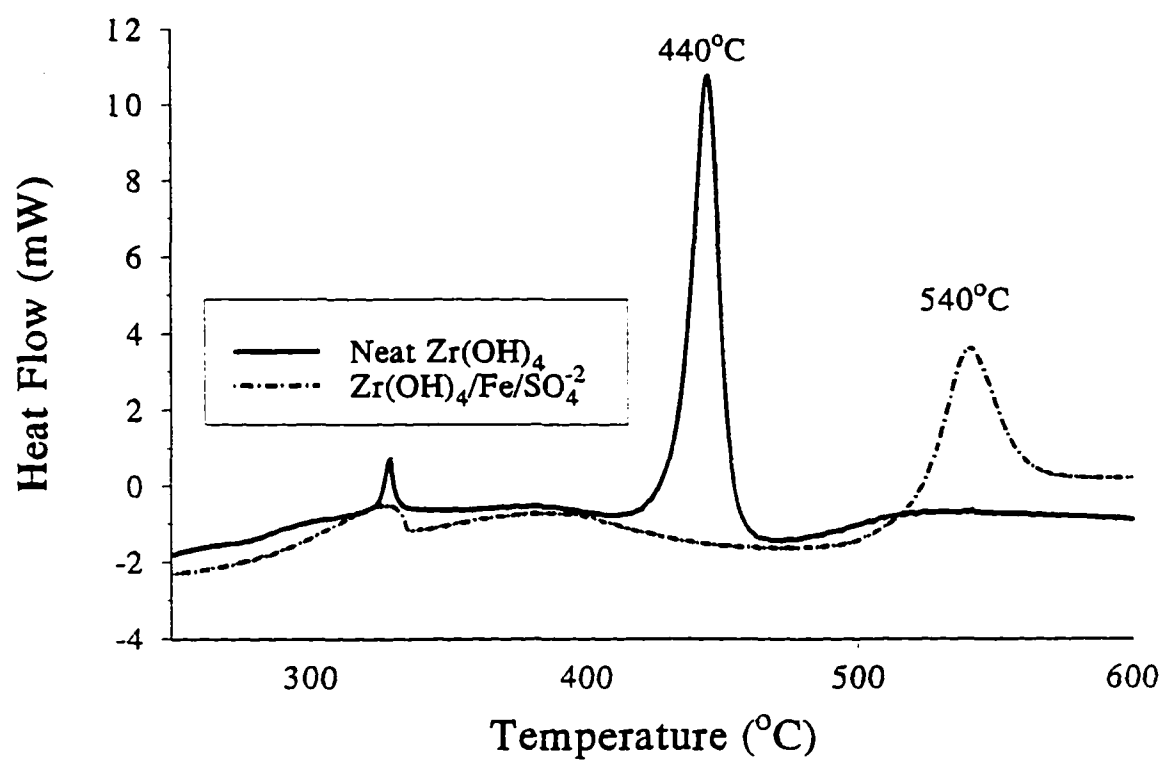


Figure 3.7 DSC curves for Zr(OH)₄ and Zr(OH)₄/Fe/sulfate crystallizations

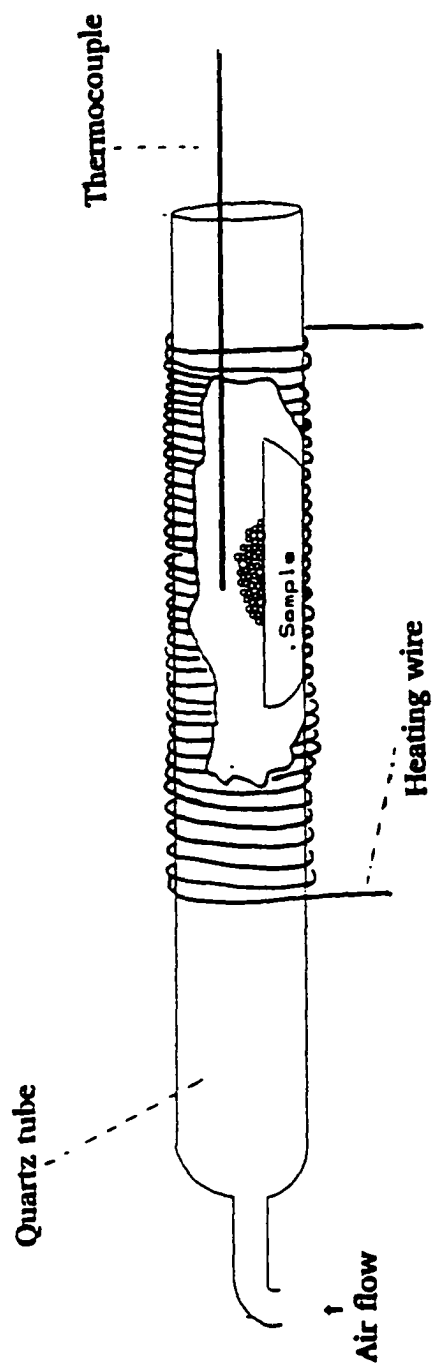


Figure 3.8 Catalyst calcination apparatus

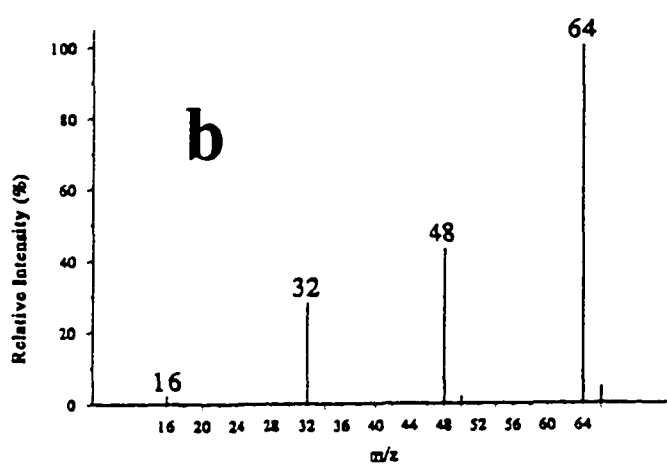
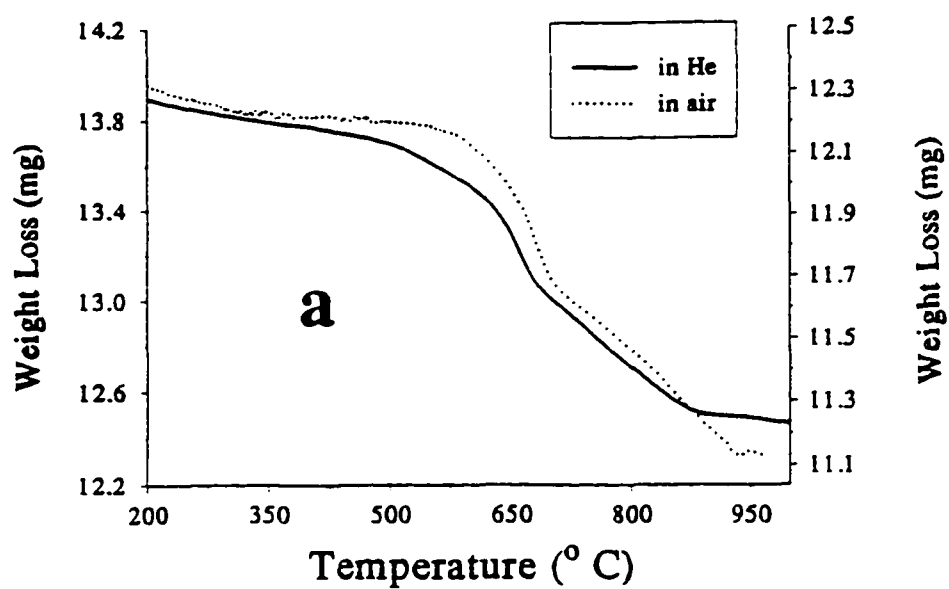


Figure 3.9 Sulfated zirconia TG-MS results

decomposed in similar manners in helium and air. The TG curves in Figure 3.9 indicate that thermal decomposition consisted of at least two steps. An evolved gas mass spectrum obtained during the TG-MS analysis conducted in helium is shown in Figure 3.9(b). Ions corresponding to m/z values of 64, 48, 32 and 16 were detected. M/z 64 was assigned to SO_2^+ and the other three ions represented SO^+ , O_2^+ and O^+ , respectively. Based on this mass spectrum, it was concluded that the thermal decomposition of unpromoted sulfated zirconias yielded primarily SO_2 and O_2 . The temperature corresponding to the maximum rate of SO_2 evolution (T_{max}) was found at 650°C .

Temperature profiles for m/z 64 ion signals representing SO_2 evolution are shown for 3 samples calcined at 500°C for varying durations and an uncalcined catalyst sample in Figure 3.10. The uncalcined catalyst (0 h) exhibited about the same T_{max} value as those for samples calcined at 500°C . One difference between the uncalcined and the calcined samples was a small peak observed at 520°C in the uncalcined sample temperature profile that was absent in calcined sample profiles. All four samples exhibited a broad shoulder between 700 and 900°C . The relative intensity of this shoulder increased as calcination time increased, suggesting that extended heating at 500°C increased the relative amount of sulfate species with greater thermal stability. A similar study of the effects of calcination time at 600°C was also performed. Figure 3.11 shows that catalysts calcined at 600°C for 2, 4, 6, and 9 hours had about the same relative SO_2 evolution temperature profiles and that the temperature of maximum SO_2 evolution ($\sim 800^\circ\text{C}$) was about the same regardless of the calcination duration.

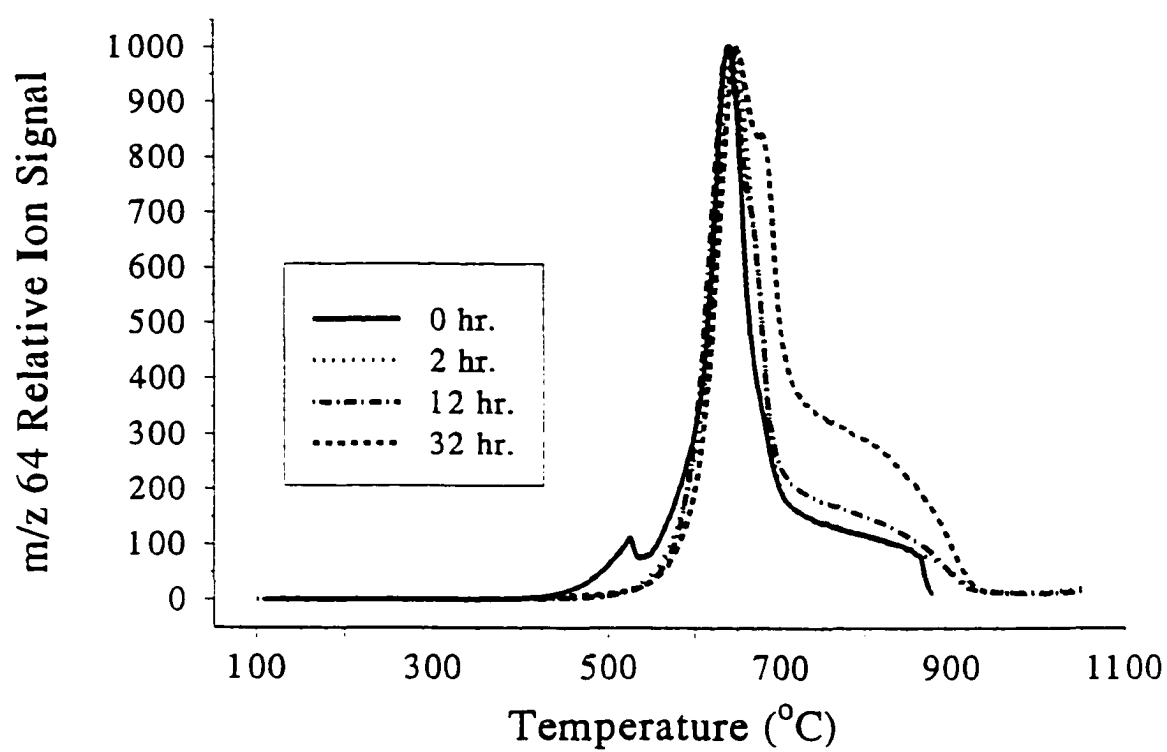


Figure 3.10 Effects of 500 °C calcination time on TG-MS SO₂ evolution

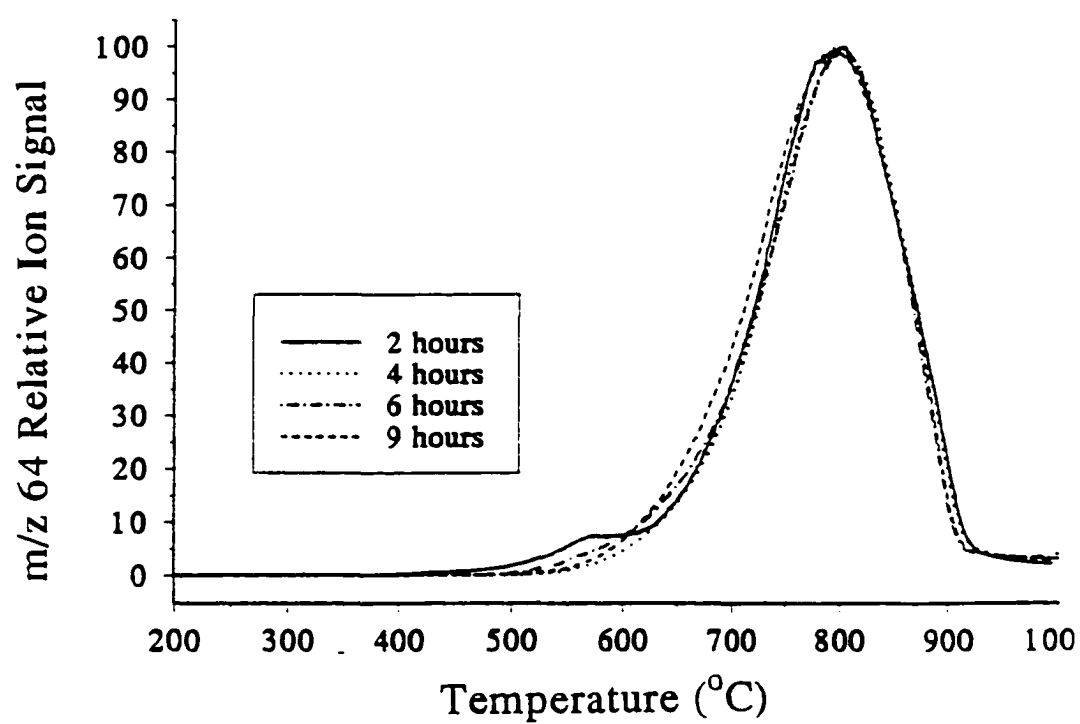


Figure 3.11 Effect of 600 °C calcination time on SO₂ evolution

TG-MS results obtained during analyses of 3 catalyst samples prepared by the "soak" method and calcined for 4 hours at 500, 600 and 700°C are shown in Figure 3.12. The thermal stabilities of catalysts were characterized by the temperatures at which the catalyst sulfate groups decomposed. The amounts of sulfate present on catalysts were determined from the weight loss measured during temperature programmed decomposition. As expected, Figure 3.12 shows that sulfate groups remaining on catalysts after calcination at 700°C were more thermally stable than those remaining on catalysts calcined at 500 or 600°C. TG mass loss results revealed that catalysts calcined at 500, 600 and 700°C contained 12, 4, and 1.7 % by weight sulfate, respectively. The results from these studies are summarized in Table 3.2.

Table 3.2 Effects of Calcination Temperature at Constant Time

$T_{\text{calcine}} (^{\circ}\text{C})$	$\text{SO}_2 T_{\text{max}} (^{\circ}\text{C})$	(%) SO_4^{2-}
500	625	12
600	795	4.0
700	850	1.7

These data confirm that the choice of calcination temperature determines the amount of sulfate remaining on synthesized catalysts.

Studies by Chen^[11], Lin^[15], and Hino^[16] showed that sulfated zirconia catalytic activity for *n*-butane isomerization depends on the sulfate content. Therefore, we used a variety of sample synthesis procedures to identify which catalyst preparation factors were most important in determining sulfate contents. First, the effects of calcination time

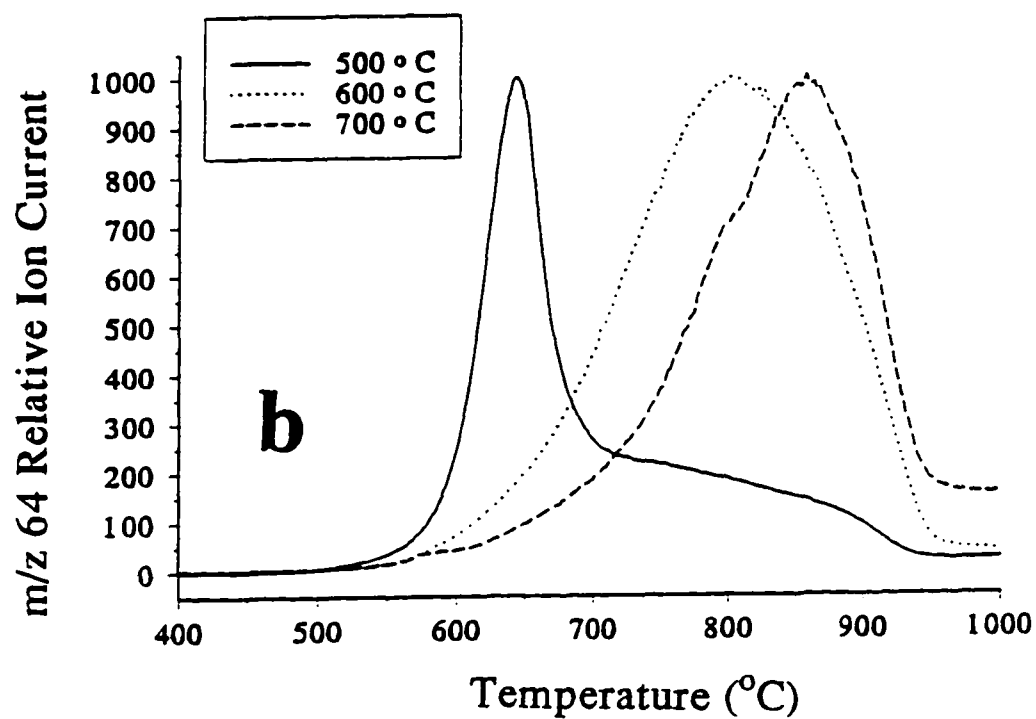


Figure 3.12 Effects of calcination temperature on TG-MS SO₂ evolution

was studied for samples prepared by incipient wetness and containing different amounts of sulfate. Catalyst samples were calcined at 600°C and characterized by TG-MS. Table 3.3 lists TG results obtained for these samples.

Table 3.3 Effects of Calcination Time on Sulfate Content

Initial Sulfate %	T _{calcine} (°C)	Duration (Hours)	Sulfate %
4.0	600	4	3.9
4.0	600	12	3.9
8.0	600	4	5.5
8.0	600	12	4.7
12.0	600	4	4.7
12.0	600	12	4.6

In Table 3.3, the column labelled "Initial Sulfate %" represents the amount of sulfate present before calcination. "Sulfate %" values were calculated from TG mass losses after samples had been calcined. Table 3.3 indicates that, regardless of the initial sulfate content and the calcination duration, the amounts of sulfate contained in calcined catalysts were between 3.9 and 5.5 % by weight. Interestingly, the catalyst prepared by using the soak method and calcined at 600°C for 4 hours (Table 3.2) was found to contain about the same sulfate content as samples prepared by incipient wetness. This suggests that the sulfate addition method was inconsequential with respect to the final catalyst sulfate content. This finding, however, was found to be true only for

unpromoted catalysts.

Sulfate addition to metal promoted catalysts was achieved solely by the incipient wetness method because metal promoters can be lost during decantation in the soak method. For example, sulfate was added by the soak method to a catalyst sample containing 1.5 % Fe and 0.5 % Mn. After calcination, the sample was analyzed by Galbraith Laboratory, Inc. and found to contain only 0.07 % Mn. The low Mn content resulted from loss of this metal during removal of excess ammonium sulfate solution.

To study the effects of metal promoters on catalyst thermal properties, samples containing 0.5, 1.0, 1.5 and 4.0 % Fe were prepared and calcined at 600°C for 4 hours. TG analyses of these samples indicated that the thermal stability of sulfated zirconia was affected by the amounts of metal promoter added. Figure 3.13 shows TG-MS results obtained from the analysis of the four Fe-promoted catalysts. The m/z 64 ion signal indicated that the SO₂ evolution T_{max} decreased as the amount of Fe was increased. Table 3.4 contains TG results that show the effects of metal promoters on catalyst thermal stability. The temperatures listed in Table 3.4 represent the temperature of maximum SO₂ evolution when the catalyst decomposed.

In conclusion, TG-MS analyses revealed that calcination temperature is the most important factor that determines sulfate content in sulfated zirconia catalysts. Based on the results described here, it was decided that catalysts used in subsequent studies would be prepared by adding sulfate and metal promoters by incipient wetness. Unless otherwise indicated, catalysts were calcined at 600°C for 4 hours. A list of catalyst compositions used for studies described in this dissertation is given in Table 3.5.

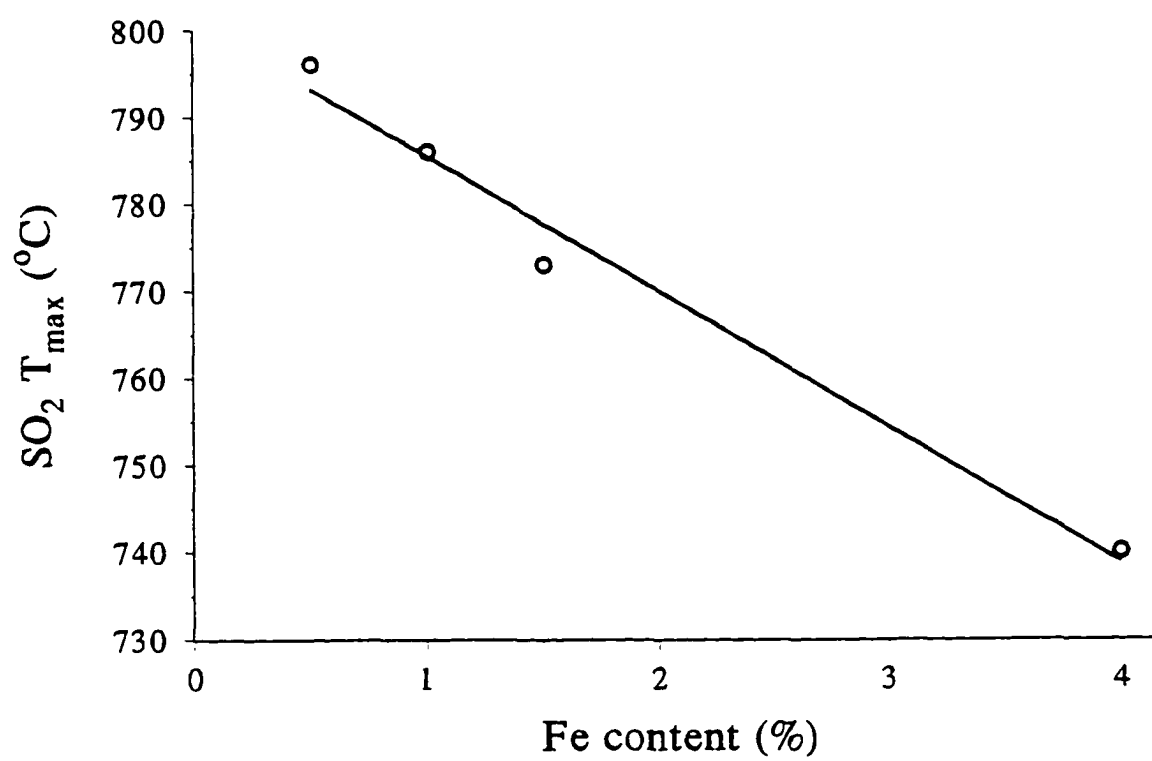


Figure 3.13 Effects of Fe content on TG-MS SO_2 evolution

Catalyst names denote their composition. For example, the SZ series are unpromoted catalysts and the SZF, SZN, SZM and SZFM series are sulfated zirconia catalysts containing iron only, nickel only, manganese only, and iron and manganese, respectively.

Table 3.4 Promoted Catalyst Thermal Stabilities

Fe Content (%)	0.5	1.0	1.5	4.0
Decomposition Temperature. (°C)	796	786	773	740

Unpromoted catalyst samples were white powders. Catalysts containing Fe were yellow when Fe content was below 1% but some red could be detected when the Fe content exceeded 1%. Samples containing Mn alone or Fe and Mn were dark grey. Samples containing Ni were pink. Surface area measurements were made on a Micromeritics ASAP 2010 adsorption apparatus by Maria Ioneva (School of Chemical Engineering and Material Science, University of Oklahoma). Zirconium hydroxide had a BET surface area of 166 m²/g. Following calcination, surface areas of sulfated zirconias ranged between 100 and 120 m²/g.

Table 3.5 Characteristics of Catalyst Samples

Catalyst Name	SO ₄ ²⁻ Content (%)	Promoters
SZ-1	4.4	0.0 % Fe
SZ-2	3.0	0.0 % Fe
SZF-1	4.7	0.5 % Fe
SZF-2	4.3	1.0 % Fe
SZF-3	4.1	1.5 % Fe
SZF-4	5.2	4.0 % Fe
SZN	5.2	1.0 % Ni
SZM	4.8	0.5 % Mn
SZFM-1	3.0	0.5% Mn/1.5% Fe

3.2 Measurement of Catalytic Activities

n-Butane isomerization has frequently been utilized to test sulfated zirconia catalytic activities^[17-22]. It is commonly reported in the literature dealing with catalytic *n*-butane isomerization that incorporation of transition metals enhances the activities of sulfated zirconias^[23-28] and that in inert atmospheres, plots of reactant conversion (or reaction rate) versus time-on-stream exhibit initial periods of increasing reaction rate followed by decreasing reaction rates. The period of increasing reaction rate constitutes an "induction period"^[23]. Reactor studies were conducted to determine the effects of varying catalyst compositions on *n*-butane isomerization reaction rates.

Materials and Procedures. Helium, hydrogen and high purity (99.99%) dry air were purchased from Sooner Air Gas, Inc. (Norman, OK). *n*-Butane was obtained from Matheson Inc. (LaPorte, TX). Isobutane (0.07 %) and propane (0.03 %) were reported by the supplier to be impurities in *n*-butane. About 200-400 mg of catalyst was packed in the reactor and activated *in situ* by maintaining a dry air flow through the reactor at 600°C for 2 hours. The reactor was cooled to 100°C, which was the selected reaction temperature, and then flushed with helium. The desired *n*-butane molar fraction in the reactant stream was achieved by adjusting *n*-butane and helium flow rates. For instance, to achieve an *n*-butane partial pressure of 0.35 atm, flow rates of 5.5 mL/min and 10.4 mL/min were selected for *n*-butane and helium, respectively. Reaction products were analyzed by using an HP 5890 gas chromatograph. During catalytic isomerizations, 50

μL injections from the reactor into the GC were made at 1 minute intervals in order to monitor the conversion of feed over the catalyst. The GC column was maintained at 80°C during separations. Effluent from the catalytic reactor was found to consist primarily of isobutane and *n*-butane. The chromatographic conditions used did not permit the observation of minor by-products such as C_3 and C_5 hydrocarbons that are also produced during the reactions^[22]. Gas chromatographic integrated peak areas were used to calculate the relative abundances of each component. Catalytic test reactions were conducted in collaboration with Mario Coelho in the laboratory of Dr. Daniel Resasco, School of Chemical Engineering and Material Science at the University of Oklahoma.

Results and Discussion. Figure 3.14 shows successive gas chromatograms obtained for catalytic reactor effluent as a function of time on stream when using a 1.5 wt. % Fe, 0.5 wt. % Mn sulfated zirconia catalyst (SZFM-1) at 100°C . The first peak in chromatograms represents isobutane elutions. The second peak in chromatograms represents *n*-butane. The isobutane concentration in the reactor effluent increased with increasing time on stream until it reached a maximum at 18 minutes. After 18 minutes, the isobutane concentration in the catalytic reactor effluent began to decrease.

Isobutane percent conversion as a function of time was calculated from chromatographic peak areas and the results are shown in Figure 3.15. The evolution of the catalytic activity of SZFM-1 as a function of time on stream exhibits an initial induction period during which the activity increases. The induction period is followed by a period of decreasing activity. The decrease in activity is indicative of catalyst

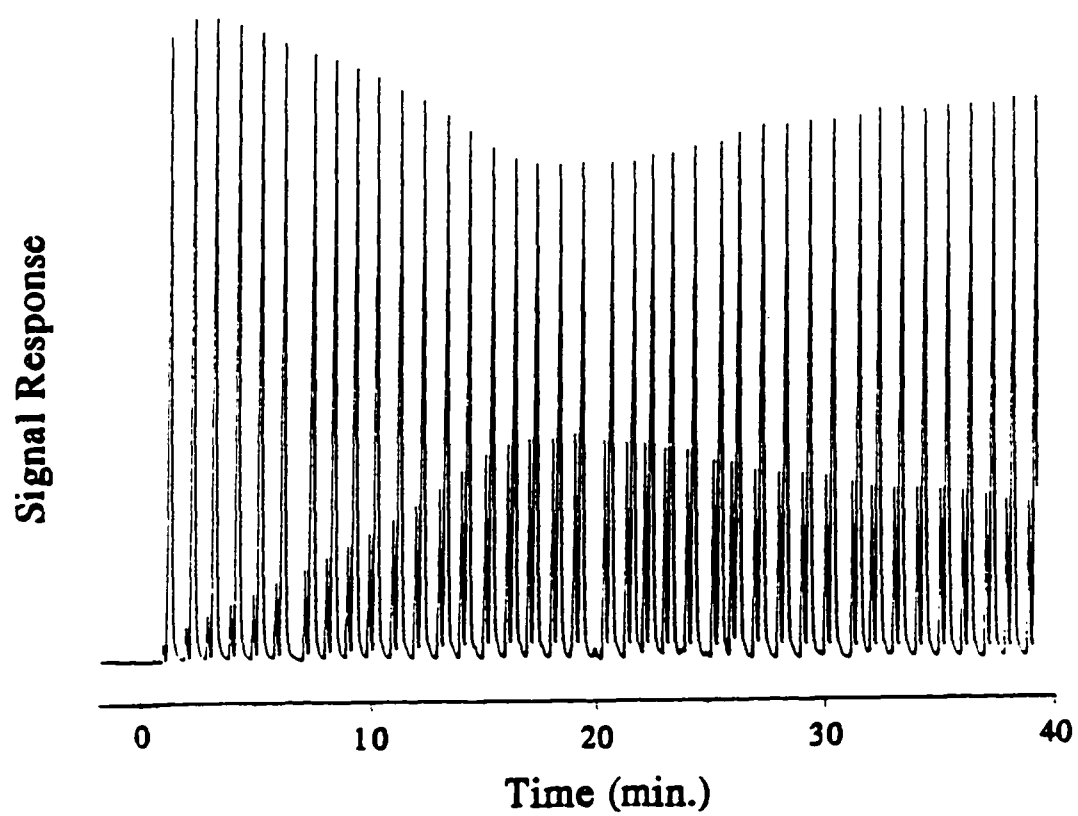


Figure 3.14 Microcatalytic reactor gas chromatograms

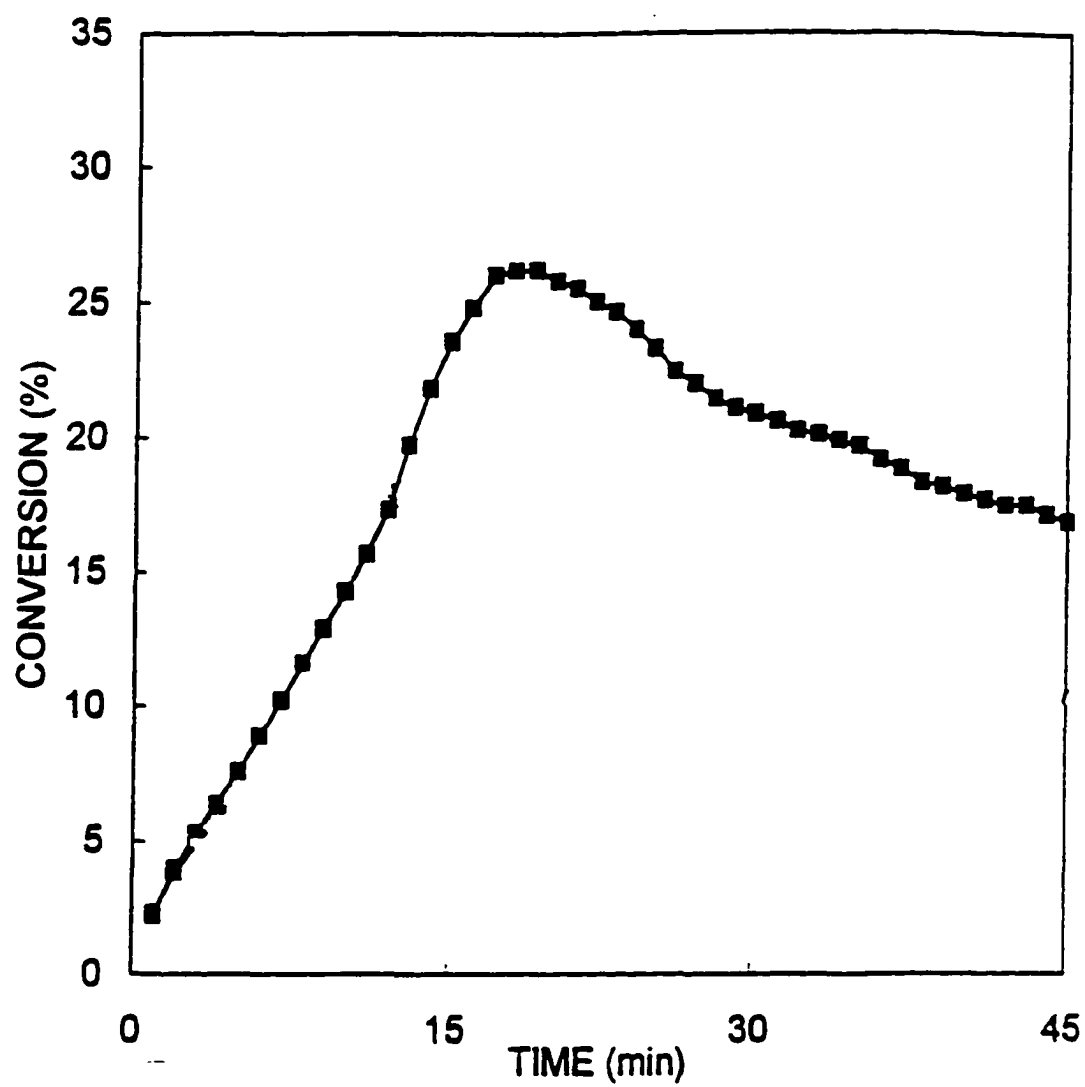


Figure 3.15 *n*-Butane conversion versus time-on-stream for the ZSFM-1 catalyst

deactivation. The shape of the conversion-time curve reveals important information concerning the way the catalyst operates. In particular, the induction period may result from slow accumulation of reaction intermediates on the catalyst surface^[23,24,28].

The effects of various reactor conditions on conversion-time curves were investigated. First, *n*-butane isomerization was conducted at different temperatures. The resulting conversion-time curves are plotted in Figure 3.16. The conversion-time curves obtained at different temperatures exhibit differences in shape. The induction period duration decreased when the reaction temperature was increased. Times required to reach maximum conversion and maximum conversions achieved at different reactor temperatures are listed in Table 3.6.

Table 3.6 Effects of Temperature on *n*-Butane Conversion

Reaction Temperature (°C)	Time (min.)	Maximum Conversion (%)
90	13.2	9.8
110	6.4	18.6
130	2.2	17.8
150	t.s. ^(a)	12.7

^(a)time was too short to be measured.

Although the time required to reach maximum conversion for the SZFM-1 catalyst decreased with increasing temperature, the maximum conversion attained decreased at high reactor temperatures. Reactions conducted at 110°C exhibited the highest

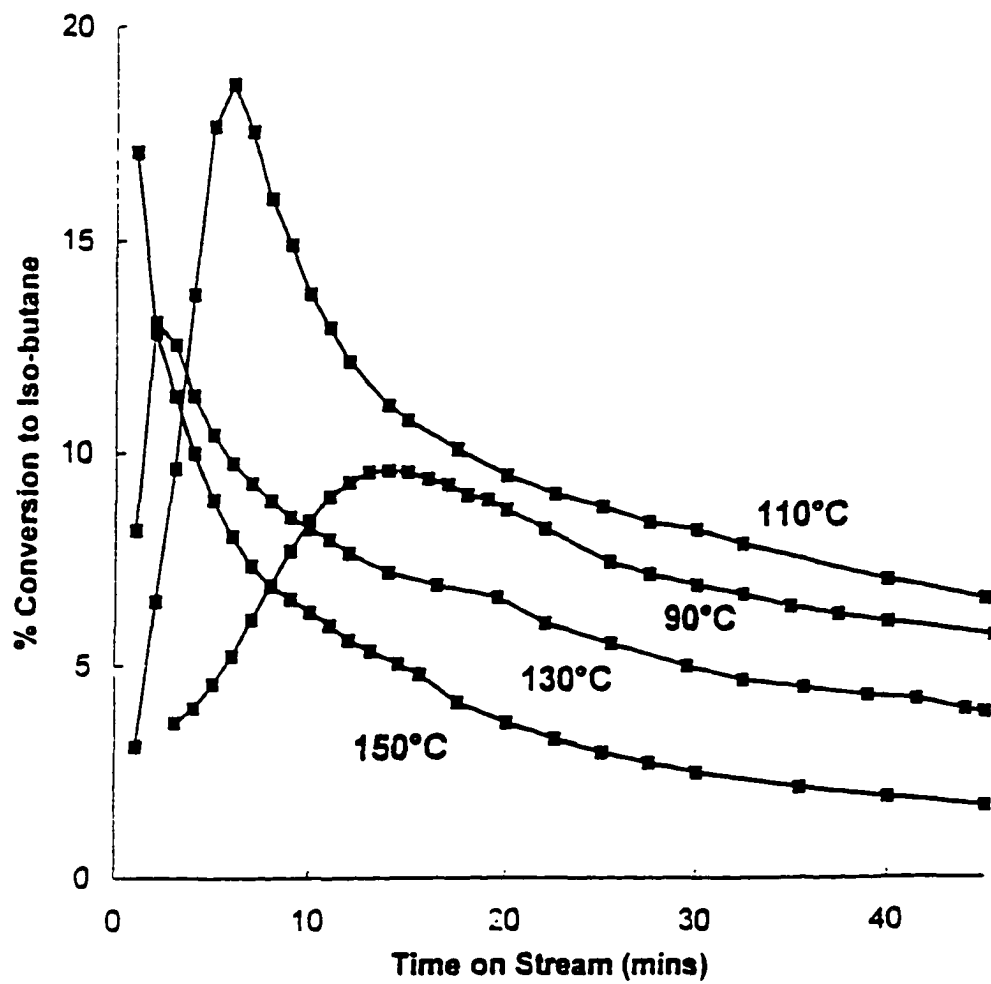


Figure 3.16 Effects of reactor temperature on conversion versus time-on-stream curves

conversion rates. Temperatures lower or higher than 110°C led to lower maximum conversion rates. Increasing the reactor temperature also led to an increase in the rate of the catalyst deactivation.

Figure 3.17 depicts the effects of varying the *n*-butane molar fraction for reactions conducted at 100°C on the SZFM-1 catalyst. The induction period was shortened and higher conversion rates were obtained as the mole fraction increased. When molar fractions of at least 0.47 were employed, the induction period was absent but higher deactivation rates were detected. The fact that the induction period was shortened by increasing the *n*-butane molar fraction is consistent with a hypothesis that the induction period is due to accumulation of reaction intermediates^[30].

Reactor temperature and *n*-butane molar fraction were found to determine the catalyst deactivation rate. Catalyst regeneration was attempted by maintaining the used catalyst at 600°C for 12 hours under flowing air. Figure 3.18 shows differences in *n*-butane conversions for freshly prepared and regenerated SZFM-1 catalysts obtained under identical reaction conditions. The fresh catalyst (curve a) exhibited an initial sharp increase in activity whereas the regenerated catalyst showed a longer induction period and a lower maximum activity. It appears that the initial high activity of the fresh catalyst cannot be regenerated, suggesting that catalyst sites responsible for this high conversion rate may be irreversibly deactivated during catalytic reactions^[31,32]. However, the fact that catalytic activity was still obtained after catalyst regeneration indicates that the catalyst possessed at least two types of active sites and that only the less active sites could be regenerated.

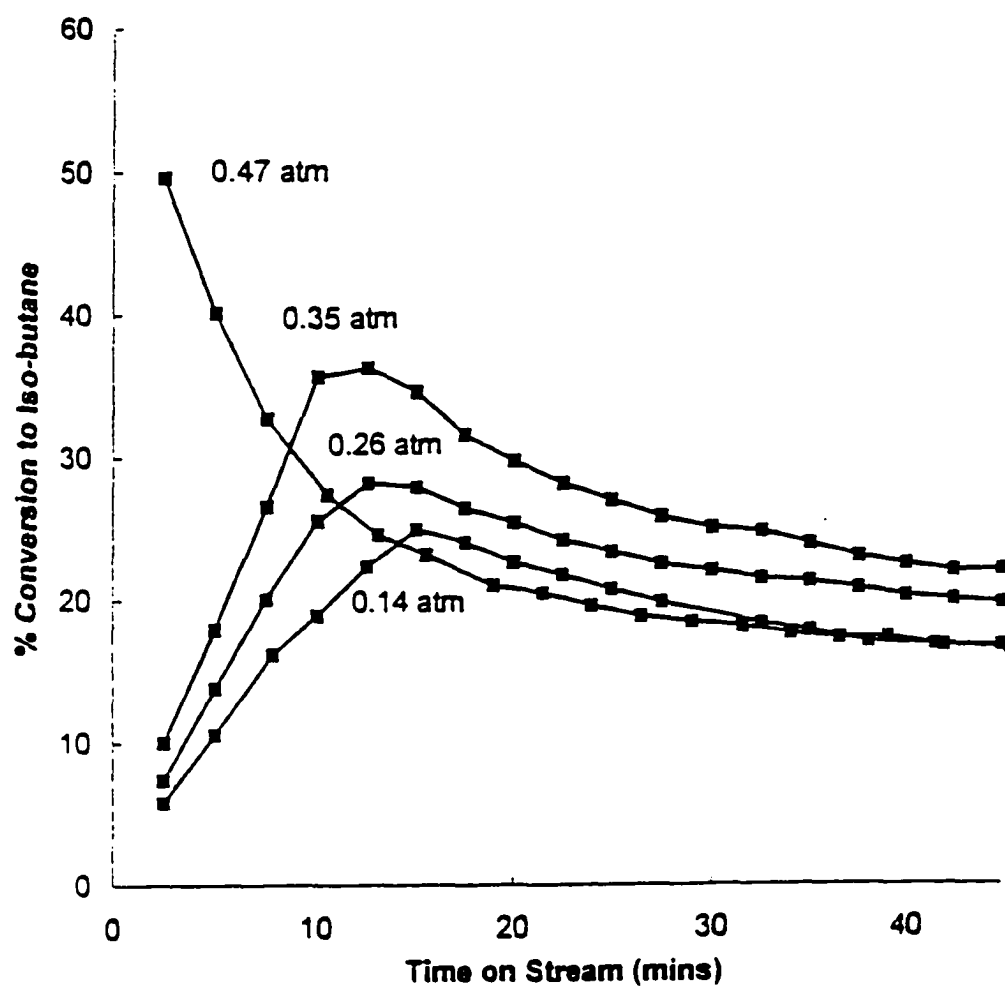


Figure 3.17 Effects of *n*-butane partial pressure on conversion versus time-on-stream curves

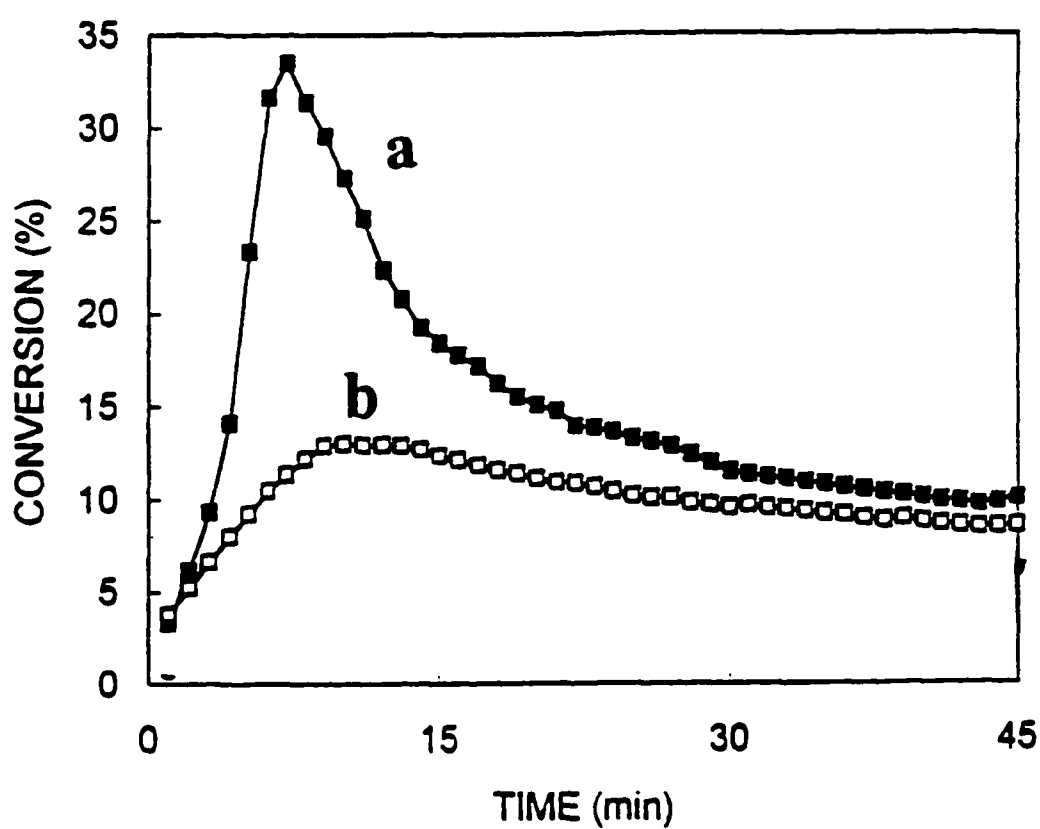


Figure 3.18 Conversion versus time-on-stream curves for (a) fresh and (b) regenerated catalyst samples

n-Butane catalytic isomerization was also affected by catalyst pretreatment conditions. For example, when SZFM-1 catalyst was preheated in flowing helium at 600°C for 2 hours, the activity dropped by several orders of magnitude and was not recovered by subsequent treatments in air at 600°C. The effects of different catalyst pretreatments are summarized in Table 3.7.

Table 3.7 Effects of Thermal Pretreatment on SZFM-1 Activities

In-Situ Pretreatment	Maximum conversion (%)
(1) = air, 600°C, 2 h	36
(2) = (1) + He, 600°C, 2 h	0.6
(3) = (2) + air, 600°C, 2 h	1.5

The loss of activity after the catalyst had been in contact with helium at 600°C may indicate a loss of some sulfate species due to catalyst decomposition^[30].

The effects of catalyst preparation variables were investigated for a series of catalysts containing the same Fe and Mn content as SZFM-1 but prepared by different impregnation procedures (Table 3.8). A catalyst made by co-impregnation of Fe and Mn exhibited the highest activity. For catalysts impregnated sequentially, the catalyst for which Mn was added first (SZFM-2) was more active than the catalyst for which impregnation by Fe preceded Mn. Catalytic activity was defined as the percent conversion attained after the catalyst had been in contact with the feed for 5 minutes. For comparison, the activity of an unpromoted catalyst (SZ-1) is also listed in Table 3.8.

Table 3.8 Effects of Promoter Addition Sequence

Sample	Description	Conversion (%)
SZFM-1	Fe, Mn co-impregnated	11.0
SZFM-2	Mn (first), Fe (last)	8.2
SZFM-3	Fe (first), Mn (last)	5.0
SZM	Mn only	1.8
SZ-1	Unpromoted catalyst	2.5

In agreement with results reported by Jatia *et al*⁽²¹⁾, it was found that Mn alone did not enhance sulfated zirconia activity for *n*-butane isomerization. *n*-Butane isomerization studies were also conducted with catalysts containing no Mn but varying amounts of Fe. Unlike the Mn-promoted catalyst, results indicated that Fe-promoted catalysts (SZF) were more active than unpromoted catalysts. Under identical reaction conditions, higher conversion was achieved for a catalyst containing 0.5 % Fe than for those containing 0.2, 1.0, 1.5, 2.0, and 4.0 % Fe. The promoting effects exhibited by (Fe/Mn) and "Fe only" catalysts were also observed when Ni was used as a promoter. Reactor studies for catalysts containing Ni (SZN) were conducted under conditions identical to those used for Fe/Mn and Fe-promoted catalysts. The activities of catalysts containing varying amounts of Ni only and Fe only were measured at 250°C. Figure 3.19 shows conversion versus metal content curves obtained by plotting the highest conversion achieved for each catalyst as a function of the metal promoter content in the catalyst. For nickel containing catalysts, activity increased with promoter content from 0.2 to 1.0 % by weight Ni. Fe-

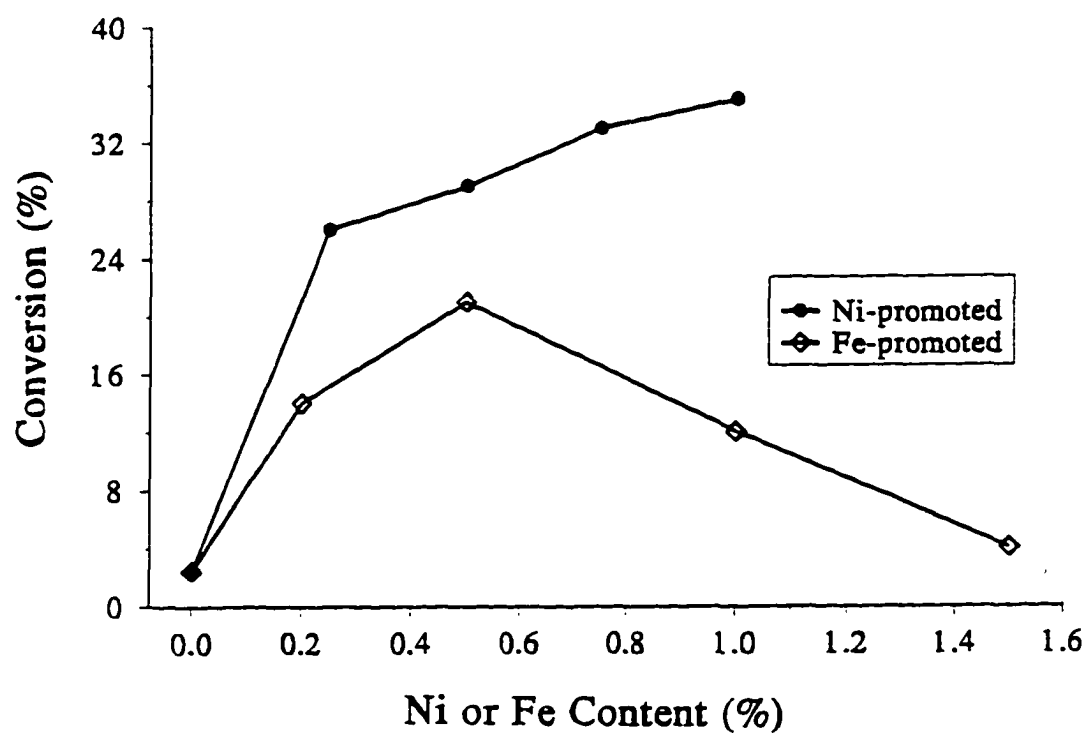


Figure 3.19 Effects of metal content on *n*-butane conversions

promoted catalysts exhibited a maximum at 0.5 wt. % Fe, after which activities decreased as Fe contents increased. In all cases, Ni-promoted catalysts exhibited higher conversion rates than Fe-promoted catalysts containing the same weight percent of metal promoter. These findings suggest that the extent of catalytic activity enhancement derived from metal promoters depends heavily on the metal employed.

n-Butane isomerization is believed to proceed via the formation of carbenium ion intermediates^[33]. The formation of such ions would be expected to be inhibited by the presence of hydrogen in the feedstock. When hydrogen was added to the feed, the *n*-butane isomerization rate was found to decrease with increasing hydrogen partial pressure. Figure 3.20 shows the effects of increasing H₂ partial pressure in the feed on the activity of the SZFM-1 catalyst at a constant partial pressure of *n*-butane at 100 °C. When H₂ was added without helium, *n*-butane conversion at 100°C was effectively quenched. However, catalytic activity was measured after raising the reaction temperature to 250°C. The activities of 3 catalysts for *n*-butane isomerization at 250°C in hydrogen are compared in Figure 3.21. The performance of the Ni-promoted catalyst surpassed those for the unpromoted and the (Fe/Mn)-promoted catalysts. Furthermore, the induction periods observed in helium were not observed in hydrogen.

The dependence of catalytic activity on sulfate content was also investigated. A (Fe/Mn)-promoted catalyst was prepared with an initially large amount of sulfate by the soak method described earlier. Calcination at 600°C for several hours led to the partial removal of sulfate species. TG measurements of the catalyst after it had been heated for 2 hours yielded a sulfate content of 19.5 % by weight. Reactor measurements for *n*-

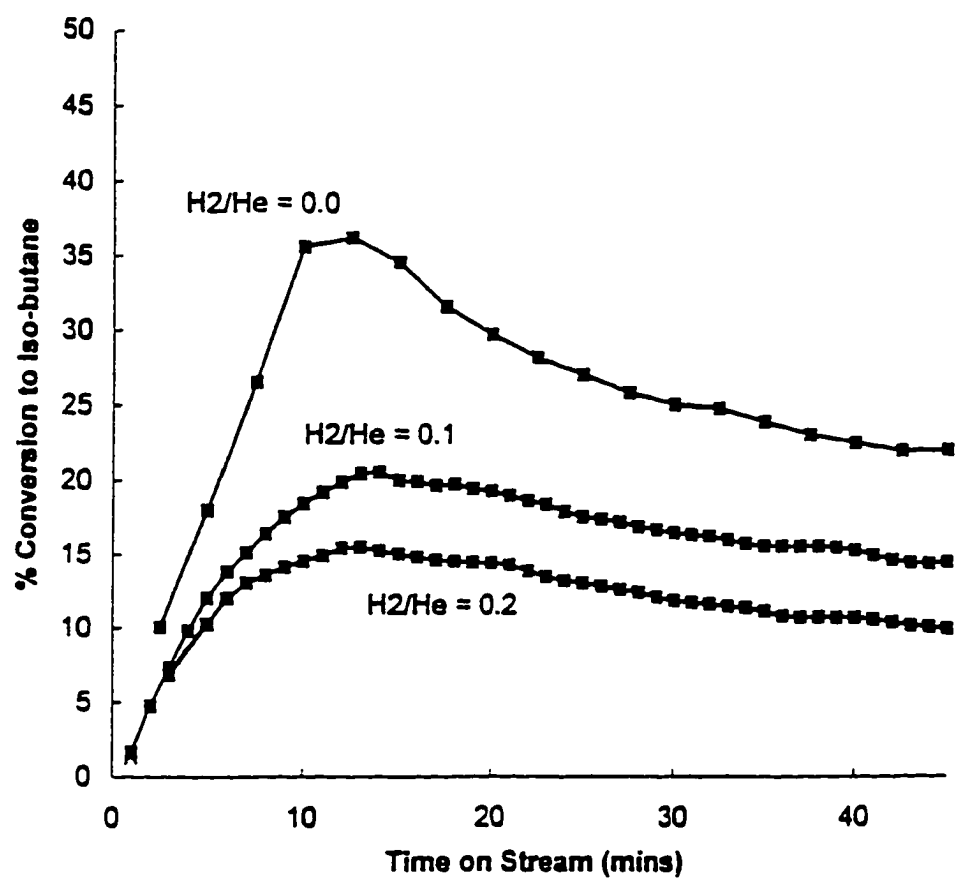


Figure 3.20 Effects of hydrogen on *n*-butane conversions

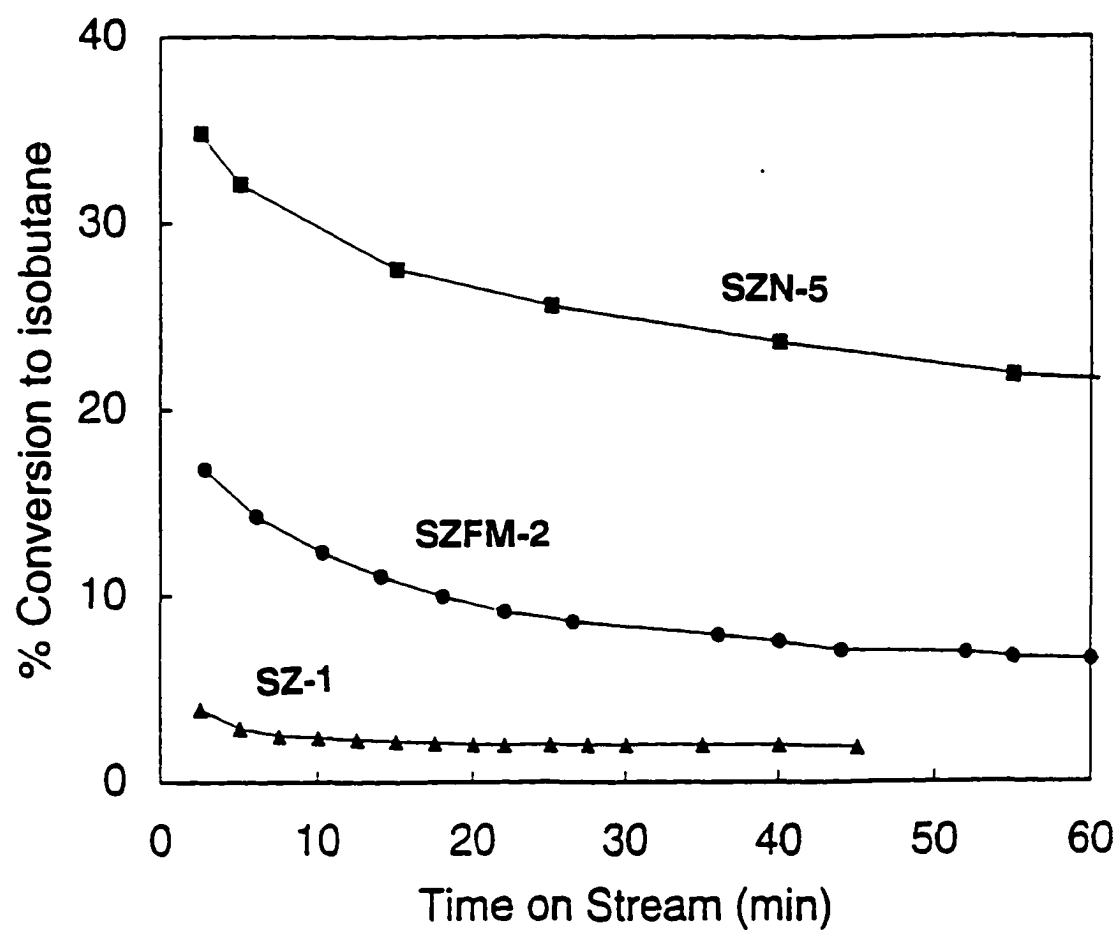


Figure 3.21 Effects of metal promoters on *n*-butane conversion at 250 °C in He

butane isomerization conducted at 100 °C after the catalyst had been calcined for 2 hours revealed a 1.8 % maximum conversion. Subsequent calcination of this catalyst led to different sulfate contents and *n*-butane maximum conversions. After 12 hours, the sulfate content decreased to 9.3 % and the catalyst had a conversion efficiency 15.4 %. The results of this investigation are compiled in Table 3.9.

Table 3.9 Effects of Calcination Duration on an (Fe/Mn)-promoted Catalyst Activity

Duration (hours)	Sulfate (%)	Conversion (%)
2	19.5	1.8
4	16.3	2.6
6	12.3	7.8
10	10.0	12.5
12	9.3	15.4

These findings suggest an inverse relationship between sulfate content and catalytic activity. Sulfate that was removed by prolonged calcination appeared to be inhibiting catalytic activity.

Isomerization reaction rates were calculated from *n*-butane % conversions measured at 100°C under identical feed conditions for an unpromoted and 2 metal promoted catalysts are listed in Table 3.10. The rates of *n*-butane isomerization on the Ni-promoted (SZN-4) and the (Fe/Mn)-promoted (SZFM-1) catalysts at 100°C were about 275 and 306 times greater than that of the unpromoted catalyst, respectively.

Table 3.10 Isomerization Rates for Selected Catalysts at 100°C

Catalyst	Rate (mol g ⁻¹ min ⁻¹) x 10 ⁶
SZ-1	0.06
SZFM-1	16.5
SZN-4	18.4

3.3 Summary

Various procedures for preparing sulfated zirconia catalysts were investigated. The presence of sulfate and transition metals was found to affect zirconium oxide crystallization processes. Addition of ammonium sulfate and Ni, Fe, and Mn nitrates to zirconium hydroxide by the incipient wetness method was found to provide the best means to control catalyst compositions. Calcination temperature and duration were found to be the most important factors that determined catalyst characteristics. Calcination duration affected catalyst sulfate content for promoted catalysts more significantly than it did for unpromoted catalysts.

Microcatalytic reactor studies of *n*-butane isomerization were performed to better understand the roles of metal promoters on the rate of this reaction. Although unpromoted and metal promoted sulfated zirconias catalyzed *n*-butane isomerization,

promoted catalysts exhibited much higher activities than unpromoted catalysts. The promoting effect of transition metals was observed with catalysts containing Ni only, Fe only, and Fe and Mn.

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CHAPTER FOUR

STRUCTURE OF THE ACID SITE

4.1 Background

In order to fully understand the origin of sulfated zirconia catalytic activity, the nature of the active site must be established. This has been the primary motivation for recent characterization studies^[1-5]. Yet, despite these efforts, the nature of sulfated zirconia active sites is still unclear^[5]. XPS results reported by Tanabe *et al.*^[6] revealed that sulfur in sulfated metal oxides was in the S^{6+} oxidation state. Two different models have been proposed for the structure of the sulfated zirconia acid site. Tanabe, Yamaguchi, and coworkers were the first to propose a bidentate sulfate species containing an $O=S=O$ moiety^[7-9]. Morrow, Lavalley, and coworkers have proposed a tridentate SO_4 species containing a single $-S=O$ moiety^[10-12]. Figure 4.1 shows the structures proposed by these two groups. Structures a and b in Figure 4.1 represent Lewis acid forms. Figure 4.2 shows the models proposed by Tanabe *et al.* (a) and Lavalley *et al.* (b) after the interaction of water with the structures in Figures 4.1 to yield Brønsted acid sites. On the basis of the structure depicted in Figure 4.1(a), Tanabe *et al.* proposed that the acidity results from the $S=O$ double bond inductive effect that leads to an electron deficient zirconium atom,

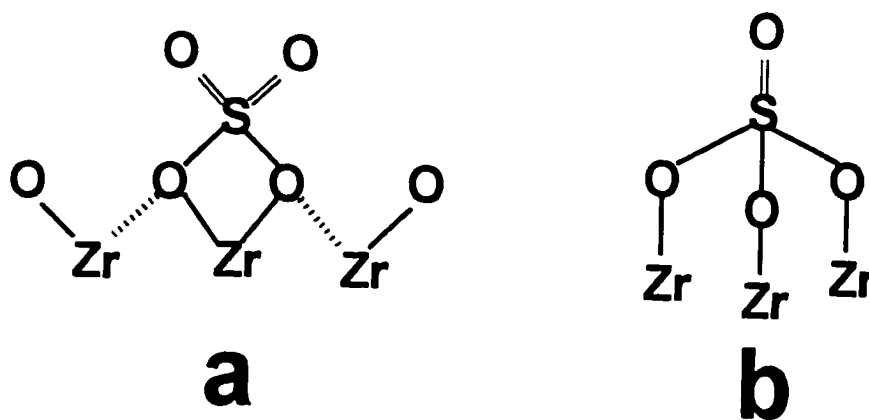


Figure 4.1 Structures proposed by (a) Tanabe and coworkers; (b) Lavalley and coworkers

thus increasing Zr^{4+} Lewis acid strength. Tanabe *et al* supported their bidentate structure by assigning infrared absorbance bands at 1390 and 1190 cm^{-1} in their sulfated zirconia infrared spectra to the asymmetric and symmetric stretching vibrations of the $\text{O}=\text{S}=\text{O}$ group^[7]. Lavalley *et al* disputed these band assignments and contended that the 1390 cm^{-1} absorbance band represents an $-\text{S}=\text{O}$ stretching vibration. They also argued that information based solely on IR studies was insufficient to establish a structural model for the species. They characterized sulfated zirconia $\text{S}=\text{O}$ species by studying the effects of ^{18}O isotope exchange from H_2^{18}O vapor at 450°C by infrared spectroscopy. For a

single S=O oscillator at 1400 cm^{-1} , a shift to lower frequency by about 40 cm^{-1} would be expected when ^{16}O is replaced by ^{18}O . If, on the other hand, two S=O species are present (as proposed by Tanabe *et al*), after 50 % isotopic substitution, IR bands corresponding to symmetric and asymmetric O=S=O stretching vibrations would split into three bands, having an intensity ratio of about 1:2:1 due to the statistical distribution of $^{16}\text{O}=\text{S}=\text{O}$, $^{16}\text{O}=\text{S}=\text{O}$, and $^{18}\text{O}=\text{S}=\text{O}$. Lavalley *et al* showed that in the presence of H_2^{18}O , the sulfated zirconia infrared band near 1400 cm^{-1} shifted without splitting to about 1360 cm^{-1} . This result is consistent with the presence of a single -S=O moiety and inconsistent with the presence of O=S=O.

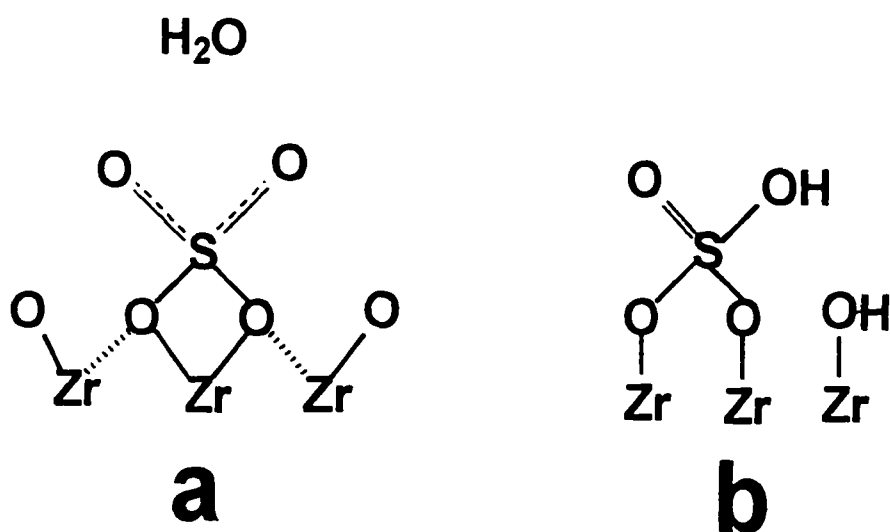


Figure 4.2 Brønsted acid sites for (a) Tanabe and (b) Lavalley Structures

The infrared band that Tanabe and coworkers assigned to the O=S=O symmetric stretching vibration was very weak in their spectrum, whereas the band that they assigned to the asymmetric stretch was very intense. It is unlikely that the dipole moment change for the symmetric stretch would be so much less than that for the asymmetric stretch. In fact, the bands corresponding to the asymmetric and symmetric stretching vibrations in sulfuric acid are of comparable intensity^[12]. Furthermore, the shoulder that Tanabe and coworkers assigned to a O=S=O symmetric stretch was not observed in our studies (vide infra) or evident in spectra of sulfated zirconia recently published by other investigators^[10,14-17]. A more likely candidate for an infrared absorbance band corresponding to a O=S=O symmetric stretching vibration appears at about 1085 cm⁻¹ in infrared spectra. However, the large frequency separation between this band and the postulated asymmetric stretching vibration (> 300 cm⁻¹) is indicative of an unreasonably large O=S=O bond angle.

Guillepsie and Robinson proposed the following empirical relationship between the oxygen-sulfur-oxygen bond angle (2α) and O=S=O stretching frequency^[18]:

$$\nu_{\text{sym}}/\nu_{\text{asym}} = [(1 + \cos^2\alpha)/(1 + \sin^2\alpha)]^{1/2} \quad [\text{Eq 4.1}]$$

where ν_{sym} is the symmetric stretching frequency and ν_{asym} is the asymmetric stretching frequency. They were able to predict bond angles for a number of sulfonyl compounds with this equation and they found that calculated bond angles were in good agreement with measured bond angles^[18]. By using the method described by Gillespie and Robinson

[Eq 4.1], the sulfated zirconia $\text{O}=\text{S}=\text{O}$ bond angle was calculated to be 137° when bands at 1390 and 1085 cm^{-1} were assigned to the asymmetric and symmetric stretching frequencies, respectively. This is much larger than corresponding bond angles for species known to contain $\text{O}=\text{S}=\text{O}$ ^[18]. Assuming that Lavalley *et al* are correct in that the acid site for sulfated zirconia contains a single $-\text{S}=\text{O}$ moiety, we suggest that a structure similar to that depicted in Figure 4.3 is consistent with the known properties of sulfated zirconia acid sites and may be responsible for the acidic properties of sulfated zirconia. In the proposed structure, each sulfur atom is surrounded by five different oxygens. The structure in Figure 4.3(a), which represents the Lewis acid form of the catalyst, can be conceptualized as arising from the insertion of a planar SO_3 molecule into the ZrO_2 crystal lattice surface. Indeed, sulfated metal oxides have been prepared by simply heating the oxide in the presence of SO_3 ^[6] (Figure 3.1). Because of its strong Lewis acidity, the SO_3 sulfur would be expected to interact strongly with oxygen lone pairs on the oxide surface. The particularly favorable orientation depicted in Figure 4.3 would permit two of the SO_3 oxygens to coordinate with surface zirconium atoms, resulting in a single $-\text{S}=\text{O}$ moiety oriented with the $-\text{S}=\text{O}$ bond perpendicular to the oxide surface. Water can attack the structure shown in Figure 4.3(a) to produce the structure shown in Figure 4.3(b), which represents the Brönsted acid form of the catalytic site. The proton associated with the sulfur-containing group would be easily accessible to species approaching the catalyst surface, would be weakly held by an $\text{S}-\text{O}-\text{H}$ bond, and could form weak multiple hydrogen bonds with neighboring oxide oxygens as well as with the $-\text{S}=\text{O}$ oxygen.

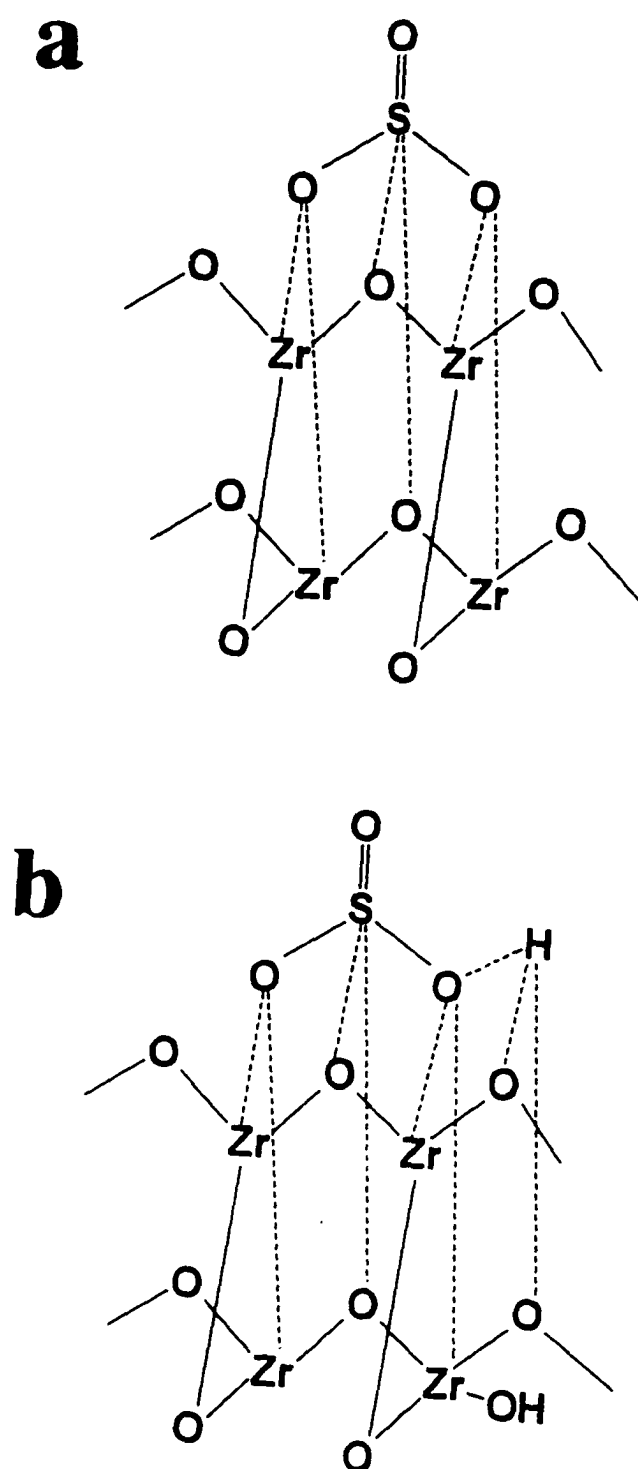


Figure 4.3 Proposed active site structure. Dotted lines represent bonds to SO_3 in (a) and to the proton in (b)

4.2 Experimental Conditions

Unpromoted catalysts were prepared by the methods described in section 3.1. Dry ammonia was obtained in a lecture bottle from Sooner Air Gas (Norman, OK). Variable temperature diffuse reflectance infrared spectroscopy (VT-DRIFTS), thermogravimetric analysis coupled with mass spectrometric detection of evolved products (TG-MS), and temperature programmed desorption (TPD) of NH_3 were employed to investigate the properties of unpromoted sulfated zirconia. For VT-DRIFTS measurements and ammonia desorption studies, catalysts were pretreated in-situ to remove impurities by heating them at a rate of $30^\circ\text{C}/\text{min}$ from ambient temperature to 600°C in air. Catalysts were then evacuated ($< 1 \times 10^{-6}$ Torr) and maintained at 600°C for 30 minutes. Neat catalyst infrared measurements were made by diffuse reflectance infrared spectroscopy (DRIFTS) by signal averaging 8 cm^{-1} resolution interferograms for 15 min. For ammonia TPD studies, enough NH_3 was added to the vacuum chamber to achieve a pressure of about 100 Torr and then samples were allowed to cool to 100°C . VT-DRIFTS infrared spectra were acquired at a rate of 1 spectrum/min at 8 cm^{-1} resolution while samples were heated in N_2 (10 mL/min) at $10^\circ\text{C}/\text{min}$ from 100 to 600°C . For TG-MS TPD studies, the TG-MS interface was maintained at 200°C and the helium flow rate was 50 mL/min. Catalysts were heated from 50 to 900°C at a rate of $10^\circ\text{C}/\text{min}$ and mass spectra were acquired by using 70 eV electron bombardment ionization and scanning from m/z 10 to m/z 200 at a rate of 3 spectra/min.

4.3 Infrared Results

Figure 4.4 shows a diffuse reflectance infrared spectrum for sulfated zirconia. The spectrum exhibits a band in the OH stretching region at 3665 cm^{-1} . This band was not found for ZrO_2 and was assigned to an OH group created after sulfate was added to zirconia^[19]. Two strong bands due to sulfate species are found in the $1500\text{--}1000\text{ cm}^{-1}$ region. The band at 1393 cm^{-1} was assigned to an -S=O stretching vibration and the band at 1026 cm^{-1} was assigned to an S-O- stretching vibration.

High temperature infrared measurements indicated that decomposition involved the loss of absorbance attributed to OH groups and sulfur containing species. The difference spectrum in Figure 4.5 reflects the effects of heating sulfated zirconia from 400 to 700°C . Only negative features, denoting species lost by heating, were obtained by spectral subtraction. The difference spectrum in Figure 4.5 has distinct bands at 3658 , 1393 , 1084 , 1026 , and 987 cm^{-1} . Absorbance bands below 950 cm^{-1} could not be detected in difference spectra because of excessive noise resulting from the high absorbance background from zirconium oxide. Unlike infrared spectral results reported by Tanabe and coworkers^[6], no infrared absorbance band was detected at 1190 cm^{-1} . However, the S-O- bands at 1084 , 1026 , and 987 cm^{-1} in Figure 4.5 can be correlated with similar absorbance bands reported by Bensitel *et al*^[10]. In their study, small amounts of SO_2 in excess O_2 were added to a ZrO_2 sample and infrared spectra were measured after each increment of SO_2 was added. In addition to an intense band near 1400 cm^{-1} , Bensitel *et al*^[10] reported S-O- infrared absorbance bands at 1082 , 1035 , 1004 , 968 , 937 , and 910 cm^{-1} after moderate amounts of SO_2 were admitted to the zirconia

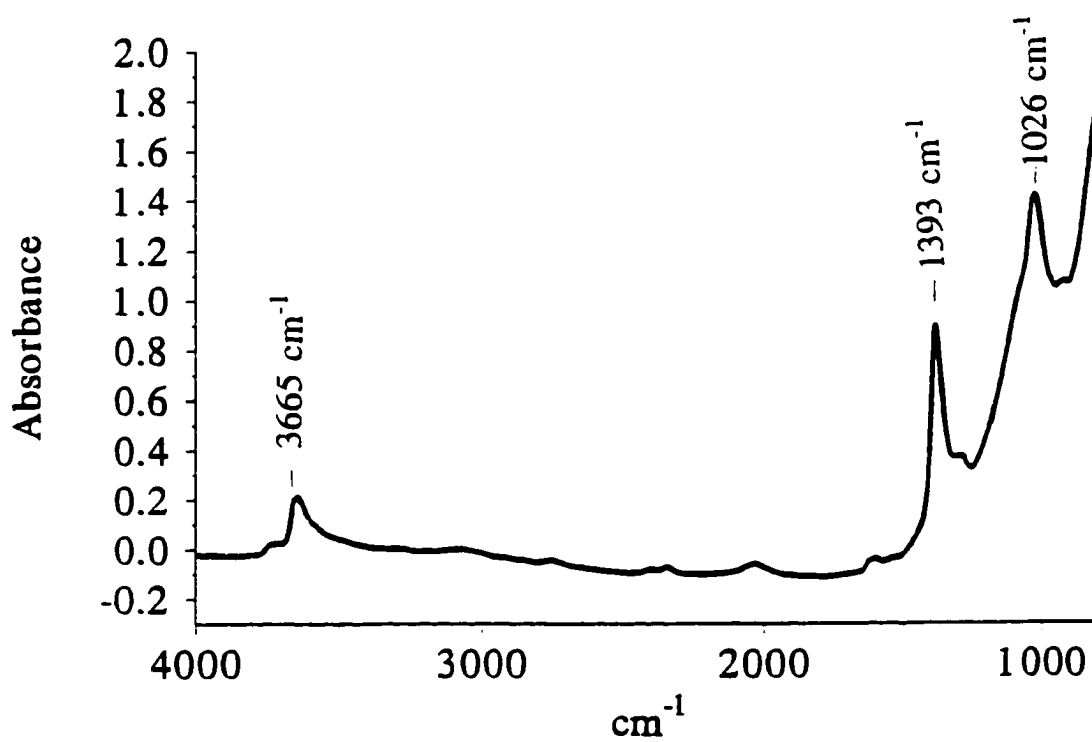


Figure 4.4 Sulfated zirconia VT-DRIFTS infrared spectrum

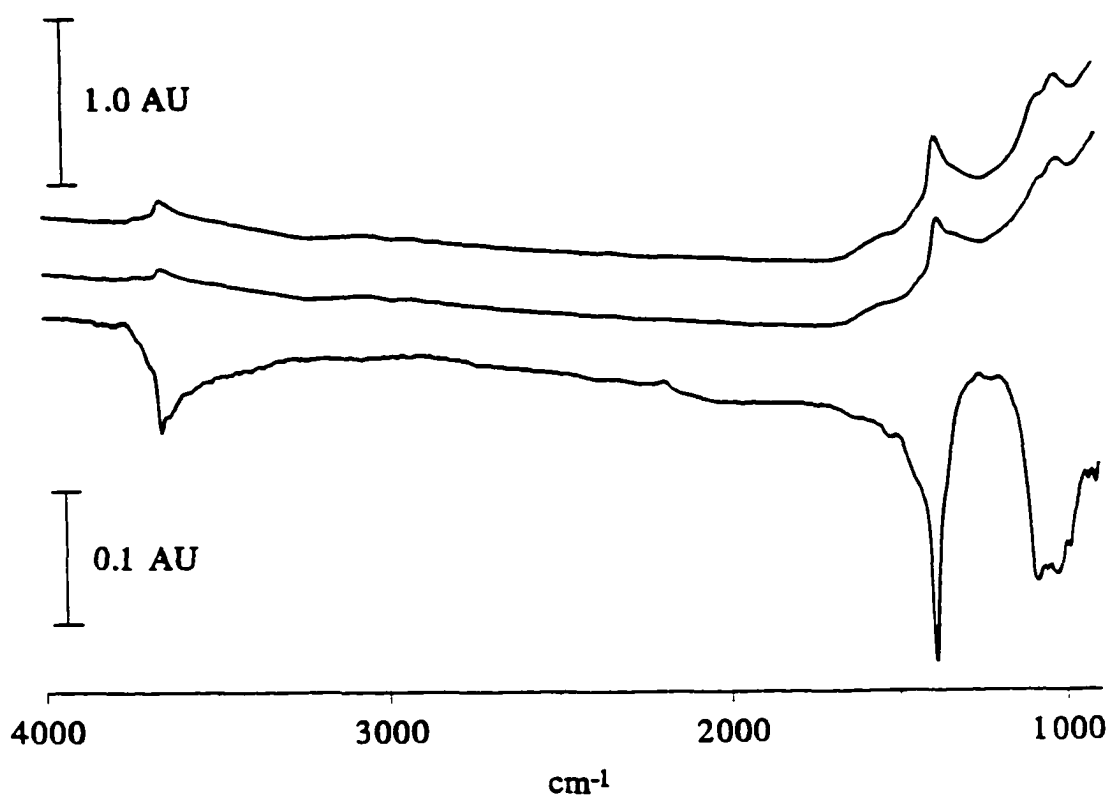


Figure 4.5 Top: Sulfated zirconia VT-DRIFTS spectra obtained at 700 and 400 °C. Bottom: Difference spectrum

sample.

4.4 TG-MS Results

Previously reported thermogravimetric studies indicated that the thermal decomposition of sulfated oxides made by reacting oxides with SO_2 and O_2 leaves the oxide with the same mass as was measured before sulfur-containing groups were formed^[11], suggesting a stoichiometric reversible reaction. By using TG-MS, we determined that the primary products of sulfated zirconia thermal decomposition are SO_2 and O_2 , which is consistent with previously reported mass spectrometric results^[20]. As noted in the previous section, absorbance band losses indicated in Figure 4.5 correlate with spectral changes observed when sulfated zirconia is made by adsorption of SO_2 in excess O_2 . These facts suggest that the decomposition process may be the reverse of the formation reaction when SO_2 and O_2 are used as reactants. Accounting for differences in ionization cross-sections of SO_2 and O_2 , relative mass spectral ion intensities indicated that the amount of SO_2 formed during sulfated zirconia thermal decomposition exceeded the amount of O_2 formed by a little more than a factor of 2. A 2:1 SO_2/O_2 ratio would suggest that thermal decomposition resulted in a stoichiometric loss of SO_3 from sulfated zirconia samples. This would be expected for the thermal decomposition of the structures shown in Figure 4.3. Interestingly, it has been shown that sulfated iron oxide can be prepared by heating the oxide in the presence of SO_3 , whereas a similar thermal treatment in the presence of SO_2 without added O_2 was unsuccessful^[22]. This finding supports the hypothesis that sulfation results in the incorporation of SO_3 into the oxide

structure. The fact that TG-MS results indicated that the SO_2/O_2 ratio exceeded 2:1 suggests that not all oxygen atoms produced by SO_3 decomposition formed O_2 . Some oxygen atoms likely reacted with surface impurities to form oxygenated species instead of O_2 .

With heating, zirconium hydroxide is converted into amorphous zirconium oxide that subsequently crystallizes into a tetragonal form. At higher temperatures, the tetragonal form converts to a monoclinic phase^[23,24]. The temperature corresponding to the tetragonal to monoclinic transition is lower for sulfated zirconia than for ZrO_2 ^[26-29]. Recent evidence suggests that sulfated zirconia exists only in the tetragonal form. In this tetragonal form, each bulk phase zirconium atom is coordinated to eight different oxygens. Four Zr-O bonds are significantly shorter than the other four. The four short Zr-O bonds constitute one distorted tetrahedron and the four longer Zr-O bonds constitute another distorted tetrahedron^[30]. At the surface, zirconium atoms of tetragonal zirconium oxide are coordinated to only six oxygens. Each zirconium atom can therefore coordinate to surface adsorbates through two vacant coordination sites^[30]. These surface coordination sites can be occupied by oxygenated sulfur species as shown in Figure 4.3. The fact that sulfated zirconia is not stable in the monoclinic form^[31] suggests that the acid site structure is sensitive to the spacing between zirconium and oxygen atoms at the oxide surface. Monoclinic ZrO_2 is less dense than tetragonal ZrO_2 and therefore its unit cell is larger^[30]. Because Zr-O-Zr spacings are larger for monoclinic than for tetragonal ZrO_2 , the multiple interactions depicted in Figure 4.3 may not be possible.

4.5 Ammonia TPD Results

Various Lewis bases interact with sulfated oxides causing the -S=O stretching vibration to shift to lower frequencies. At the same time, infrared bands that can be attributed to the adsorbed bases appear. CO adsorption has been used to show that adding sulfate to zirconia increases its Lewis acidity^[24,32]. Infrared spectroscopic studies of H_2 and CH_4 adsorption, which probe Lewis acid-base pair polarizations, suggest that zirconia sulfation reduces its Lewis basicity^[32]. The strong interactions between the sulfur atom and Zr-O oxygens in our proposed structure (Figure 4 3) would be expected to reduce the Lewis basicity of oxide oxygens and increase the Lewis acidity of zirconium atoms bonded to these oxygens via an inductive effect. Conversely, coordination of zirconium atoms by S-O oxygens would be expected to reduce their Lewis acidity. The observed increase in Lewis acidity for sulfated zirconia may occur because the magnitude of the Lewis acidity reduction is less pronounced than the Lewis acidity enhancement. It would be expected that adsorption of CO on Lewis acid sites would affect catalytic activity if these sites participate in reactions. In fact, Pinna *et al* have shown that sulfated zirconia activity for n-butane isomerization can be reversibly quenched by adsorption of CO^[33].

Infrared spectroscopy of adsorbed ammonia can be used to distinguish Lewis and Brønsted acid sites^[34]. By measuring infrared spectra while heating samples containing adsorbed ammonia, differences in the behavior of Brønsted and Lewis acid sites were observed. The partial removal of adsorbed ammonia from a catalyst by heating it from 100 to 200°C resulted in the infrared spectral changes depicted by the difference

spectrum in Figure 4.6. Partial ammonia desorption caused an O-H stretching vibration at 3695 cm^{-1} to shift to 3665 cm^{-1} , a broad loss of absorbance due to N-H stretching vibrations near 3000 cm^{-1} , loss of absorbance at 1610 cm^{-1} due to NH_3 that desorbed from Lewis acid sites, loss of absorbance at 1470 cm^{-1} due to NH_3 that desorbed from Brønsted acid sites, the appearance of a band near 1360 cm^{-1} , and a broad loss of absorbance near 1200 cm^{-1} . Because the positive $-\text{S}=\text{O}$ (1380 cm^{-1}) and negative NH_4^+ (1450 cm^{-1}) spectral features overlap in the difference spectrum, the band center intensities and peak frequencies corresponding to these species are not accurately represented by the absorbance maximum at 1360 cm^{-1} and at 1470 cm^{-1} in the difference spectrum. The broad negative spectral feature near 1200 cm^{-1} arises from a reduction in the number of $-\text{S}=\text{O}$ groups interacting with ammonia. The positive absorbance band at 1360 cm^{-1} represents $-\text{S}=\text{O}$ groups that were released from interactions with ammonia by heating the catalyst.

The fact that the O-H band was present in infrared spectra before and after partial ammonia desorption suggests that the acidity of this hydroxyl was not sufficient to protonate ammonia at 100°C . The fact that the O-H stretching vibration band shifted to a lower frequency when ammonia desorbed indicated that the O-H stretching vibration force constant was greater when ammonia was present. This is the opposite of what would be expected for acidic O-H protons interacting with ammonia. Based on these observations, it seems likely that the O-H band shift shown in the difference spectrum in Figure 4.6 resulted from a change in the environment of Zr-O-H moieties that were not responsible for Brønsted acidity. In the structure shown in Figure 4.3(b), the proton

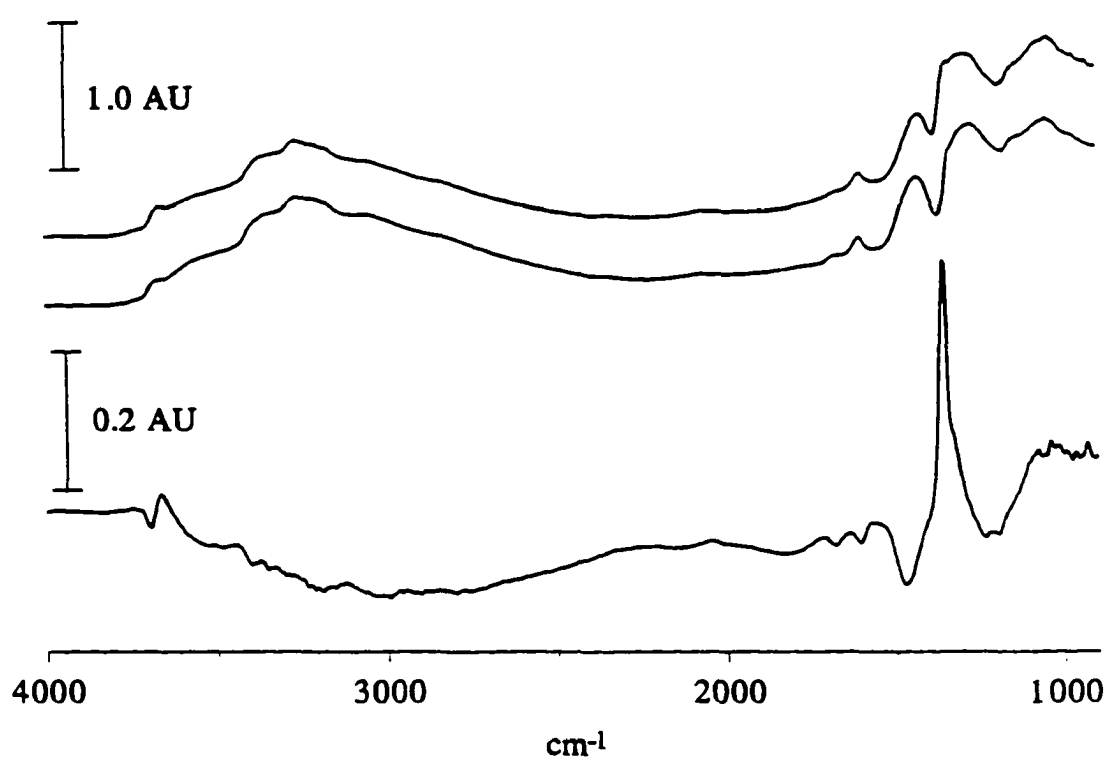


Figure 4.6 Top: Sulfated zirconia with adsorbed NH₃ VT-DRIFTS spectra measured at 200 and 100 °C.
Bottom: Difference spectrum

associated with the S-O oxygen would more likely be responsible for Brönsted acidity than the Zr-O-H proton. Because of the variable environment that the S-O-H proton may experience, O-H stretching vibration bands for this proton would be expected to be very broad and difficult to detect by infrared spectroscopy.

4.6 Comparison with Thionyl Tetrafluoride

The penta-coordinate sulfur in the Figure 4.3 structures is found in the thionyl tetrafluoride molecule, in which sulfur also exists in a +6 oxidation state.

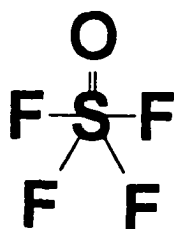


Figure 4.7 Thionyl tetrafluoride structure

The structure of this molecule might be expected to have features in common with the proposed sulfated zirconia acid sites shown in Figure 4.3. The SF₄O molecule is trigonal bipyramidal, has C_{2v} symmetry, and the -S=O moiety is located at the equatorial position^[21]. Two of the O=S-F bond angles are 90° and the other two O=S-F bond angles are 120°^[35]. The infrared spectrum of SF₄O contains a strong absorbance band at about 1380 cm⁻¹ that is assigned to the -S=O stretching vibration^[21,35]. The acid site structure shown in Figure 4.3 can be considered a distortion of the SF₄O structure in

which oxygen atoms replace fluorines and the two 90° O=S-F bond angles are increased.

4.7 Summary

A potential structure for the sulfated zirconia acid site was described. Thermogravimetric studies revealed that sulfated zirconia decomposed to produce SO_2 and O_2 in about a 2:1 ratio. Spectroscopic studies suggested that sulfur containing moieties possess a single -S=O group, in contrast to proposed bidentate structures. These findings, crystal phase temperature dependencies, and the similarity of the sulfated zirconia -S=O infrared band to that for SF_4O suggest that the sulfated zirconia acid site structure may be conceptualized as originating from the insertion of a planar SO_3 molecule into the ZrO_2 surface.

4.5 References

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CHAPTER FIVE

CATALYST ACIDITY MEASUREMENTS

As described in Chapter Three, *n*-butane reactor studies revealed that metal-promoted sulfated zirconia catalysts were much more active than unpromoted catalysts. It has been postulated that this enhanced catalytic activity may result from metal promoted catalysts being stronger solid acids than unpromoted catalysts^[1,2]. To explain differences in observed catalytic activities and to investigate the role of metal promoters in the overall reactivity of promoted catalysts, catalyst acidity was examined in detail.

5.1 Background

When catalytic activity for hydrocarbon isomerization or alkylation is enhanced by a change in the catalyst preparation method, the enhancement is often brought about by a change in catalyst acidity^[3]. This is particularly true for some aluminosilicate catalysts^[4]. For sulfated zirconia, the relationship between acidity and activity has not yet been established^[5]. The complexity of the acidic nature of sulfated zirconia catalysts has led to a controversy between those who claim that sulfated zirconia is a superacid^[6-8] and others who maintain that its acidity may not be any greater than that of sulfuric

acid^[9,10]. For instance, Arata *et al*^[11] used Hammet indicators and concluded that, depending on the preparation method, sulfated zirconia can be a superacid with H_0 values as low as -16. On the other hand, Adeeva reported NMR results that suggested that sulfated zirconia does not possess exceptionally strong acidity^[10].

The nature of sulfated zirconia acidity is also controversial. There have been claims that catalytic activity derives mainly from Lewis acid sites^[12]. Others contend that Brönsted acid sites are responsible for sulfated zirconia activity^[13]. Tanabe *et al*^[14] reported that both Brönsted and Lewis acid sites are found on the catalyst with relative ratios that depend on preparation conditions. Nascimento *et al*^[15] also reported that both acid types were present and that the maximum catalytic activity was achieved when the ratio of Brönsted to Lewis acid sites approached unity.

The issue concerning the relationship between acidity and activity is further complicated by the fact that incorporation of transition metal promoters (e.g. Fe, Mn) has been shown to increase the *n*-butane isomerization rate by as much as three orders of magnitude^[16]. The role of metal promoters in relation to sulfated zirconia acidity has been postulated by several researchers. Hsu *et al*^[6] and Cheung *et al*^[17] postulate that sites responsible for increased catalytic activity are of higher acid strength than those found in unpromoted catalysts. Adeeva^[10], on the other hand, presented results that indicated that the acidities of unpromoted and Fe/Mn-promoted catalysts were similar. Farneth and Gorte^[18] suggested that factors other than acid strength may contribute to the enhanced activities of the catalysts. Clearly, despite considerable efforts^[19-25], the origin and nature of sulfated zirconia acidity is not well understood.

The term "acidity" has been used to designate the nature of acidic sites (Brönsted or Lewis sites), the number or density of sites, and the strength of these sites^[4]. Infrared spectroscopy has been used extensively to distinguish the two types of acid sites found on solid acid catalysts^[26-28]. Eischens and Pliskens^[26] first observed that ammonia adsorbed on the surface of aluminosilicates produced infrared bands that could be used to distinguish Lewis and Brönsted acid sites. Adsorption of ammonia produces several infrared bands that are absent in gas phase NH₃ spectra. A band near 1610 cm⁻¹ is assigned to the asymmetric H-N-H stretching vibration of coordinatively bound ammonia. This band has been used to confirm the presence of Lewis acid sites. A band near 1450 cm⁻¹ is due to adsorbed NH₄⁺ species, which is indicative of Brönsted acid sites^[4]. Similar results are obtained when pyridine is adsorbed on acid catalyst surfaces. In this case, pyridinium ion bands signifying the presence of Brönsted sites are observed at 1630 and 1545 cm⁻¹ and a band at 1440 cm⁻¹ is characteristic of coordinatively bound pyridine^[28].

5.2 Hammet Indicators

For Brönsted sites, acid strength determines the ability of these sites to convert an adsorbed neutral base into its conjugate acid^[25]. Thus, acid strength can be measured by using basic indicators^[24,29]. Acid strength may be expressed quantitatively by the Hammet acidity function, H₀:

$$H_0 = pK_{BH^+} - \log [BH^+]/[B] \quad [Eq\ 5.1]$$

where $[B]$ is the concentration of the indicator, $[BH^+]$ is the concentration of its conjugate acid, and K_{BH^+} represents the equilibrium constant for the reaction :



For liquid acids, the ratio $[BH^+]/[B]$ in Eq 5.1. can be obtained spectrophotometrically. A more negative value for H_o corresponds to greater acid strength. Figure 5.1 shows an H_o scale listing various liquid and solid acids^[30]. Sites with different acid strength may be present on a solid catalyst surface. The total surface acidity may then be characterized in terms of an acid strength distribution, in which the abundances of sites with similar strengths are reported^[31].

Hammet indicators have been used to characterize both liquid and solid acids. To measure solid acid strength, indicators having various pK_a values are dissolved in solvents in their basic forms. Indicator solutions are then dropped on samples of solid acids. If the indicator color changes to that for the acid form, then the value for the H_o function for the catalyst is assumed to be at least equal to the pK_a of the indicator conjugate acid^[4]. Table 5.1 lists indicators frequently used to measure solid acidities. According to the data compiled in Table 5.1, a solid acid catalyst that turns 2,4-dinitrotoluene from colorless (basic form) to red (acidic form) would have an H_o value of at least -13.75.

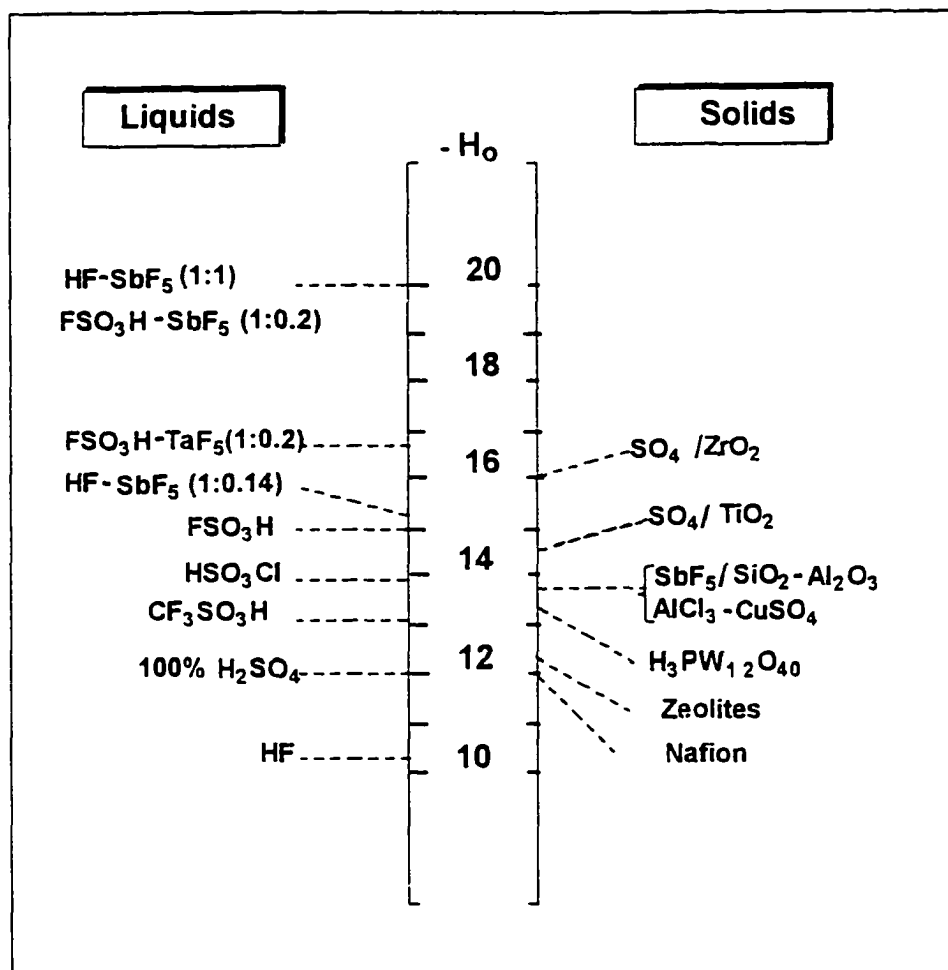


Figure 5.1 H_0 values for some strong acids

Table 5.1 Acid Strength Indicators

Indicator	pK _a
p-Nitrotoluene	-11.35
m-Nitrotoluene	-11.99
p-Nitrofluorobenzene	-12.44
p-Nitrochlorobenzene	-12.70
m-Nitrochlorobenzene	-13.16
2,4-Dinitrotoluene	-13.75
2,4-Dinitrofluorobenzene	-14.52
1,3,5-Trinitrotoluene	-16.04
2,4,6-Trinitrotoluene	-18.36
p-Methoxybenzaldehyde	-19.50

Hammet indicators have been used by several^[32-34] who have concluded that sulfated zirconia is a superacid with an acid strength 10^4 times greater than that of 100 % H₂SO₄. However, the use of Hammet indicators to measure solid catalyst acidities has been criticized^[35]. For example, Hammet bases are sometimes so strongly adsorbed that conjugate acids responsible for color changes are not formed^[10]. Their use for characterizing transition metal-promoted sulfated zirconias is handicapped by the fact that these catalysts are colored, making it difficult to detect indicator color changes^[36]. Further limitations of Hammet indicators are described in recent reports that they incorrectly attribute superacidity to ZrO₂^[37].

5.3 Infrared Acidity Measurements

Infrared measurements of catalyst OH stretching vibrations have been used to characterize Brönsted acid strengths. The absolute measurement of OH stretching frequencies gives no information about the acid strengths. However, the magnitudes of frequency shifts of these vibrations caused by interactions with hydrogen-bonded adsorbates can be informative^[38]. On the other hand, considerable doubt has been raised about the assumption that OH stretching frequencies can be directly correlated with acidities for all solid catalysts^[25,39].

Carbon monoxide is a Lewis base and can be used to probe Lewis acid sites on catalyst surfaces^[40-43]. The C≡O stretching vibration frequency shifts when CO coordinates with surface species. At low spectral resolution, vapor phase CO yields a vibrational/rotational infrared band centered near 2143 cm⁻¹ with side lobes at 2118 and 2180 cm⁻¹. After adsorption, CO molecules lose their rotational freedom and only vibrational transitions are observed in infrared spectra. The magnitude of CO frequency shifts are indicative of the strengths of surface interactions.

The strength of a solid catalyst Lewis acid site (L) can be quantitatively characterized by the enthalpy (ΔH) of its interaction with an adsorbed base (:B):



However, because both protonic and aprotic sites are usually present on catalyst surfaces, enthalpy measurements are difficult because both sites can interact with adsorbates^[25].

After comparing the effects of adsorbed bases on infrared spectra of metal oxides, it has been suggested that the strengths of aprotic sites may be characterized by:

$$\Delta\nu_B = \nu_B^{\text{ads}} - \nu_B^{\text{gas}} \quad [\text{Eq 5.4}]$$

where ν_B^{ads} is the infrared band frequency for an adsorbate and ν_B^{gas} is the frequency of the corresponding vibration in the gas phase. The assumption that $\Delta\nu_B$ is a function of the extent of the interaction between **L** and **B** has been verified for carbon monoxide adsorbed on Zr^{4+} , Zn^{2+} , and Mn^{2+} in the corresponding metal oxides by Paukshtis *et al*^[39]. For the Zr^{4+} -CO interaction, the following empirical expression was established:

$$\Delta H \text{ (kJ/mol)} = 10.5 + 0.5\Delta\nu_{\text{CO}} \quad [\text{Eq 5.5}]$$

Quantitative measurements of acid site densities by using infrared spectroscopy are handicapped by the fact that these methods require accurate extinction coefficients for adsorbate bands. Also, experimental parameters such as the degree of coverage affect these measurements^[25]. In many cases, however, relative acid site densities have been measured and correlated with catalytic properties^[44].

5.4 TPD Acidity Measurements

Temperature programmed desorption (TPD) of adsorbed molecules from catalysts is a common method used for measuring acid site densities^[45-50]. When the temperature

of a catalyst containing an adsorbate is increased, adsorbed species with the lowest activation energies for desorption will evolve first, followed by species with greater activation energies^[51]. Desorbed species may be detected and identified by using an evolved gas analyzer such as a mass spectrometer. If the temperature at which adsorbates desorb is characteristic of catalyst site acidity, the area under a curve representing the rate of adsorbate desorption represents relative acid site densities. When TPD measurements are conducted by thermogravimetry, weight loss due to desorbed species as a function of temperature can be used to calculate catalyst acid site densities^[52]. Adsorbates such as ammonia, butylamine, 1-butene, benzene, pyridine, and acetonitrile have been used to characterize catalyst surface acidities by TPD^[53].

Several sulfated zirconia acid strength measurements based on TPD studies of basic adsorbates have been reported^[24,54-56]. Corma *et al*^[24] reported that sulfated zirconia was superacidic based on benzene TPD studies. Acid site density measurements of sulfated zirconia based on TPD studies have also been reported^[56-58]. However, evidence of a direct relationship between acid site density and catalytic activity has yet to be found. Clearly, more studies of sulfated zirconia acidity are warranted. The questions that are addressed here are whether TPD and infrared measurements reveal differences in acidity between promoted and unpromoted catalysts and, if so, whether these differences can be correlated with catalyst activity differences.

5.2 Experimental Conditions

Diffuse reflectance infrared spectroscopy (DRIFTS) and variable-temperature

diffuse reflectance infrared spectroscopy (VT-DRIFTS) were used to characterize sulfated zirconia acid sites. TPD measurements were employed to characterize adsorbate-catalyst interactions. For TPD measurements, mass spectrometry (MS) was employed as a thermogravimetry evolved gas detector to permit identification of volatiles.

Materials and Procedures. Ammonia and carbon monoxide were purchased from Sooner Air Gas (Norman, OK) in lecture bottles. The lecture bottles were connected to the DRIFTS adsorption chamber described in Chapter Two and the amount of gas allowed into the chamber was measured by using a pressure gauge. Catalysts used for infrared measurements were sieved prior to measurements and only particles smaller than 38 μm were analyzed. Characteristics of the catalysts used in this study are listed in Table 3.5. For VT-DRIFTS measurements, approximately 5 mg neat catalyst samples were heated in air at 30°C/min from room temperature to 600°C to remove adsorbed water and organic impurities. During this pretreatment, infrared spectra were measured periodically to assure the integrity of the sample and to confirm the removal of organics. The need for catalyst pretreatment is illustrated by Figure 5.2, which shows 3 sulfated zirconia infrared spectra obtained under different pretreatment conditions. The spectrum in Figure 5.2(a) was measured before the sample was heated. This spectrum exhibits a broad band near 3200 cm^{-1} and a band near 1600 cm^{-1} indicating the presence of adsorbed water. The spectrum in Figure 5.2(b) was measured after the sample had been heated to 600°C under flowing helium. Although water had been removed, this spectrum contains a band near 2980 cm^{-1} that is consistent with the presence of adsorbed organic

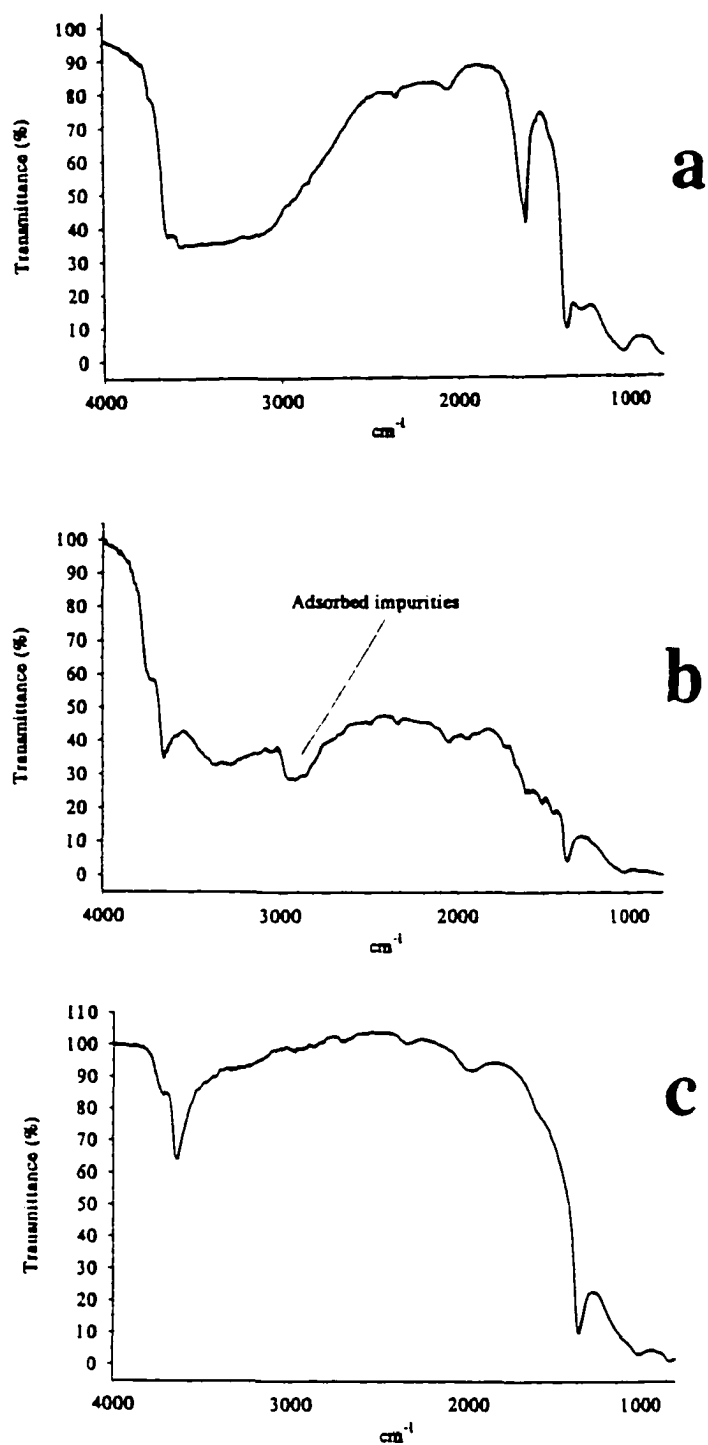


Figure 5.2 Effects of catalyst pretreatment on infrared spectra : (a) untreated sample; (b) sample heated in He; (c) sample heated in air at 600°C

impurities on the catalyst. After heating the sample to 600°C in air and then applying a vacuum (10^{-6} Torr) to the sample chamber, infrared spectra resemble that shown in Figure 5.2(c). In this spectrum, the absence of the 3200, 2980 and 1600 cm^{-1} bands indicates that water and organic species have been removed from the catalyst surface. After heating to 600°C in air, catalyst samples were cooled to 100°C and ammonia was admitted to the sample chamber until the desired pressure (usually 10 Torr) was obtained. The catalyst sample and ammonia were allowed to equilibrate for about 10 minutes, then the chamber was purged with He at 10 mL/min. By monitoring the gas phase NH_3 infrared bands at 970 and 935 cm^{-1} , it was possible to determine when all ammonia vapor was purged. A similar procedure was followed for the adsorption of carbon monoxide, except that in this case, CO was introduced into the chamber at 30°C. For benzene and amine adsorption studies, about 1 mL was placed into a glass tube (4 mm diameter, 100 mm long). After 5 freeze-evacuation-thaw cycles, the organic vapor was admitted into the chamber until the pressure reached 10 Torr. After adding adsorbates and purging vapor phase species, VT-DRIFTS spectra were acquired at a rate of 1 spectrum/min at 8 cm^{-1} spectral resolution while the sample was heated at a rate of 10°C/min.

Temperature-programmed desorption (TPD) measurements were made by using a DuPont model 951 TGA connected to a Hewlett Packard (Palo Alto, CA) 5985 mass spectrometer as described in Chapter Two. About 10 to 20 mg catalyst samples were placed in the TG sample pan. Samples were heated in air at 30°C/min to 600°C. Air flow was then shut off and the TG chamber was evacuated. Samples were left at 600°C under vacuum for 30 minutes. After cooling samples to 100°C, adsorbates were

introduced. Introduction of liquid adsorbates such as pyridine and benzene was accomplished by following the freeze and thaw method described previously. Organic vapors were removed by purging the TGA with helium at 50 mL/min. Helium purge was maintained until the mass spectrometer no longer detected the presence of organics in the effluent. During TPD-MS measurements, adsorbate desorption was accomplished by heating samples at 10°C/min from 100 to 800°C.

5.6 Infrared Spectroscopic Results

Reported hydroxyl group stretching frequencies and shifts resulting from interactions between zirconia, sulfated zirconias, and HY zeolite with benzene and acetonitrile are listed in Table 5.2. Frequency shifts obtained when pyridine was used as the adsorbate during the present study are also listed in Table 5.2.

Table 5.2 Effects of adsorbates on $\nu_{\text{(OH)}}$

Catalyst	$\nu_{\text{(OH)}}$ (cm ⁻¹)	Adsorbate	$\Delta\nu_{\text{(OH)}}$ (cm ⁻¹)	Reference
ZrO ₂	3670	Benzene	100	40
SO ₄ ²⁻ /ZrO ₂	3640	Benzene	200	40
SO ₄ ²⁻ /ZrO ₂	3630	Acetonitrile	430	10
Fe,Mn/SO ₄ ²⁻ /ZrO ₂	3630	Acetonitrile	430	10
SO ₄ ²⁻ /ZrO ₂	3665	pyridine	150	this work
Fe,Mn/SO ₄ ²⁻ /ZrO ₂	3665	pyridine	150	this work
HY zeolite	3640	Benzene	300	29

The fact that the magnitude of the frequency shift for benzene in Table 5.2 is greater on HY zeolite than on unpromoted sulfated zirconia suggests that HY hydroxyls are stronger acids than those for unpromoted sulfated zirconia. The larger frequency shift for sulfated zirconia hydroxyls than for ZrO_2 hydroxyls after benzene adsorption suggests that hydroxyls on sulfated zirconia are more acidic than hydroxyls on ZrO_2 ^[40]. After acetonitrile adsorption, Adeeva *et al*^[10] found that unpromoted and (Fe/Mn)-promoted sulfated zirconias exhibited the same frequency shift (Table 5.2), suggesting that there is no difference in acid site strength.

Sulfated zirconia acid strengths were characterized by using infrared measurements of adsorbed NH_3 , CO, and pyridine. An infrared spectrum of ammonia adsorbed on unpromoted sulfated zirconia at 100°C is shown in Figure 5.3. A band located at 1450 cm^{-1} is consistent with the formation of NH_4^+ , indicating that Brönsted acid sites were present on the SZ catalyst. Coordinatively bound NH_3 was responsible for the band at 1610 cm^{-1} in Figure 5.3.

Figure 5.4 shows a spectrum of adsorbed pyridine on unpromoted sulfated zirconia. Pyridine adsorbed on the catalyst surface by coordinating with Lewis acid sites exhibited a band at 1445 cm^{-1} due to the ring stretching ν_{19b} infrared vibration^[59]. Reactions of pyridine with Brönsted sites forming adsorbed pyridinium ions was responsible for the band at 1540 cm^{-1} . These results confirm that unpromoted sulfated zirconia possesses both Lewis and Brönsted acid sites even after pretreatment at 600°C in air.

The effects of metal promoters on ammonia adsorption was also studied.

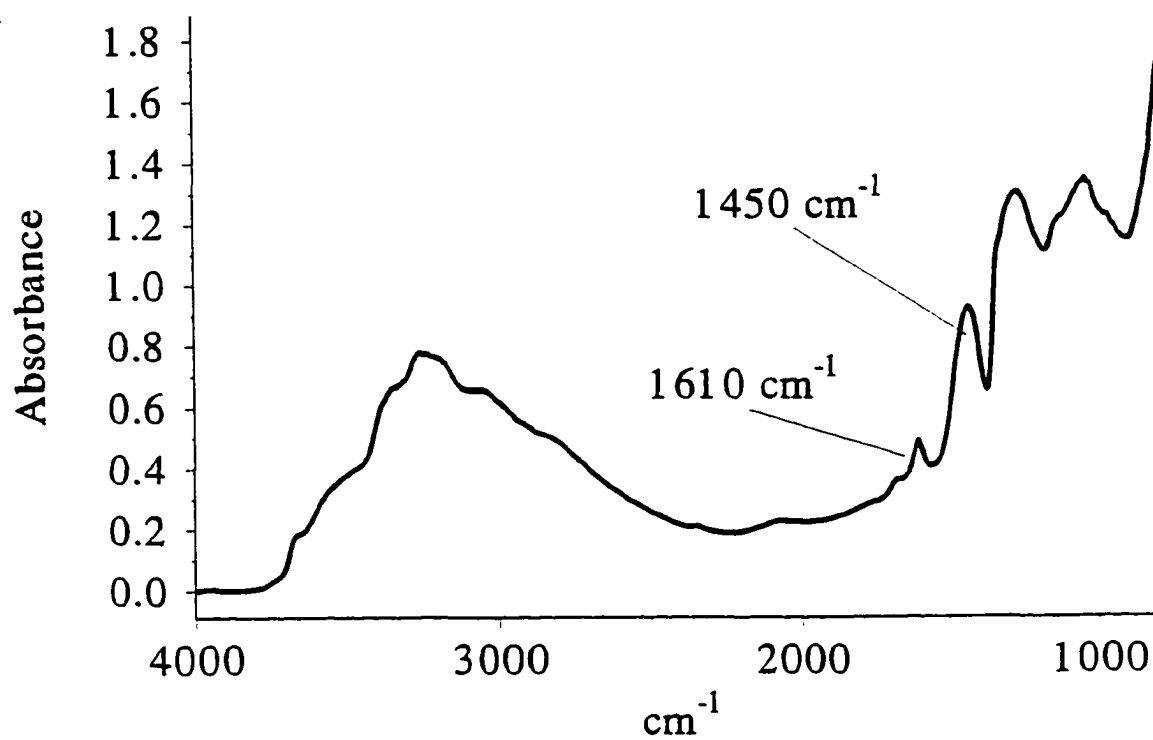


Figure 5.3 Infrared spectrum of ammonia adsorbed on an unpromoted catalyst

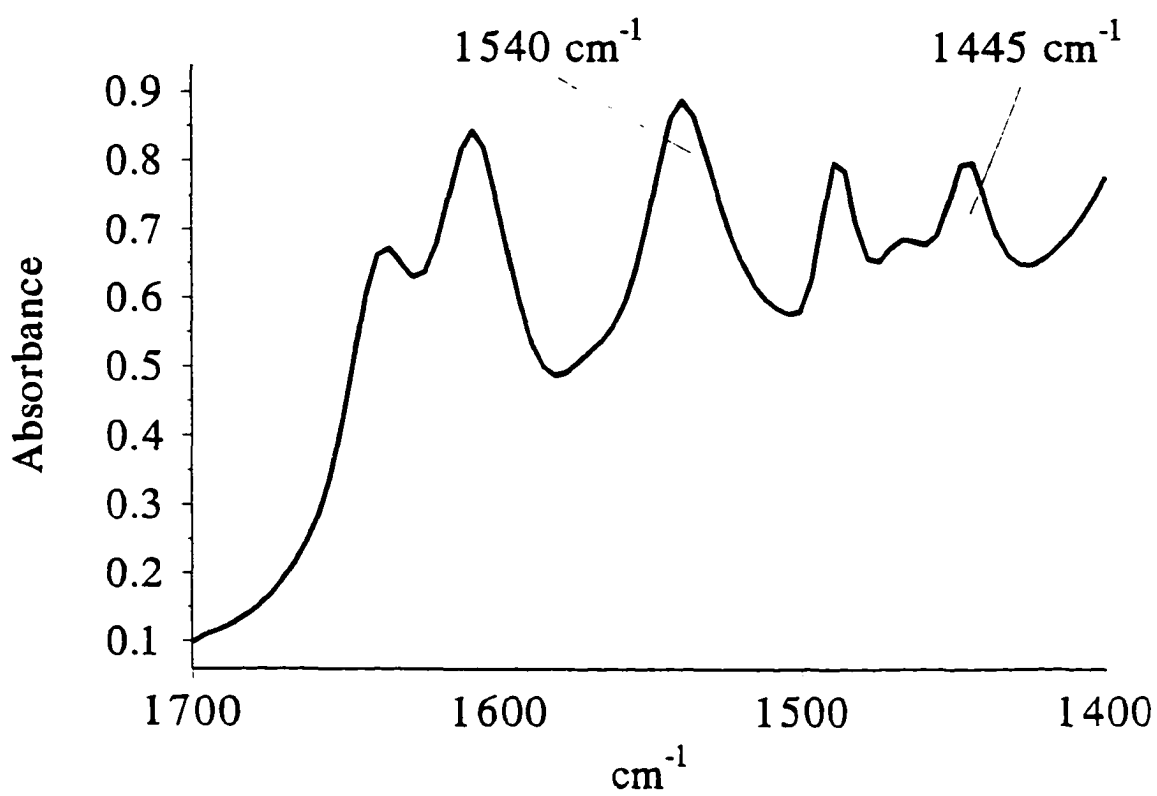


Figure 5.4 Infrared spectrum of pyridine adsorbed on an unpromoted catalyst

Adsorption of NH_3 on metal promoted catalysts produced the spectrum shown in Figure 5.5. Metal promoted catalysts exhibited spectral features similar to those found for NH_3 adsorbed on the unpromoted catalyst. Adsorbed ammonia spectra exhibited unresolved bands with maximum absorbance near 3271 cm^{-1} and shoulders at 3360 and 3040 cm^{-1} assigned to vibrational stretching modes of adsorbed NH_3 and NH_4^+ ^[27]. In the O-H stretching vibration region, the catalyst band at 3665 cm^{-1} was buried under a broad N-H stretching vibration band. This broad band precluded acid strength comparisons based on adsorbed ammonia induced O-H stretching frequency shifts. The most significant vibrational frequency shifts were observed for a band associated with -S=O vibrations. After ammonia adsorption, the -S=O band shifted to lower frequency, suggesting a direct interaction between adsorbate and -S=O groups. Frequency shifts observed for unpromoted and metal promoted catalysts are listed in Table 5.3.

Table 5.3 Effects of Adsorbed Ammonia on -S=O Stretching Frequency

Catalyst	Composition	$\nu_{(\text{S=O})}$ Before ads. (cm^{-1})	$\nu_{(\text{S=O})}$ After ads. (cm^{-1})	$\Delta\nu_{(\text{S=O})}$ (cm^{-1})
SZ-1	unpromoted	1386	1274	112
SZFM-2	1.5 % Fe, 0.5 % Mn	1382	1313	69
SZF-2	0.5 % Fe	1386	1258	128
SZN-5	1.0 % Ni	1390	1280	110

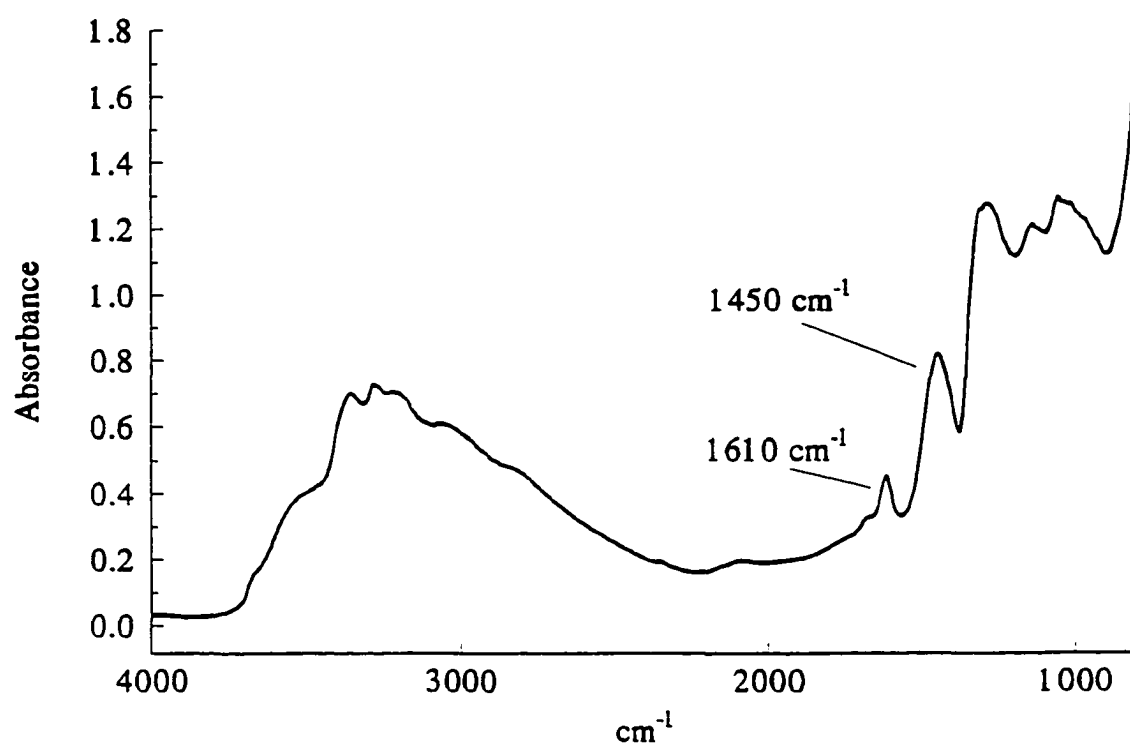


Figure 5.5 Infrared spectrum of ammonia adsorbed on a Ni-promoted catalyst

The data in Table 5.3 indicate that sulfate groups interact strongly with adsorbates. However, these results do not demonstrate significant catalyst-adsorbate interaction differences between promoted and unpromoted catalysts.

Because pyridine lacks N-H vibrations, adsorbed pyridine infrared spectra exhibit no bands above 3100 cm^{-1} . After pyridine adsorption on SZ-1, the catalyst O-H stretching vibration band was observed to shift from 3665 cm^{-1} to 3515 cm^{-1} . Pyridine adsorption on a sample of the (Fe/Mn)-promoted catalyst also yielded a band at 3515 cm^{-1} , suggesting similar interactions between pyridine and promoted catalyst OH groups. This conclusion is consistent with results described by Adeeva *et al*^[10] who reported the same acetonitrile frequency shifts for promoted and unpromoted sulfated zirconia catalysts (Table 5.2).

Variable temperature infrared measurements of adsorbed NH_3 were employed to characterize acid sites on unpromoted and promoted sulfated zirconias. Figure 5.6 is a difference infrared spectrum for the O-H vibration spectral range that was obtained by subtracting a spectrum obtained at 200°C from a spectrum obtained at 100°C for a catalyst sample containing adsorbed NH_3 . When the sample temperature was raised from 100°C to 200°C , ammonia partially desorbed. The positive peak in the difference spectrum represents an infrared band that was recovered after partial removal of ammonia whereas the negative band represents species lost due to adsorbate removal. The spectrum exhibits a loss of intensity at 3693 cm^{-1} and a gain at 3665 cm^{-1} that can be attributed to O-H stretching vibrations. Removal of adsorbed NH_3 shifted the O-H band from 3693 cm^{-1} to 3665 cm^{-1} . If adsorbed NH_3 had interacted with OH hydrogens,

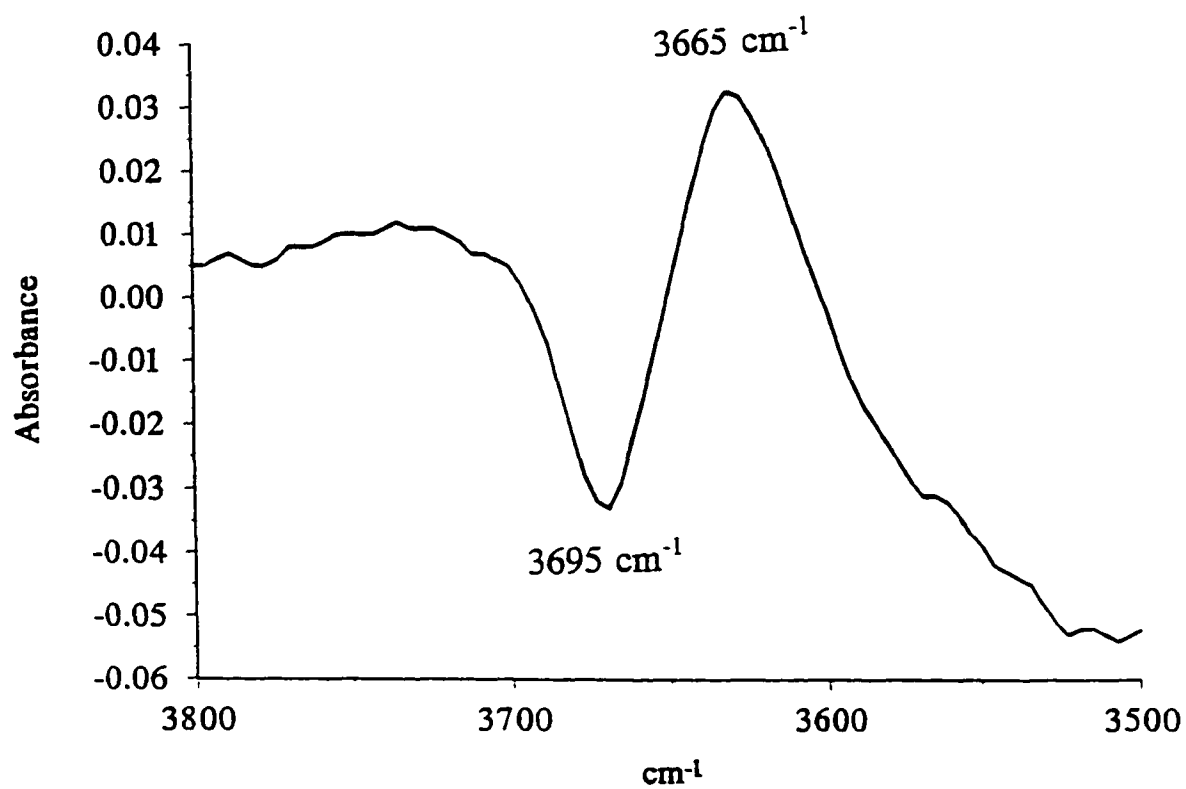


Figure 5.6 Difference spectrum obtained after partial ammonia desorption

the O-H bond would have been weakened and the O-H frequency would have shifted to lower frequency^[60]. The shift to a higher O-H stretching frequency suggests that NH₃ did not interact with OH groups through hydrogen atoms.

VT-DRIFTS studies were conducted for three metal promoted catalysts for which *n*-butane isomerization catalytic activities had been measured in an attempt to correlate Lewis and Brönsted acid strength distributions with catalytic activity. Infrared measurements of adsorbed ammonia were made during sample heating at 10°C/min and fifty infrared spectra were collected at one minute intervals from 100 to 600°C. Curve fitting software described in Chapter Two was employed to obtain absorbance versus temperature profiles for bands at 1450 and 1610 cm⁻¹. To facilitate comparisons between spectra, adsorbed ammonia absorbance bands were normalized to the S=O absorbance band intensity in each spectrum. Normalized absorbances plotted as a function of catalyst temperature for catalyst samples listed in Table 5.3 are shown in Figure 5.7. These graphs depict changes in the relative amounts of ammonia remaining on Brönsted and Lewis acid sites as a function of temperature. As shown in Figure 5.7, Brönsted and Lewis band intensity profiles for the unpromoted (SZ-1) and nickel-promoted (SZN-5) catalyst samples were similar. Thus, if catalyst acid strength distribution determined catalytic activity, SZ-1 and SZN-5 would have similar activities. However catalytic reactor studies revealed that SZ-1 was much less active for *n*-butane isomerization than SZN-5. The ratios of Brönsted to Lewis absorbance band intensities are plotted against desorption temperature in Figure 5.8. These ratios are relatively constant throughout the entire temperature range for the SZF-2, SZFM-2, and SZ-1 catalysts with average values

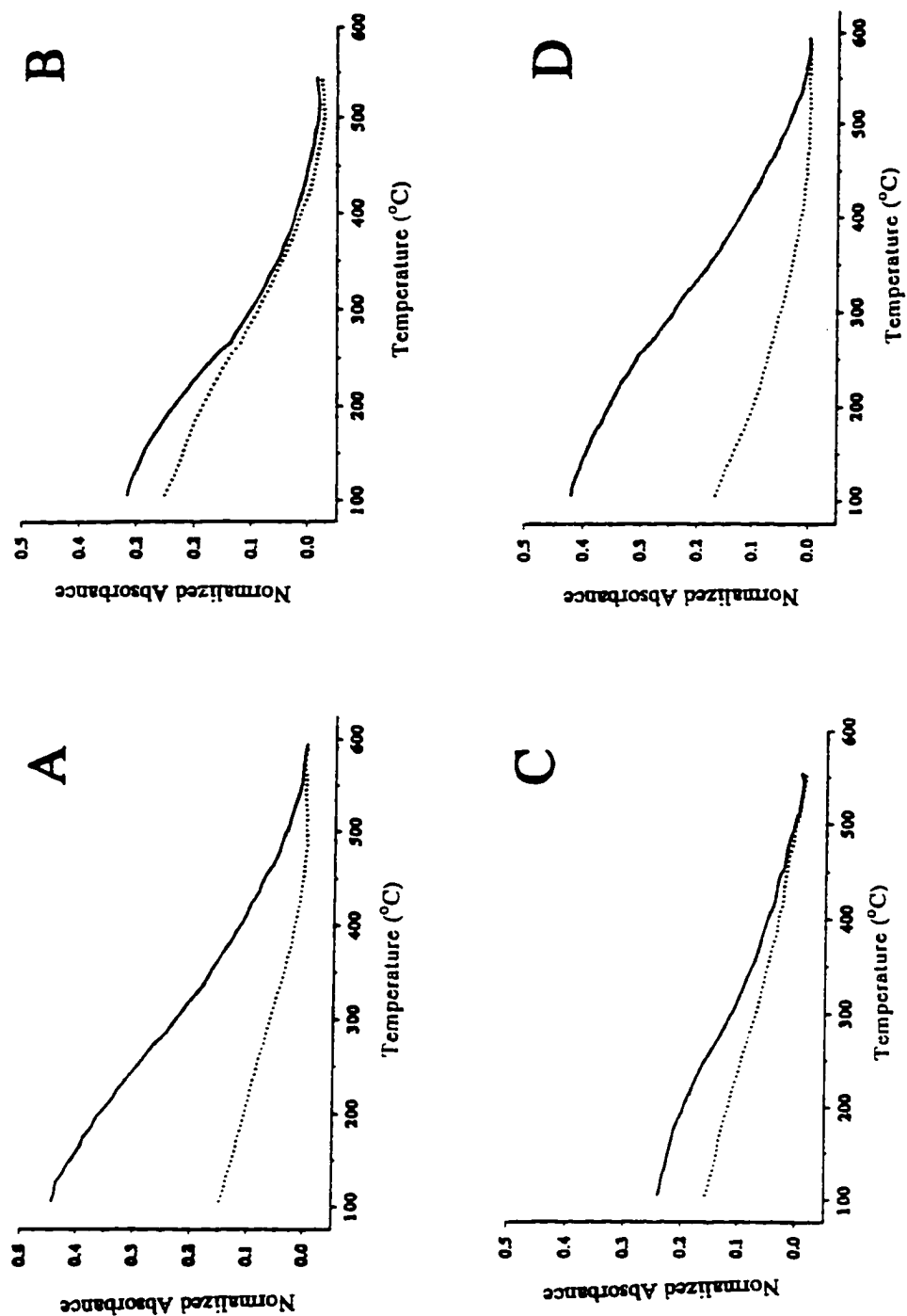


Figure 5.7 Brønsted (solid lines) and Lewis (dotted lines) ammonia absorbance band intensity profiles for (A) SZ-1; (B) SZF-2; (C) SZFM-1; and (D) SZN-5 catalysts

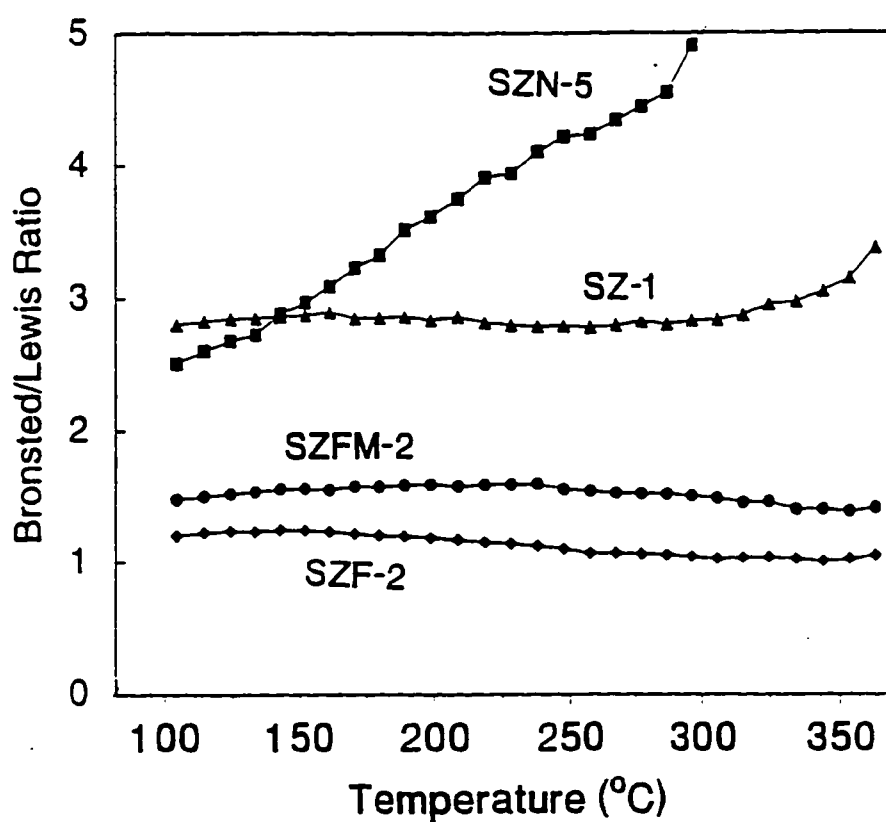


Figure 5.8 Temperature dependencies of Brønsted/Lewis absorbance band intensity ratios

of 1.2, 1.4, and 2.8, respectively. In contrast, SZN exhibited increasing absorbance for Brönsted sites relative to Lewis sites as desorption temperature increased. Table 5.4 lists initial Brönsted-to-Lewis ammonia absorption band intensity ratios along with catalytic activities at 250°C for *n*-butane isomerization. Clearly, there is no correlation between these ratios and catalytic activity.

Figure 5.9 shows difference spectra obtained after admitting enough CO to unpromoted sulfated zirconia to achieve vapor pressures of 5, 8, and 12 Torr. CO adsorption resulted in the appearance of bands at 2193 and 2166 cm⁻¹. The fact that two adsorbed CO infrared bands were detected suggests that there were at least two types of interactions between CO and SZ-1.

Table 5.4 Catalyst Activity and Acidity Relationship

Catalyst	Conversion(%) at 250°C	Initial B/L
SZ-1	1.9	2.8
SZFM-1	18	1.5
SZF-2	22	1.3
SZN-5	35	2.6

The band at 2193 cm⁻¹ was assigned to CO adsorbed on Zr⁴⁺ centers. Speilbauer *et al*^[61] have assigned the band near 2166 cm⁻¹ to hydrogen bonded CO.

An infrared spectrum of CO adsorbed on SZFM-2 is shown in Figure 5.10. CO

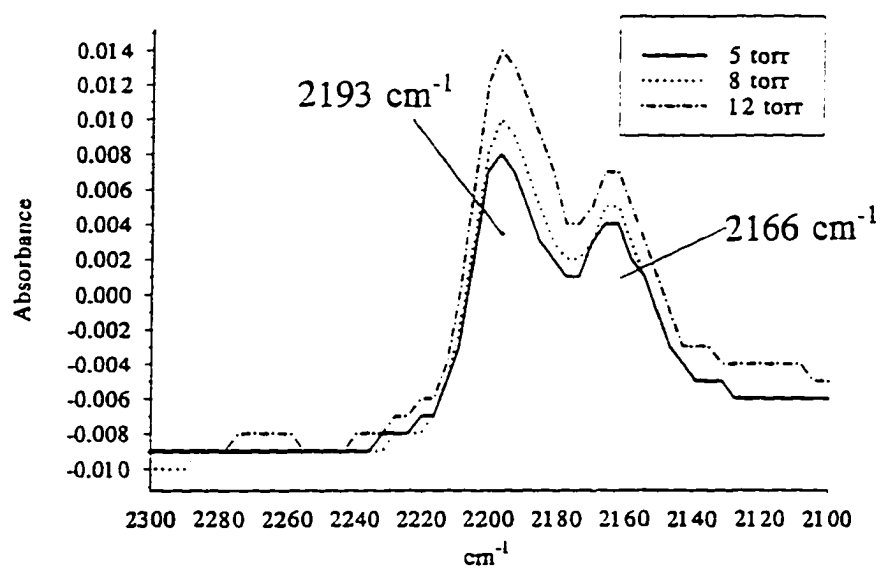


Figure 5.9 Infrared difference spectra representing CO adsorbed on SZ-1 catalyst

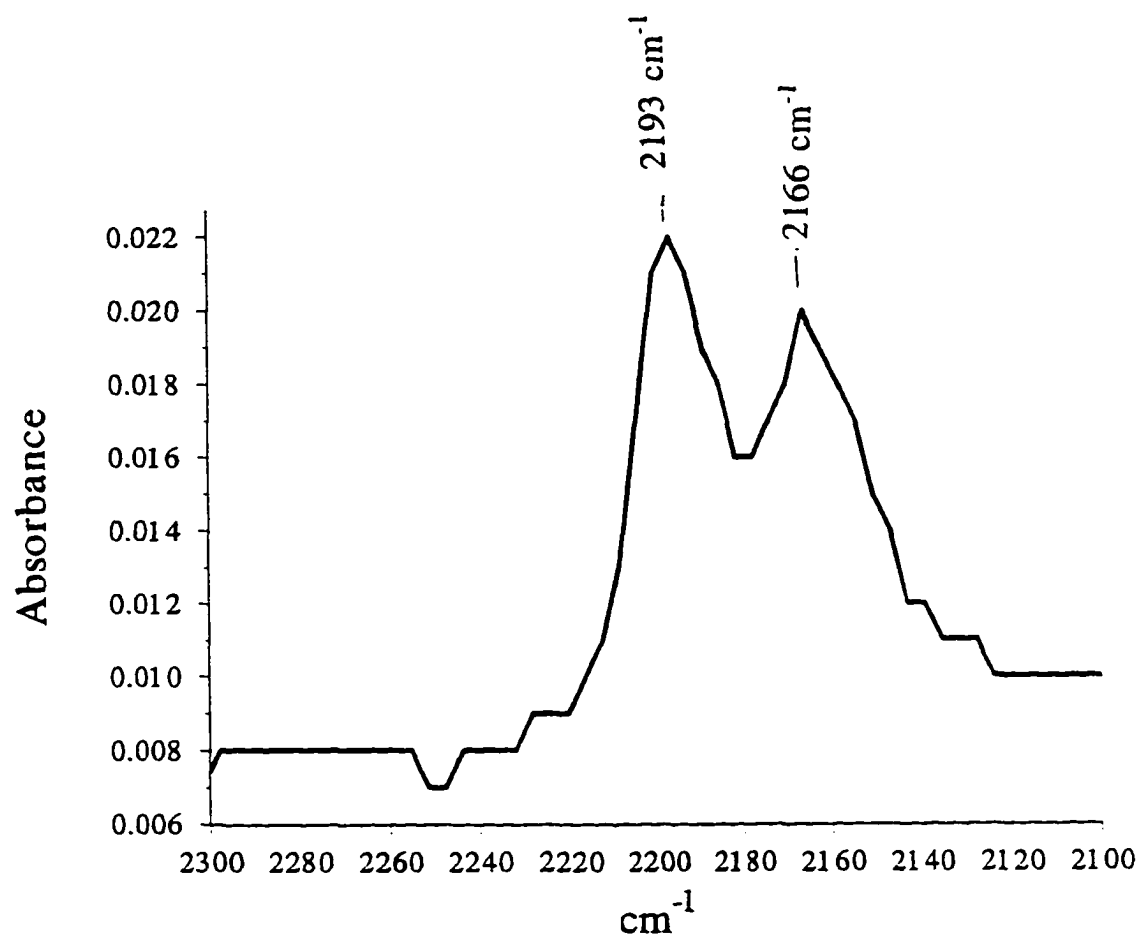


Figure 5.10 Infrared spectrum for CO adsorbed on SZFM-2 catalyst

adsorption on SZFM-2 also resulted in infrared bands at 2193 and 2166 cm^{-1} , suggesting that interactions between CO and the SZFM-2 catalyst were similar to those between CO and the SZ catalyst. Tabora and Davis^[25] measured infrared spectra of ZrO_2 and unpromoted and (Fe/Mn)-promoted sulfated zirconias and found $\text{C}\equiv\text{O}$ stretching bands at 2199, 2201, and 2201, respectively, which is consistent with the spectral results in Figure 5.10. Assuming that Eq 5.5 is valid, the strength of CO interactions with Lewis acid sites on unpromoted and promoted sulfated zirconias were both 35.5 kJ/mol of CO.

Arata *et al*^[11] contend that adsorption of water on sulfated zirconia increases Brönsted acid site densities whereas Garin *et al*^[62] reported no increase in Brönsted acid site density when catalysts were hydrated. Catalyst rehydration has been reported to both improve^[63] and quench^[64] catalytic activity of sulfated zirconia catalysts. More recently, studies have indicated that partial rehydration enhances catalytic activity but that excessive amounts of water renders the catalyst inactive^[65]. Figure 5.11 shows infrared spectra of sulfated zirconia before and after exposure to water vapor. Infrared bands at 3580, 1610 and 1250 cm^{-1} appear in the spectrum obtained for the catalyst after exposure to water vapor. When more water vapor was admitted, the absorbance band assigned to the to $-\text{S}=\text{O}$ stretching vibration shifted to lower frequency as a result of interactions with water. Lewis acid sites were characterized by comparing infrared spectra for catalysts with adsorbed CO to spectra of similarly treated catalysts exposed to water vapor prior to adsorption of CO. As shown in Figure 5.12, a spectrum measured after the catalyst was exposed to water vapor exhibited a much lower CO uptake, reflecting a loss of Lewis acid sites, particularly those that were responsible for the 2193 cm^{-1}

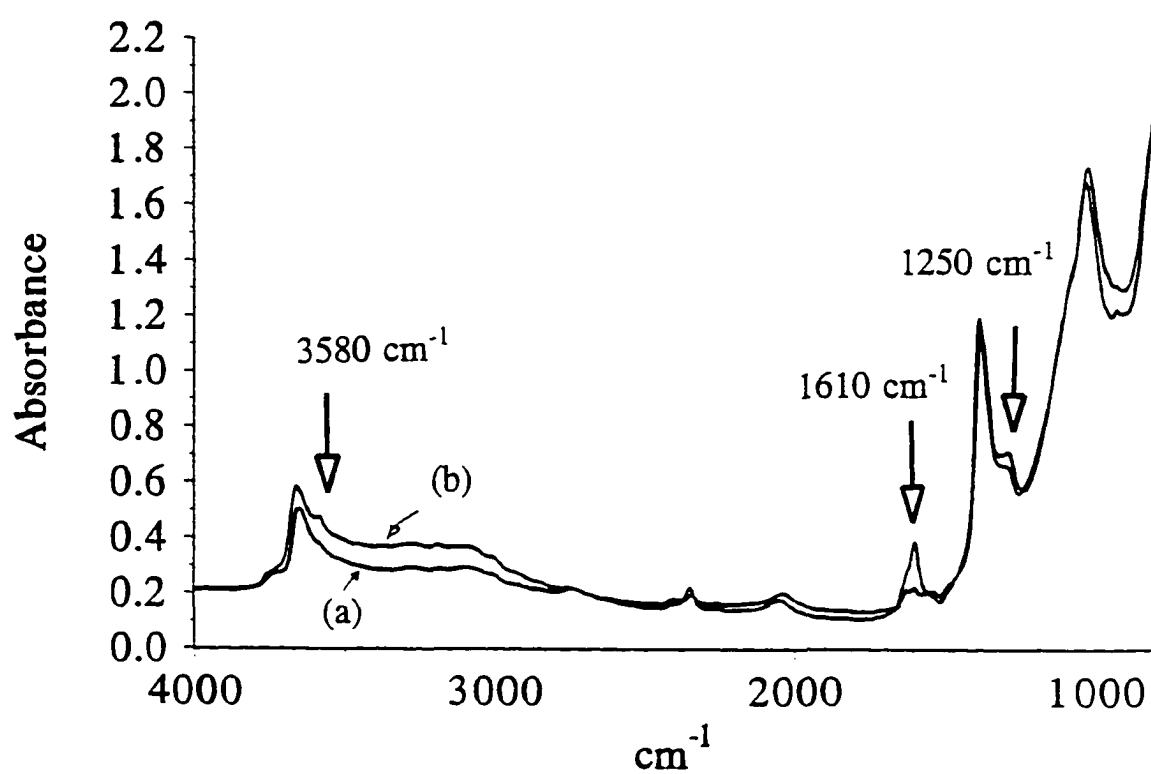


Figure 5.11 Infrared spectra for SZ-1 (a) before and (b) after water vapor adsorption

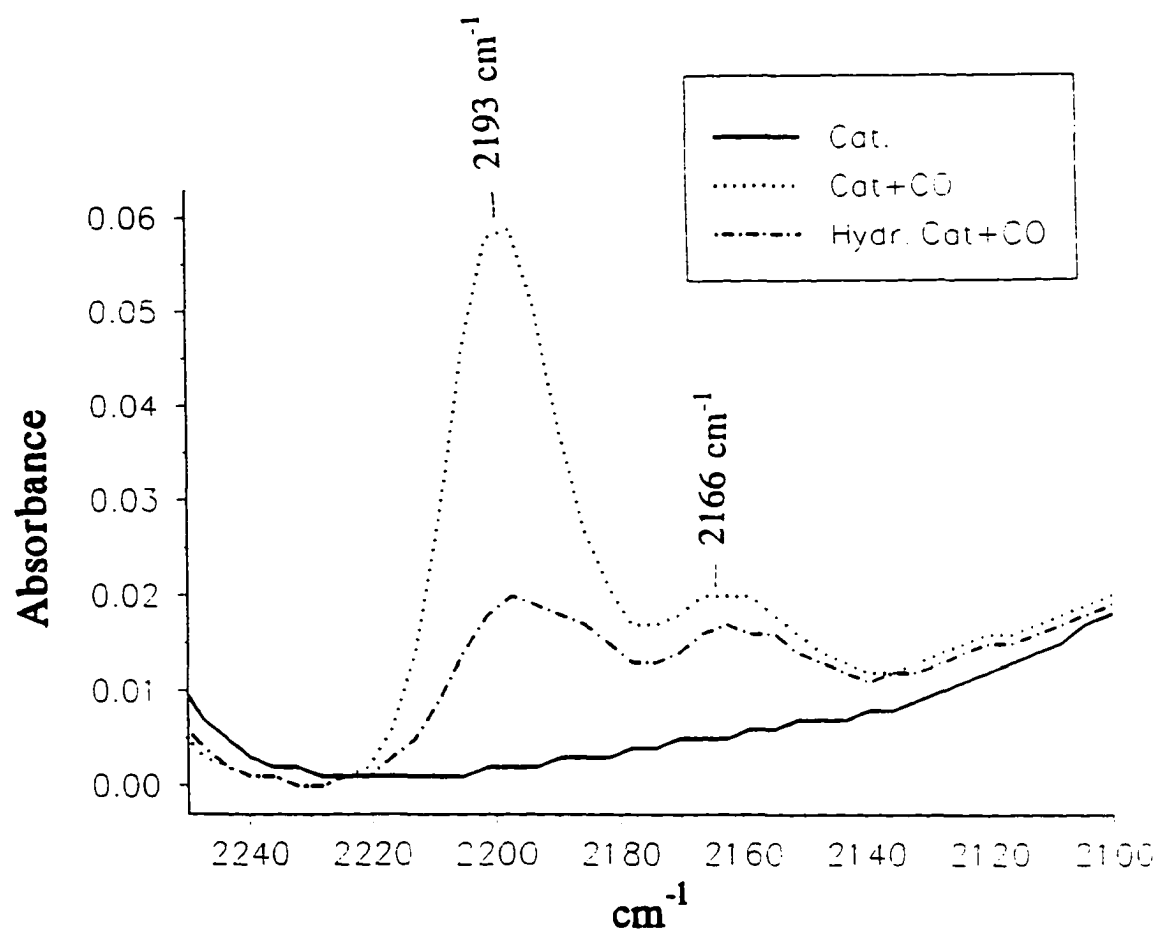


Figure 5.12 Effects of water on CO adsorption on SZ-1

band. The 2166 cm^{-1} band, which represents hydrogen bonded CO, was not significantly affected by exposure to water vapor. The loss of the 2193 cm^{-1} band is consistent with conversion of Lewis acid sites to Brönsted acid sites as a result of their reaction with water vapor.

5.7 TPD Results

Corma *et al*^[24] reported ammonia TPD results for sulfated zirconia in which they observed desorption maxima at 200, 330 and 540°C . The 540°C maximum was ascribed to strong acid sites that they identified as "superacid sites". Others have subsequently used ammonia TPD to measure acid site densities for sulfated zirconias. Tanabe *et al*^[31] performed adsorbed ammonia and pyridine TPD measurements and reported acid site densities of 1.1 and 1.3 sites/ nm^2 with ammonia and pyridine respectively. From ammonia TPD measurements, a total acid site density of 5.1 sites/ nm^2 was reported by Lin^[65]. In a recent ammonia TPD study by Tabora and Davis,^[25] acid site densities of 2.2, 2.0 and 1.9 sites/ nm^2 for zirconia, unpromoted sulfated zirconia, and (Fe/Mn)-promoted sulfated zirconia, respectively, were reported. Sohn and Kim^[32] measured an acid site density of about 44 sites/ nm^2 on an unpromoted catalyst sample by using ammonia TPD. However, assuming a monolayer coverage and a 0.148 nm molecular radius, a maximum of 15 ammonia molecules can occupy one nm^2 . Thus, the Sohn and Kim results exceed one monolayer.

Figure 5.13 shows TG-MS results obtained for ammonia temperature programmed desorption from the SZ-1 catalyst. Figure 5.13(a) is a TPD weight loss curve. Between

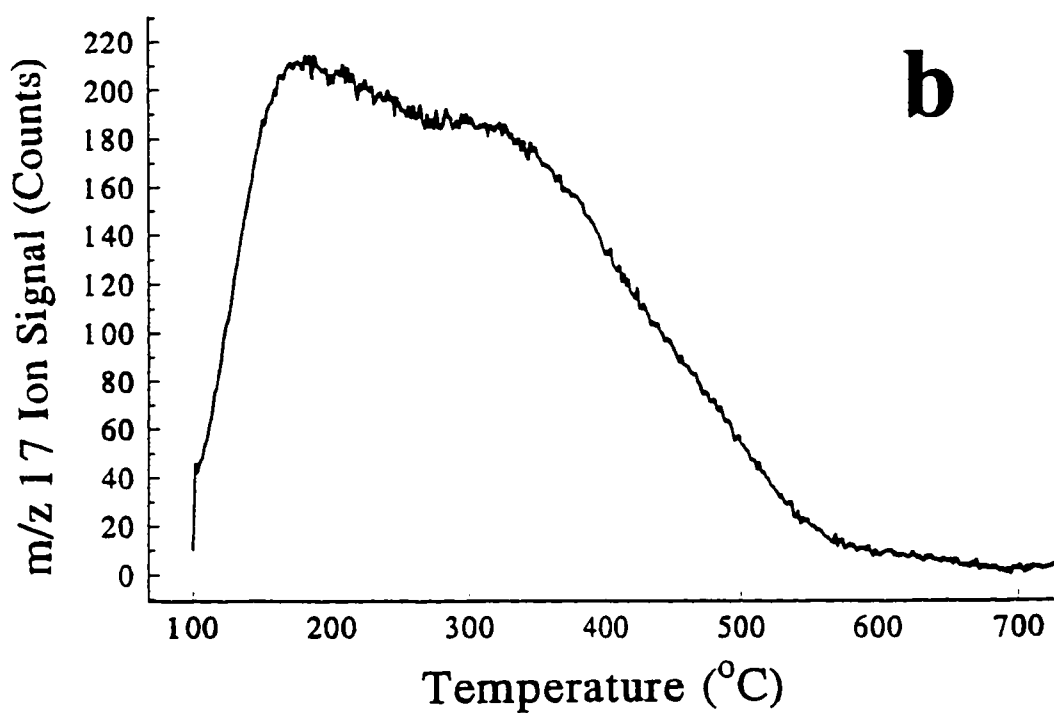
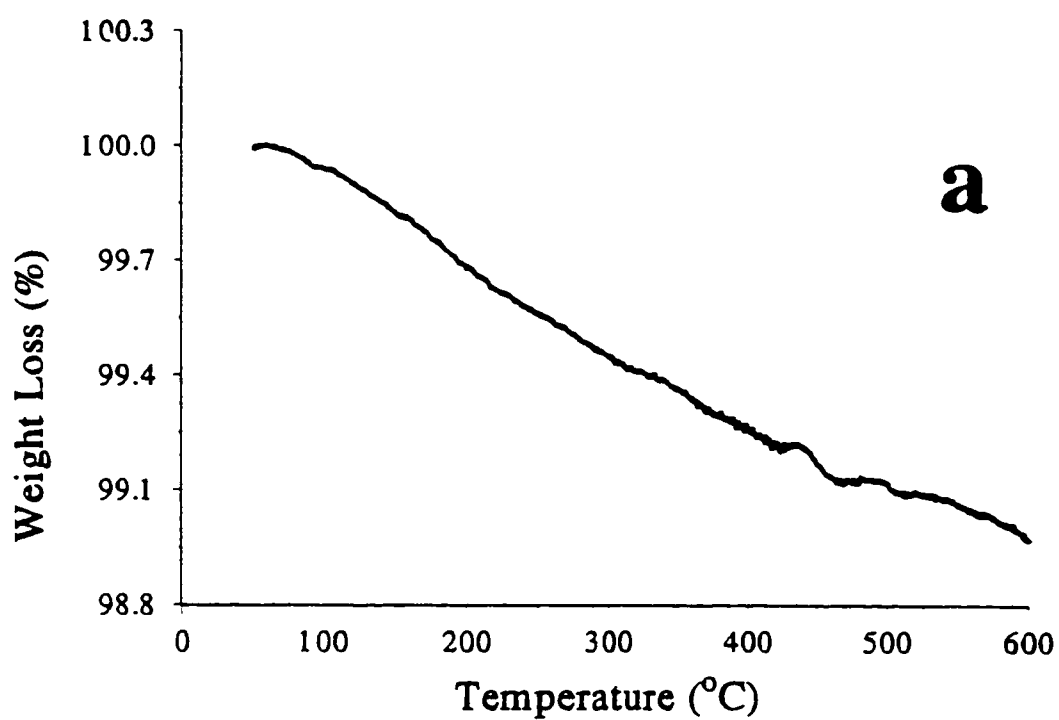


Figure 5.13 Ammonia TPD curve (a) and specific m/z 17 ion signal temperature profile (b)

100 and 500°C, the curve exhibits a gradual weight loss corresponding to ammonia and water desorption. Figure 5.13(b) shows the corresponding mass spectrometer m/z 17 ammonia specific ion signal. The water contribution to m/z 17 ion signal was removed by multiplying the m/z 18 ion signal by the ratio of m/z 17 to m/z 18 in water vapor mass spectra and subtracting these values from the total m/z 17 ion signal. Figure 5.13(b) indicates that the rate of ammonia desorption reached a maximum near 250°C and decreased at higher temperatures.

Three catalysts with metal-promoter compositions that yielded a wide range of *n*-butane isomerization catalytic activities were selected for TPD acidity measurements. The characteristics of these catalysts and those for the unpromoted catalyst are given in Table 5.5. Sulfate contents in Table 5.5 were calculated from TG weight loss measurements and percent conversions were obtained from *n*-butane isomerization reactor studies at 250°C in helium.

Table 5.5 Catalyst Characteristics

Catalyst	% SO ₄	Promoters	Conversion (%)
SZ-2	3.0	0.0	1.9
SZFM-2	5.2	0.5% Mn; 1.5% Fe	18
SZF-2	4.7	0.5 % Fe	22
SZN-5	3.0	1.0% Ni	35

Figure 5.14 shows TG-MS results derived from ammonia TPD from these catalysts. Figure 5.14 (a) shows that the rate of ammonia desorption maximized near 250°C for the nickel promoted catalyst. The catalysts that contained Fe only (b) and Fe and Mn (c) exhibited desorption profiles that were similar to that for the catalyst containing Ni. The total acid site density for each catalyst was estimated from ammonia TPD weight loss measurements. The weight difference between the beginning and the end of ammonia desorption was taken as the weight loss due to the total amount of ammonia desorbed. Table 5.6 lists the acid site densities of the sulfated zirconia catalysts and silica-alumina, which was provided for reference.

Table 5.6 Ammonia TPD Derived Catalyst Acid Site Densities

Catalyst	Composition	Density (sites/nm ²)
SZ-1	unpromoted	4.3
SZF-2	0.5% Fe	5.2
SZFM-1	0.5% Mn; 1.5% Fe	2.9
SZN-5	1.0% Ni	4.2
Silica-Alumina	S/Al : 7.5	0.97

Results indicate that the SZF-2 catalyst had the highest acid site density (5.2 sites/nm²). With 2.9 sites/nm², the SZFM-2 catalyst had the lowest acid site density of the 4 sulfated zirconia catalysts. In addition, Table 5.6 indicates that the unpromoted catalyst had a

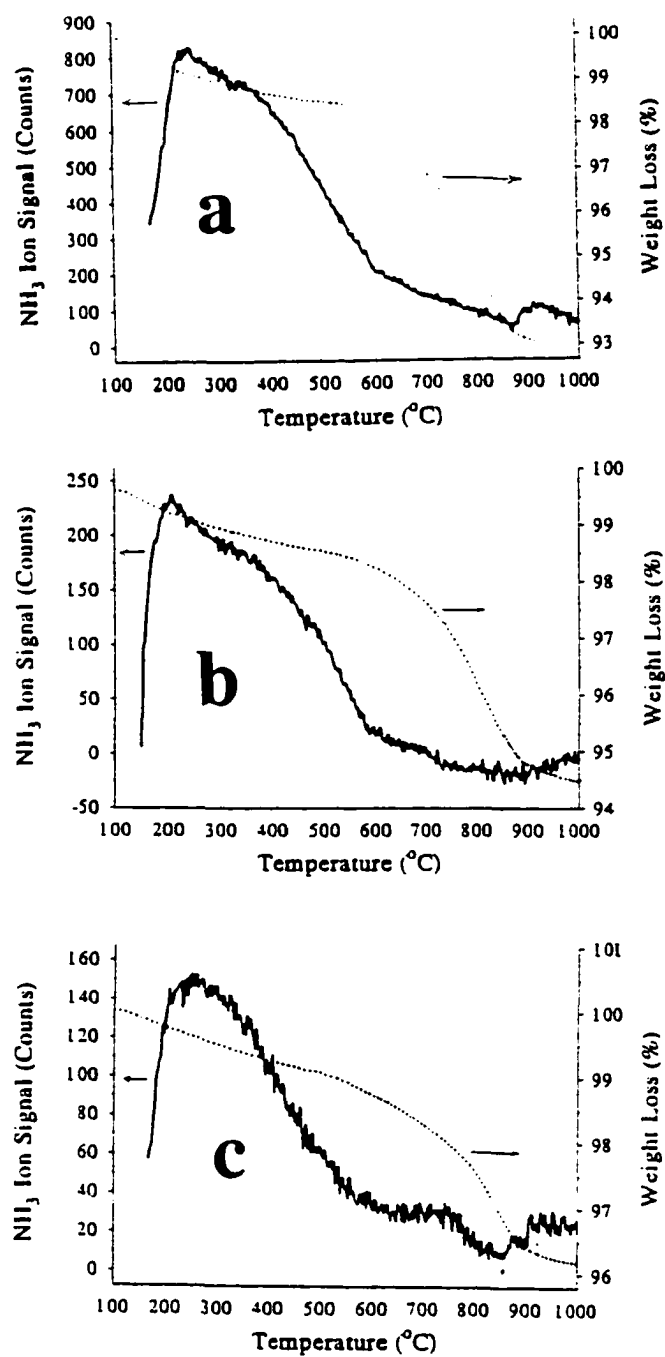


Figure 5.14 Ammonia TPD-MS results for (a) Ni-promoted; (b) Fe-promoted; and (c) Fe/Mn-promoted catalysts

higher acid site density than the SZFM-2 catalyst and that the nickel promoted catalyst had about the same acid site density as the unpromoted catalyst. All four sulfated zirconia catalysts had higher acid site densities than the silica-alumina catalyst. The acid site densities in Table 5.6 are in agreement with Lin's findings^[65] but are about 3 times higher than those reported by Tanabe *et al* and slightly higher than those reported by Tabora and Davis. Differences between our results and those reported by others may reflect differences in catalyst preparation methods. However, the relative acid site densities in Table 5.6 do not correlate with the catalytic activities for the four sulfated zirconia catalysts.

In the absence of adsorbed bases, TG-MS analyses revealed that the primary volatile product generated by the thermal decomposition of unpromoted sulfated zirconia and sulfated zirconia promoted with Fe, Fe and Mn, and Ni was SO₂ (m/z 64). It is well known that sulfated zirconia decomposes at high temperatures to yield SO₂^[67]. As shown in Figure 5.15(a), the maximum SO₂ evolution rate for a sulfated zirconia sample promoted with Fe and Mn occurred at about 825°C. The ion signal temperature profiles in Figures 5.15(b)-(d) show that the thermal stability of the (Fe/Mn)-promoted sulfated zirconia sample was affected by the presence of adsorbates. Whereas SO₂ evolution was first detected near 625°C for the sample without adsorbates, SO₂ evolution began near 500°C when ammonia was present, near 400°C when pyridine was present, and near 450°C when benzene was present.

Figure 5.15(b) shows that the rate of ammonia desorption reached a maximum near 250°C and decreased at higher temperatures. This behavior is consistent with

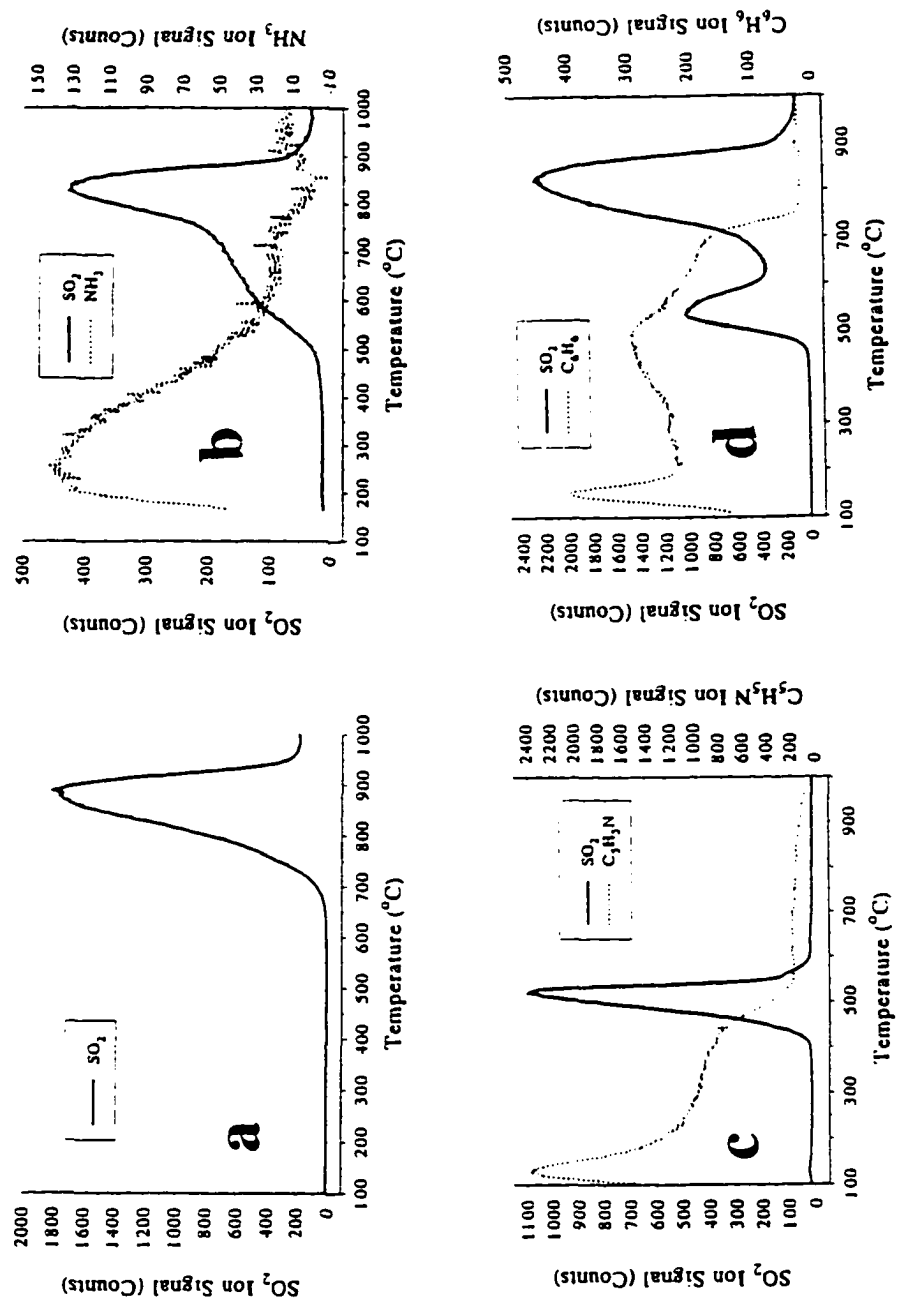


Figure 5.15 TPD-MS results for the SZFM-2 catalyst (a) without adsorbate; (b) with adsorbed ammonia; (c) with adsorbed pyridine; (d) with adsorbed benzene

previously described ammonia desorption studies of the same catalyst sample in which infrared spectroscopy was employed to selectively monitor desorption from Lewis and Brönsted acid sites (section 5.3). However, the NH_3 ion signal temperature profile shown in Figure 5.15(b) is inconsistent with results reported by Corma *et al*^[22]. Based on our findings, the increase in the rate of volatile product evolution at 540°C reported by Corma *et al* was more likely due to SO_2 formed as a result of catalyst decomposition than from ammonia desorption. Because Corma *et al* used thermal conductivity to detect species evolved during TPD, they could not distinguish SO_2 from ammonia. The fact that we observed no catalyst decomposition below 625°C in the absence of adsorbates (Figure 5.15(a)) is consistent with the fact that Corma *et al* found no TPD peak at 540°C during their TPD of the catalyst without adsorbed ammonia (the blank measurement). Similar findings have also been reported by others. From studies employing a mass spectrometer for detection of evolved species, Lee and Park found^[66] that adsorbed ammonia and pyridine cause sulfated iron oxide catalysts to decompose at lower temperatures. Their pyridine TPD studies indicated that significant quantities of CO_2 were produced at about the same temperature at which catalyst decomposition began. Also using mass spectrometric detection, Jutia *et al*^[67] found that benzene decomposed to CO_2 at 525°C on an (Fe/Mn)-promoted sulfated zirconia and that the catalyst decomposed to yield SO_2 in the presence of benzene at about 575°C. Because these decomposition temperatures are close to those previously attributed by others to ammonia and benzene desorption from promoted sulfated zirconia, it is possible that volatile decomposition products were mistaken for ammonia and benzene desorption in those

studies.

The ion signal temperature profiles for desorbed bases and SO₂ shown in Figure 5.15(b-d) indicate that each of the bases had a different effect on the thermal stability of the catalyst. Pyridine had the most dramatic effect on catalyst stability. As shown in Figure 5.15(c), the TPD ion signal temperature profile for SO₂ obtained for the sample with adsorbed pyridine exhibited a maximum near 525°C. Catalyst decomposition for this sample was complete by 600°C and no pyridine was evolved above 540°C. The SO₂ ion signal temperature profile obtained by benzene TPD exhibited two distinct maxima. The first TPD maximum occurred near 525°C and the second maximum was found at 825°C. The fact that the second maximum in Figure 5.15(d) occurred near the SO₂ TPD peak maximum measured for the sample without adsorbates (Figure 5.15(a)) suggests that this peak represented catalyst thermal decomposition without assistance from adsorbed benzene. The presence of an SO₂ evolution maximum near 525°C in Figure 5.15(d) suggests that the large benzene TPD peak reported by Lin and Hsu at 560°C for a (Fe/Mn)-promoted sulfated zirconia may have been caused by catalyst decomposition and is consistent with the claim made by Jatia *et al* that this TPD peak was due to a combination of CO₂ from benzene decomposition and catalyst decomposition, which resulted in SO₂ and O₂^[67].

Figure 5.16 shows mass spectra obtained by TG-MS analysis during TPD studies of an (Fe/Mn)-promoted sulfated zirconia sample. The mass spectrum in Figure 5.16(a) was obtained during ammonia TPD at 575°C. Ion intensities at m/z 64 and m/z 48 were due to SO₂ and represented SO₂⁺ and SO⁺, respectively. The ion detected at m/z 44

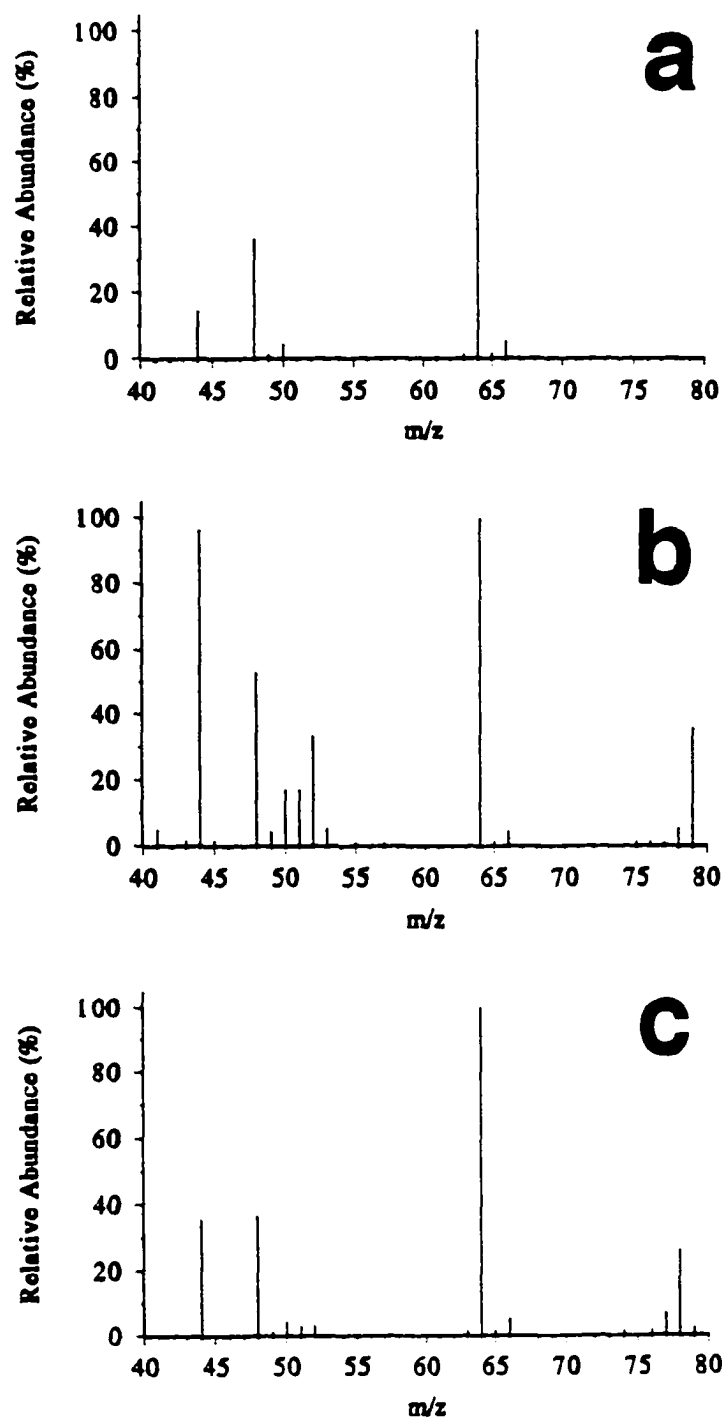


Figure 5.16 Mass spectra derived by TPD-MS for (a) no adsorbate; (b) adsorbed pyridine; and (c) adsorbed benzene

most likely represented CO_2 . Because CO_2 cannot be produced by reactions between the pristine catalyst and NH_3 , the carbon dioxide formed during catalyst decomposition likely resulted from oxidation of organic impurities on the catalyst surface, which were apparently present despite heating the samples at 600°C prior to ammonia adsorption. The mass spectrum shown in Figure 5.16(b) was obtained during pyridine TPD of an (Fe/Mn)-promoted catalyst sample at 520°C , the temperature at which the SO_2 evolution rate was highest. Ions at m/z 50, 51, 52, 53, 78, and 79 are representative of pyridine. The CO_2 ion intensity at m/z 44 in this mass spectrum is nearly as large as the SO_2 ion intensity, suggesting that significant oxidation of adsorbates on the catalyst surface occurred at this temperature. Figure 5.16(c) is a mass spectrum obtained at the temperature corresponding to the first SO_2 evolution maximum (525°C) during benzene TPD. Ions at m/z 50, 51, 52, 77, and 78 are representative of benzene. Again, this mass spectrum shows that CO_2 was detected in significant quantities when the catalyst decomposed.

Figure 5.17 shows ion signal-temperature profiles for the evolution of SO_2 , CO_2 and O_2 . In Figure 5.17(a), the ion signal for O_2 exceeds that for CO_2 , suggesting that in the absence of the adsorbate, SO_2 and O_2 were the primary products obtained during decomposition of the (Fe/Mn)-promoted catalyst. In the presence of benzene, Figure 5.17(b) shows that the relative amount of CO_2 produced increased, suggesting that CO_2 was produced by benzene oxidation. The two SO_2 evolution peaks in Figure 5.17(b) and the fact that CO_2 was observed at both SO_2 evolution maxima indicate the presence of two types of adsorption sites.

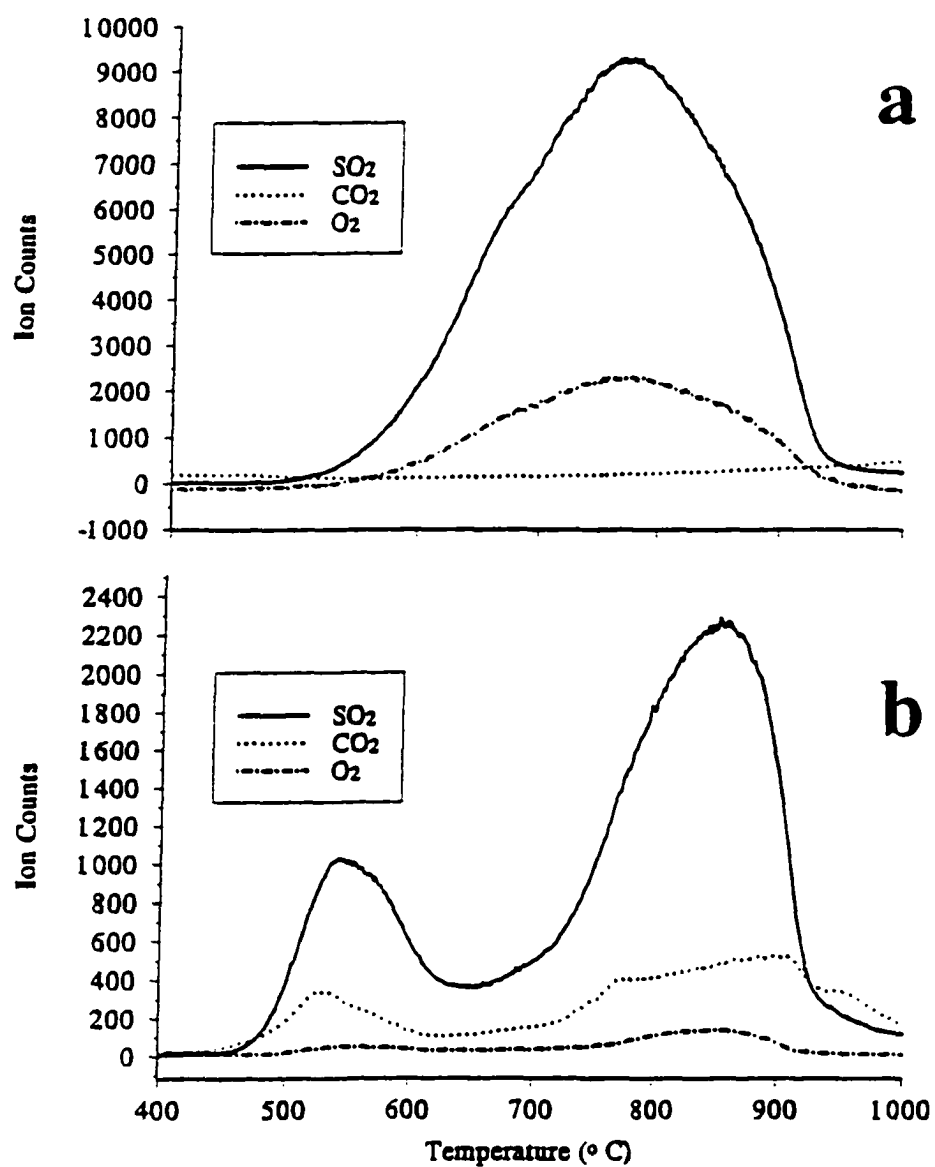
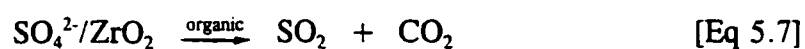
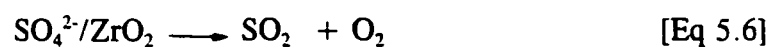


Figure 5.17 TPD-MS ion signal temperature profiles (a) without adsorbate; (b) with adsorbed benzene

Reaction between catalyst and adsorbates can be summarized by the following equations:



The areas under the ion signal curves representing O_2 and CO_2 were calculated and ratios between these areas and that for SO_2 evolution were computed. The results are compiled in Table 5.7.

Table 5.7 Evolved Volatiles from Benzene TPD.

Sample	$R_1(\text{O}_2)$	$R_2(\text{O}_2)$	$R_1(\text{CO}_2)$	$R_2(\text{CO}_2)$
SZ-1	-	26.1	-	0
SZFM-2	-	26.0	-	0
SZF-2	-	30.7	-	0
SZN-5	-	53.0	-	0
SZ-1 + Benzene	-	4.0	-	1.3
SZFM-2 + Benzene	4.0	5.0	28.4	16.6
SZF-2 + Benzene	3.3	5.7	27.3	13.5
SZN-5 + Benzene	2.8	4.2	22.0	31.0
$(\text{NH}_4)_2\text{SO}_4$	12.1	-	1.3	-

R_1 and R_2 in Table 5.7 denote ratios for species detected in the first and second peaks derived from the profiles shown in Figure 5.17, respectively. In the absence of adsorbates, catalysts produced no appreciable CO_2 . In the presence of benzene, the SZF, SZFM and SZN catalysts produced similar amounts of CO_2 in the first peak, but more CO_2 was produced in the second peak for the most active catalyst (SZN). Interestingly, the SZ-1 catalyst produced more O_2 than CO_2 even in the presence of benzene. This suggests that adsorbates interacted differently with promoted and unpromoted catalysts.

Figure 5.18 contains ion signal temperature profiles obtained from TPD measurements for a Ni promoted sulfated zirconia. In general, the same features exhibited by the temperature profiles in Figure 5.15 are evident in the profiles in Figure 5.18. However, unlike the (Fe/Mn)-promoted catalyst, the ammonia TPD temperature profile for SO_2 obtained for the Ni-promoted catalyst contained two distinct maxima. The low temperature maximum occurred at 580°C , which is close to the temperature at which Corma *et al* previously reported ammonia TPD peaks^[22].

Microcatalytic reactor studies for *n*-butane isomerization by metal promoted catalysts revealed the following order of activities:



Figure 5.19 shows ion signals for SO_2 evolution resulting from pyridine decomposition on (Fe/Mn), Fe only, and Ni only promoted catalysts. SO_2 evolution for the most active catalyst (SZN-5) maximized at 590°C , the next active catalyst (SZF-2) exhibited a

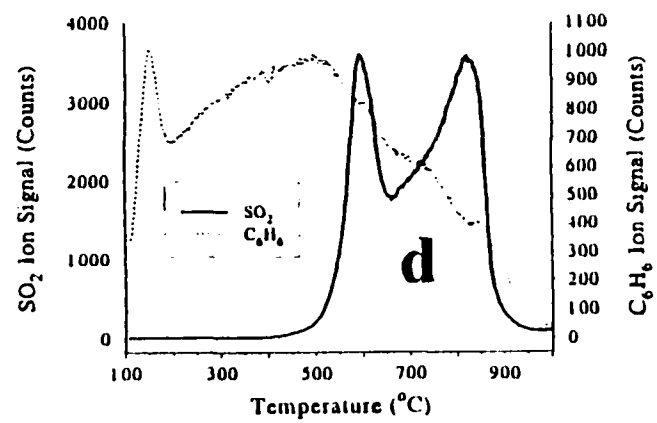
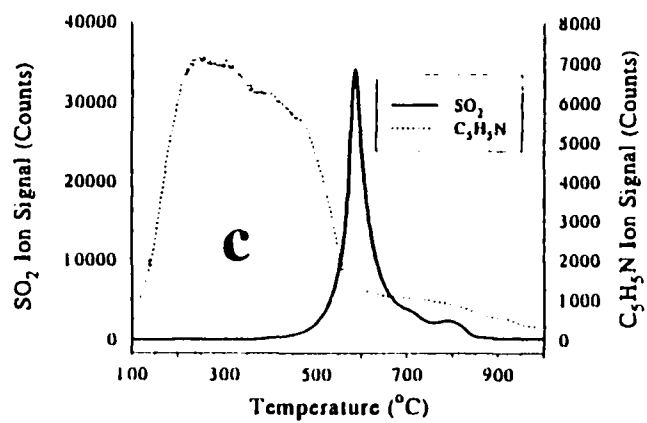
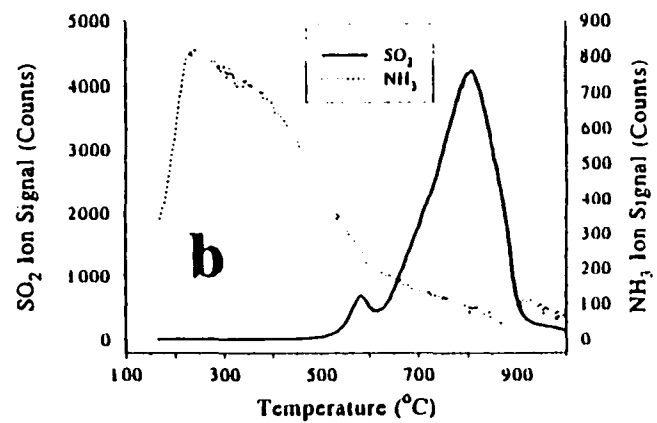
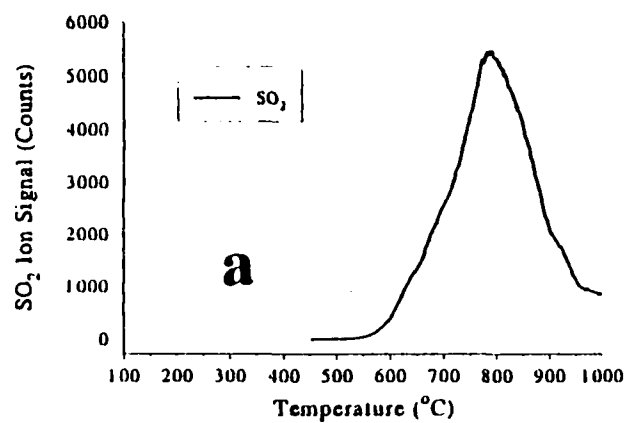


Figure 5.18 TPD-MS results for SZN-5 (a) without adsorbate; (b) with adsorbed ammonia; (c) with adsorbed pyridine; (d) with adsorbed benzene

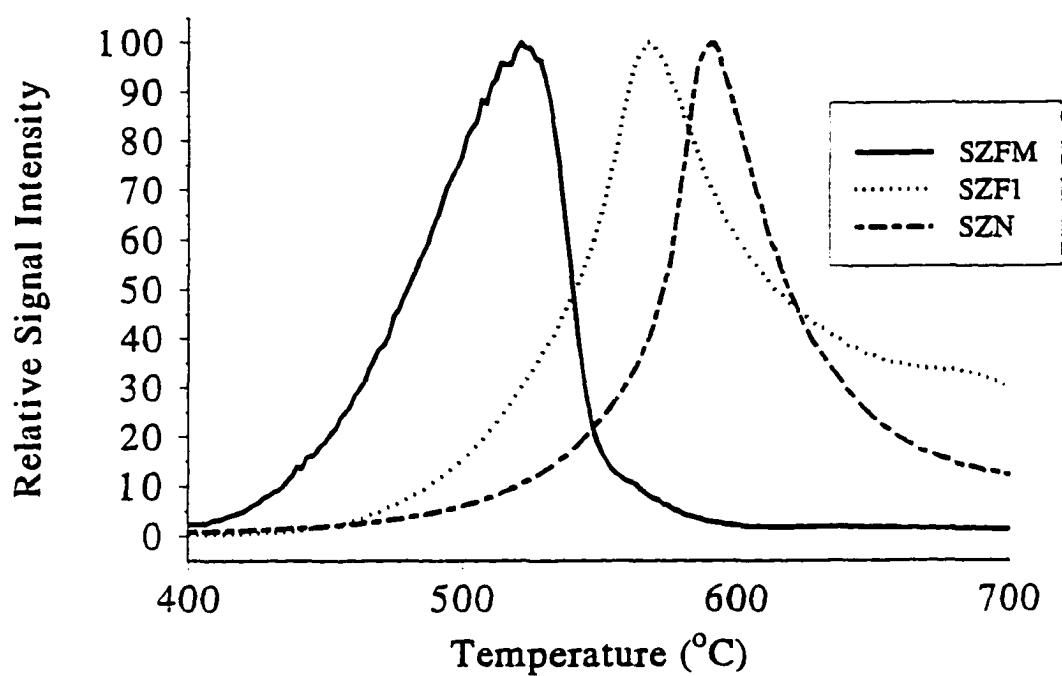


Figure 5.19 Effects of pyridine on SO_2 evolution for metal promoted catalysts

maximum at 568°C, and SO₂ evolution for the least active catalyst (SZFM-2) maximized at 520°C. Pyridine TPD-MS results suggest that catalyst decomposition may be dependent on the oxide surface sulfate environment, which is altered by the presence of metal promoters.

The effects of adsorbed benzene on the thermal decomposition of unpromoted and nickel-promoted sulfated zirconia catalysts are compared in Figure 5.20. In contrast to pyridine TPD, the shape of the ion signal temperature profile for SO₂ evolution from the nickel-promoted catalyst (solid line) exhibited two maxima. The low temperature maximum occurred at 557°C and the second maximum occurred at 823°C. The two maxima in the ion signal temperature profile suggest the presence of two sulfate species. Results similar to those obtained during benzene TPD-MS measurements for the nickel promoted sample were also obtained for Fe and Fe/Mn promoted catalysts. Whereas benzene discriminated between two acid sites with different acidities, pyridine, a much stronger base, interacted strongly with both sites. The ion signal temperature profile in Figure 5.20 representing SO₂ evolution from the unpromoted catalyst when benzene was present shows that benzene had little effect on the decomposition of the unpromoted catalyst (dotted line). Thus, the unpromoted catalyst exhibited a behavior different from the other catalysts, suggesting different interactions between unpromoted catalyst and benzene. Figure 5.21 compares ion signal temperature profiles for SO₂ evolution below 650°C (first maximum) for three metal promoted sulfated zirconias. SO₂ evolution maximized at 544°C for the (Fe/Mn)-promoted catalyst, 557°C for the Fe-promoted catalyst, and at 596°C for the Ni-promoted catalyst. In contrast, the high temperature

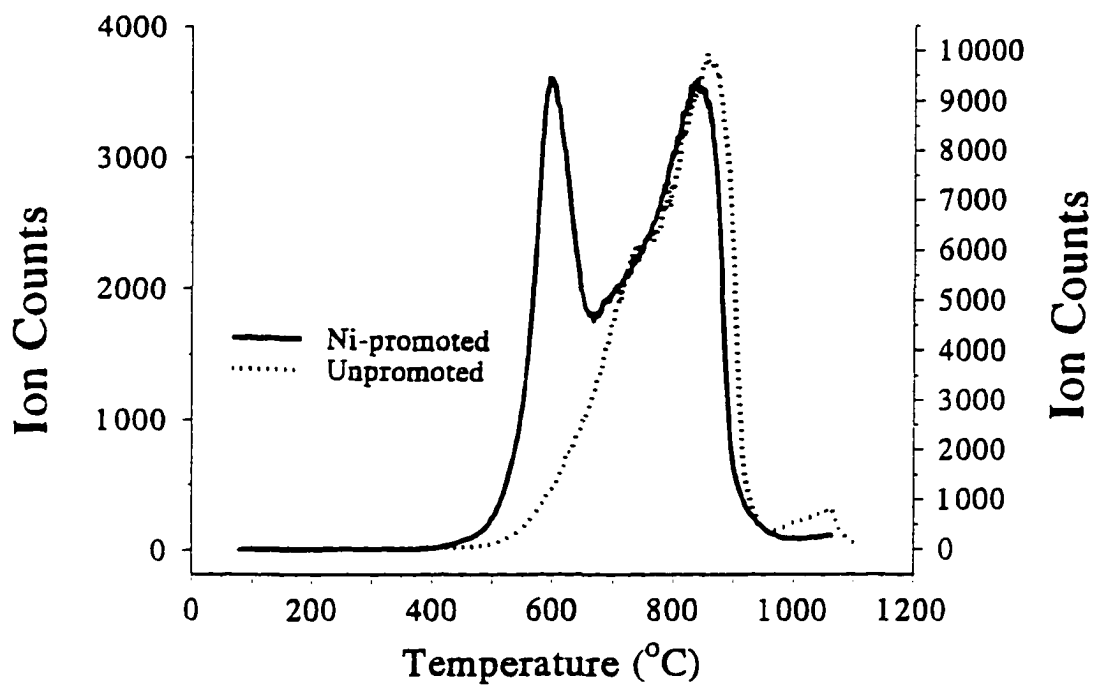


Figure 5.20 SO_2 evolution profiles for an unpromoted catalyst and a Ni-promoted catalyst containing adsorbed benzene

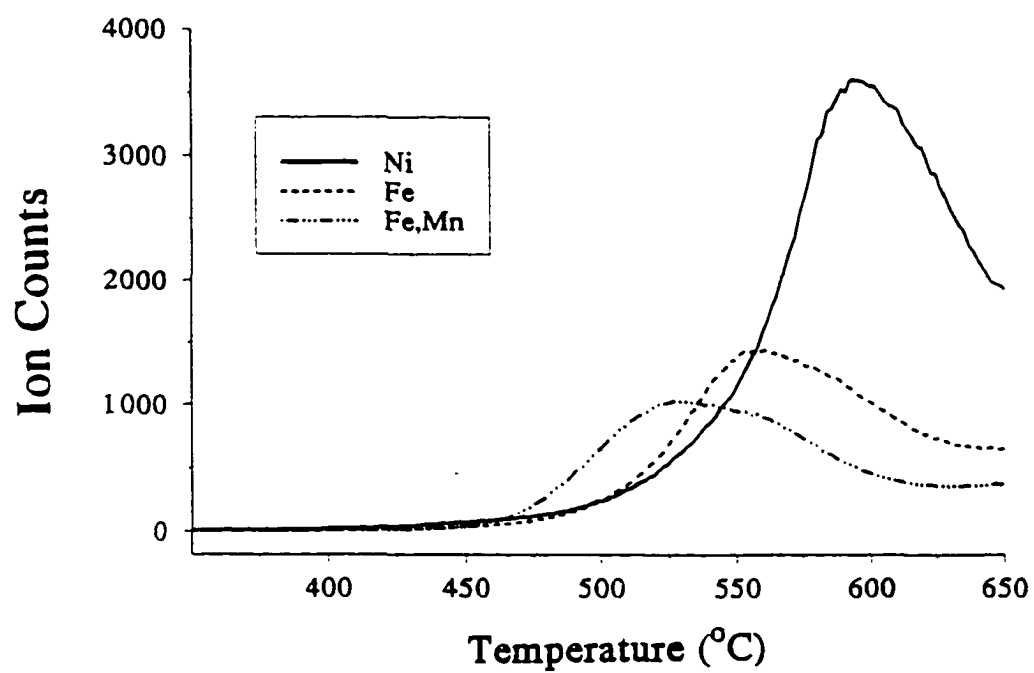


Figure 5.21 SO₂ evolution profiles for metal promoted catalysts containing adsorbed benzene

SO₂ evolution (not shown in Figure 5.21) maximized at about the same temperature in all three TPD curves. The trend in SO₂ evolution T_{max} values was found to correlate with catalytic activities. For the Ni-promoted catalyst, the area under the peak shown in Figure 5.21 represented about 40 % of the total area under the SO₂ ion signal temperature profile. The SO₂ peak areas for the Fe and the (Fe/Mn)-promoted catalysts were about 20 % of the total SO₂ ion signal temperature profile areas. The large area under the first peak for the Ni-promoted catalyst compared to the Fe and (Fe/Mn)-promoted catalysts may be indicative of catalyst property differences that are responsible for their different catalytic activities. Table 5.8 summarizes the effects of the ammonia, benzene, and pyridine adsorbates on SO₂ evolution for metal-promoted catalysts.

Table 5.8 Effects of Adsorbates on SO₂ T_{max} Values (°C)

Catalyst Sample	No Adsorbate	Ammonia	Benzene	Pyridine
SZ-1	850	870	- 850	812
SZFM-2	835	845	544 834	520
SZF-2	796	800	557 823	568
SZN-5	808	812	596 834	590

5.8 Summary

The surface acidities of sulfated zirconias were examined by studying interactions of metal promoted and unpromoted sulfated zirconias with ammonia, pyridine, carbon monoxide, and benzene. Infrared measurements of adsorbed ammonia and pyridine revealed the presence of both Brönsted and Lewis acid sites on all catalysts. Measurements of acid site densities and acid strength distributions based on the interactions with adsorbates could not account for differences in *n*-butane isomerization catalytic activities. Results from temperature programmed desorption measurements suggest that two types of sulfate species may be present on metal promoted catalysts. Interactions between catalysts and adsorbates typically led to catalyst decomposition and CO₂ evolution, indicating that adsorption was irreversible and that adsorbate oxidation occurred during desorption.

The initial objective for these studies was to establish a relationship between catalytic activity and sulfated zirconia acidity. Unfortunately, catalyst acidity measurements failed to reveal relationships between acidity and activity. However, TPD studies suggested that a correlation may exist between catalytic activity and the temperature at which catalysts decomposed. Clearly, catalyst-adsorbate interactions differ for transition metal promoted catalysts and unpromoted catalysts.

In conclusion, the role of metal promoters may not be to increase acidity, but rather to modify other catalyst properties^[68]. Therefore, surface reaction studies may be useful for determining the role of metal promoters in the enhanced *n*-butane isomerization catalytic activity.

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CHAPTER SIX

THE EFFECTS OF IRON PROMOTER ON 1-BUTENE REACTIONS

6.1 Background

The catalytic isomerization of *n*-butane to isobutane is widely accepted as an acid catalyzed process^[1-6]. However, attempts to correlate sulfated zirconia acidities with unpromoted and metal promoted catalyst activities have been unsuccessful. Alternatively, it has been proposed that metal promoters facilitate the dehydrogenation of butane to butene, which subsequently oligomerizes to form a C₈ intermediate that rearranges and cracks to produce isobutane^[7-11]. Coelho *et al* have further postulated that metal promoters facilitate accumulation of hydrogen deficient species on catalyst surfaces^[12]. Tabora and Davis^[13] and Wan *et al*^[14] suggest that butane isomerization occurs by a bi-functional mechanism and that differences between unpromoted and promoted catalysts are not due to differences catalyst acidities.

Oligomerization reactions such as those that have been proposed to form C₈ intermediates in the isomerization of *n*-butane involve reactions of carbenium ions. Olefins react with Brönsted acid sites to form carbenium ions and negative alkoxide surface ions. Therefore, TPD studies of catalysts containing adsorbed olefins should

provide insight into the stabilities and reactions of surface carbenium ions. In fact, studies using small olefins have previously been employed to characterize zeolite reactivities^[15-17]. Volatile species detected during TPD studies typically include oligomers and oligomer cracking products and reflect the reactivities of surface carbenium ions as well as interactions between carbenium ions and alkoxide surface ions^[18-21]. In this chapter, results derived from 1-butene temperature programmed desorption from promoted and unpromoted sulfated zirconia catalysts are described.

6.2 Experimental Conditions

1-Butene was obtained in lecture bottles from Sooner Air Gas (Norman, OK) and the adsorption procedure that was used was the same as that described in section 5.5. Diffuse reflectance infrared spectroscopy was employed to characterize interactions between catalyst surfaces and 1-butene. The combined TPD-MS and TPD-GC/MS interface employed for this study is described in detail in section 2.4. About 50 mg catalyst samples were placed in the TG sample pan for TPD-MS studies. For TPD-GC/MS studies, about 200 mg catalyst samples were placed in ceramic boats that were then placed inside the TG quartz furnace tube. Because the TG balance was not used for TPD-GC/MS studies, sample weight gain or loss information for samples studied by this method was not obtained. 1-Butene TPD studies were initiated by applying a 10°C/min heating ramp to catalyst samples. For TPD-GC/MS studies, 100 μ L TG effluent samples were injected into a 10 m DB-5 capillary gas chromatography column maintained at 40°C. By making injections at 20°C catalyst sample temperature intervals,

chromatograms were obtained at 2 minute intervals. Mass spectra were acquired by using 70 eV electron bombardment ionization and scanning from m/z 10 to m/z 250.

Catalyst designations, promoter loadings, amounts of 1-butene that were adsorbed, and sulfate species concentrations for the catalysts used in this study are listed in Table 6.1.

Table 6.1 Characteristics of Sulfated Zirconia Catalysts

Catalyst Designation	Fe (%)	Butene (mmol/g)	Sulfate (mmol/g)
SZ-2	---	0.38	0.21
SZF-2	0.5	0.60	0.56
ZSF-4	1.5	0.61	0.54
ZSF-5	4.0	0.50	0.65

6.3 Results and Discussion

Infrared spectra for promoted and unpromoted catalyst samples obtained after catalysts were exposed to 10 Torr of 1-butene were similar. Figure 6.1 shows infrared difference spectra for adsorbed 1-butene in the presence of 10 Torr 1-butene vapor and after vapor phase 1-butene had been removed. During He purging to remove gas phase 1-butene, absorbance bands at 3090 and 1644 cm^{-1} , which are representative of $\text{C}=(\text{CH}-\text{H})$ and $-(\text{C}=\text{C})-$ stretching vibrations respectively, disappeared leaving absorbance bands at 2877, 2935, and 2962 cm^{-1} , which are representative of protonated butene^[21] (i.e.

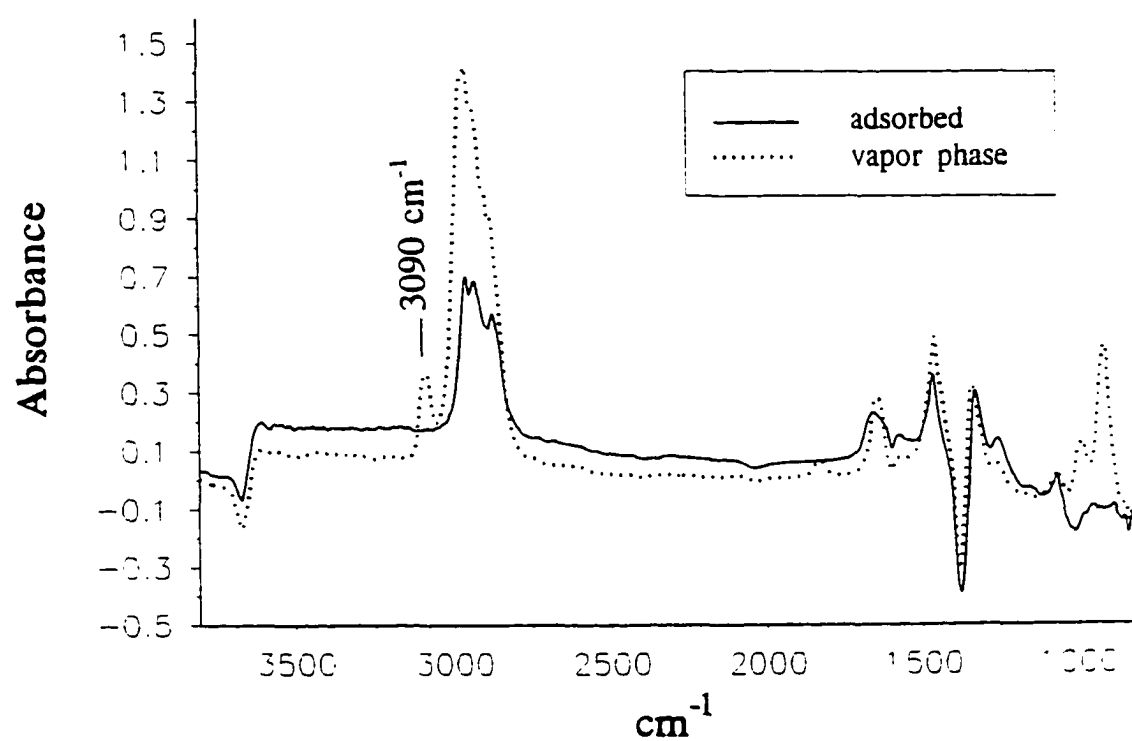


Figure 6.1 Difference infrared spectra for adsorbed 1-butene before and after removal of 1-butene vapor

$C_4H_9^+$). Spectra obtained for 1-butene adsorbed on unpromoted and Fe promoted sulfated zirconias were similar to those reported by Dakta^[23] when 1-butene was adsorbed on sodium exchanged zeolites.

For both unpromoted and Fe promoted catalyst samples, TPD-MS mass spectrometric measurements made after 1-butene was adsorbed and during sample purging with He revealed the presence of volatile hydrocarbons larger than 1-butene in the purge effluent. This suggests that oligomerization occurred during 1-butene adsorption at 50°C. For three of the four catalysts used in this study, the sample weight gain caused by 1-butene adsorption corresponded to more adsorbed butene than the number of sulfate surface sites (Table 6.1), which also suggests that oligomerization occurred at 50°C. Butene oligomerization on sulfated zirconia catalysts at 50°C was not unexpected because low temperature alkene oligomerization on zeolites has been previously reported^[24-26].

TPD-MS studies indicated that the presence of the Fe promoter facilitated volatile product evolution at lower temperatures. Figure 6.2 shows TPD-MS total ion current temperature profiles for 1-butene TPD from an unpromoted catalyst and catalysts containing 0.5, 1.5, and 4.0% Fe. Whereas the total ion current temperature profile for the unpromoted catalyst exhibits a single volatile species evolution peak, the promoted catalyst samples exhibit more asymmetric profiles with greater ion signals at lower temperatures. The Fe promoted total ion current temperature profiles appear to consist of at least two overlapping evolutions. One of these evolutions occurs near the total ion current maximum for the unpromoted catalyst sample and another evolution maximizes

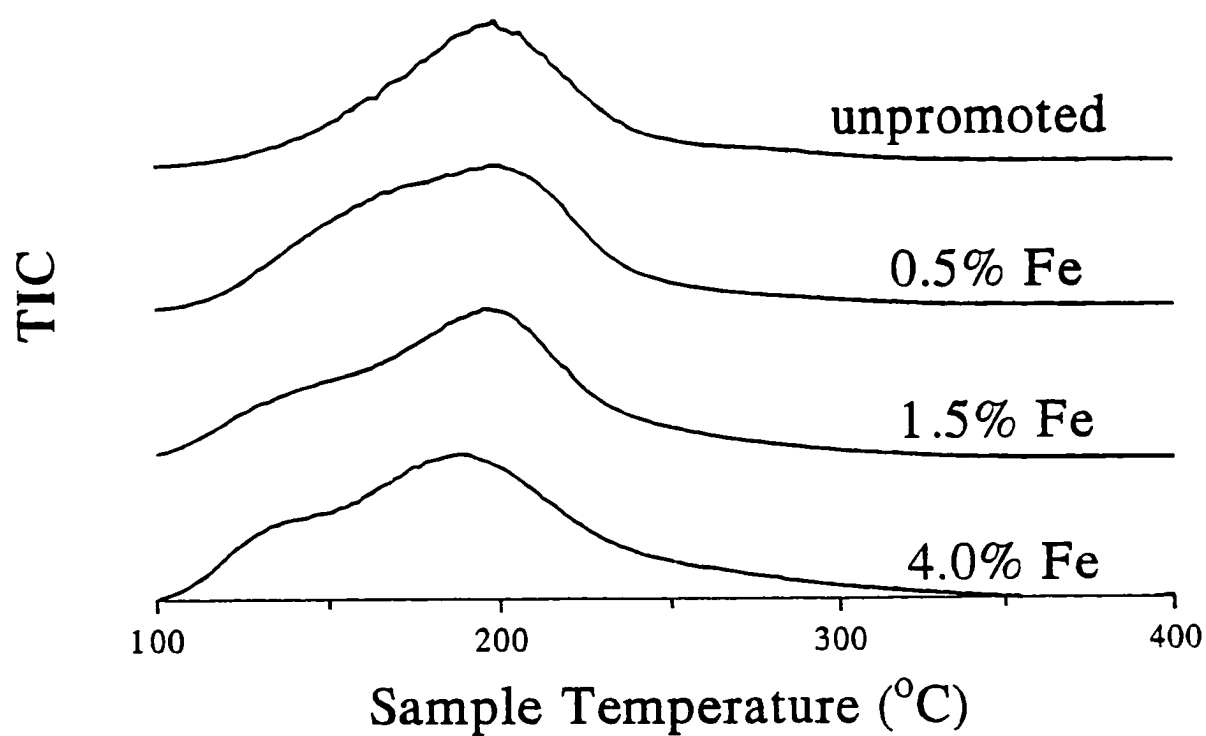


Figure 6.2 TPD-MS total ion current temperature profiles representing butene derived volatile products for four different catalysts

about 50°C lower. The relative integrated total ion current area for the low temperature evolution did not significantly increase with increased iron loading, suggesting that only some of the added iron promoter was responsible for this effect.

TPD-GC/MS studies revealed that the volatile species evolved during 1-butene TPD from unpromoted catalysts were very different from those evolved from Fe promoted catalysts. Figure 6.3 contains TPD-GC/MS chromatograms obtained during 1-butene TPD from an unpromoted catalyst sample and a catalyst containing 4.0% Fe. Results similar to those depicted in Figure 6.3 for the 4.0% Fe promoted catalyst were also obtained for the 0.5 and 1.5% Fe promoted catalysts. The tic marks in Figure 6.3 denote catalyst sample temperatures at which effluent was injected into the gas chromatograph. Successive chromatograms in Figure 6.3 are separated by two minute (20°C) intervals. Inspection of Figure 6.3 reveals that the volatile product slate for both the unpromoted and promoted catalysts changed with temperature. TPD-GC/MS results indicated that more volatile products were detected at low temperatures for the Fe promoted catalysts than for the unpromoted catalyst, which is consistent with TPD-MS results (Figure 6.2). At temperatures below 140°C, butene was a significant volatile product for both catalyst samples. At catalyst temperatures above 140°C, butene was still a significant volatile product for the Fe promoted catalysts but was not detected for the unpromoted catalyst. Above 140°C, most of the volatile species desorbed from the unpromoted catalyst were saturated hydrocarbons whereas most of the species desorbed from the Fe promoted catalysts were olefins. This is clearly illustrated in Figure 6.4, which shows TPD-GC/MS chromatograms obtained from each catalyst sample when the

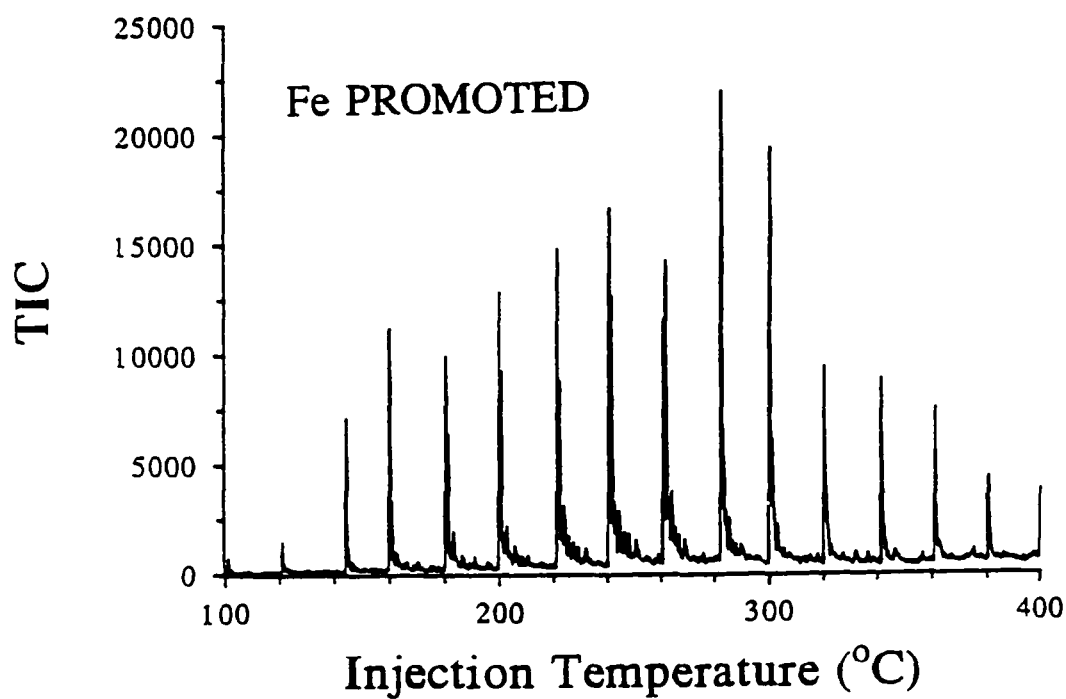
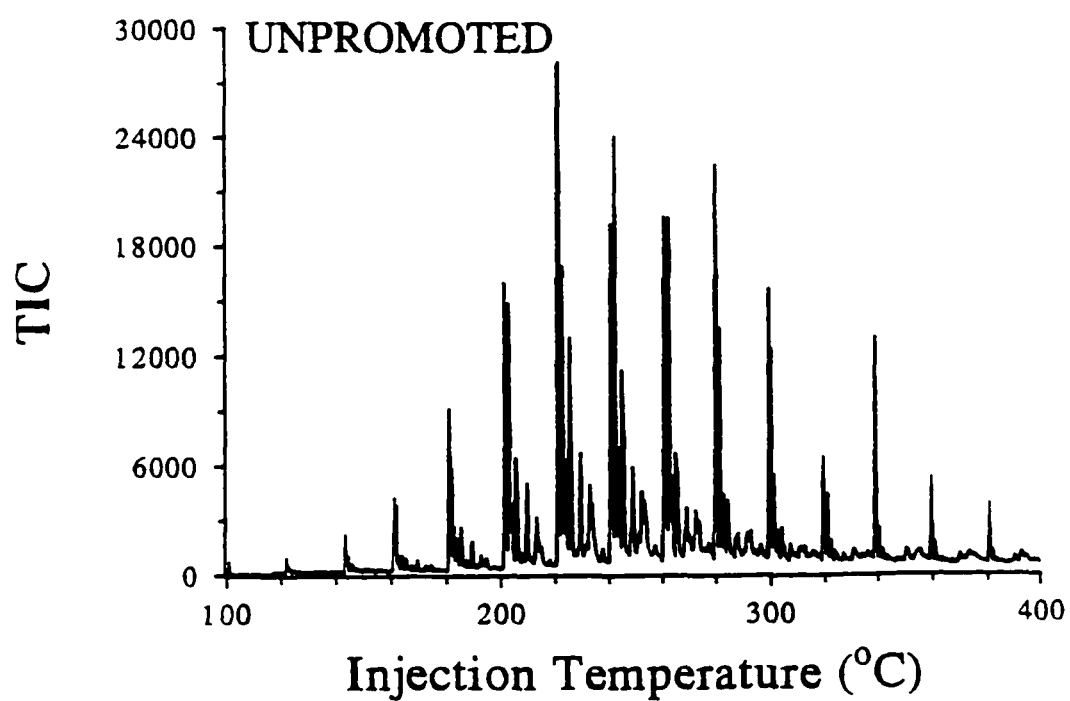


Figure 6.3 TG-GC/MS chromatograms for 1-butene TPD

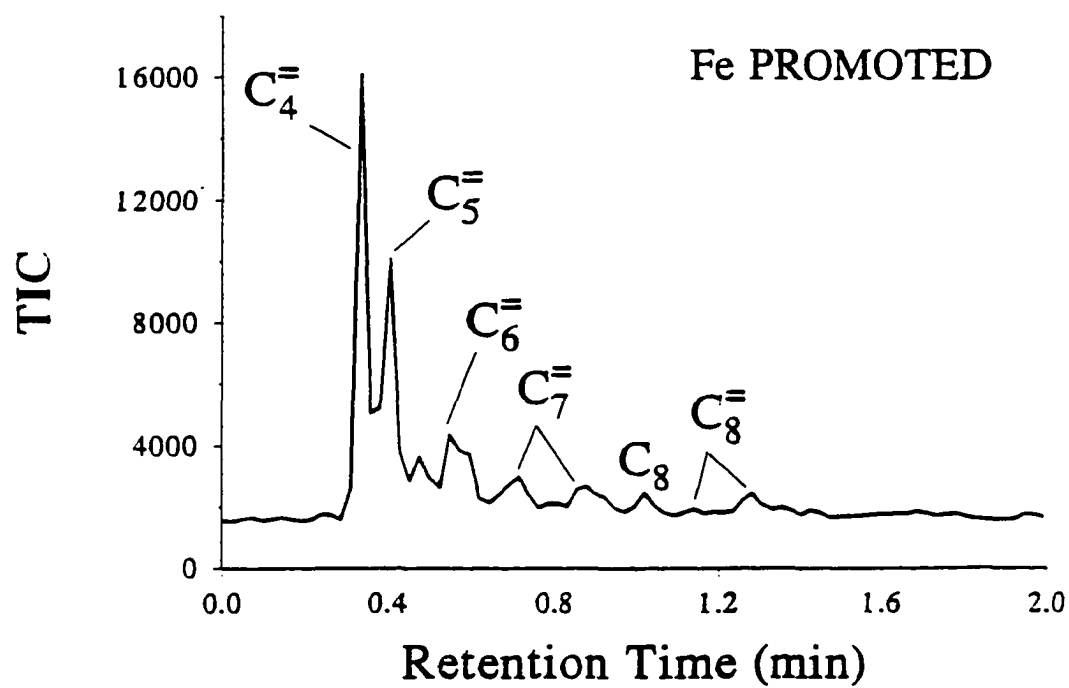
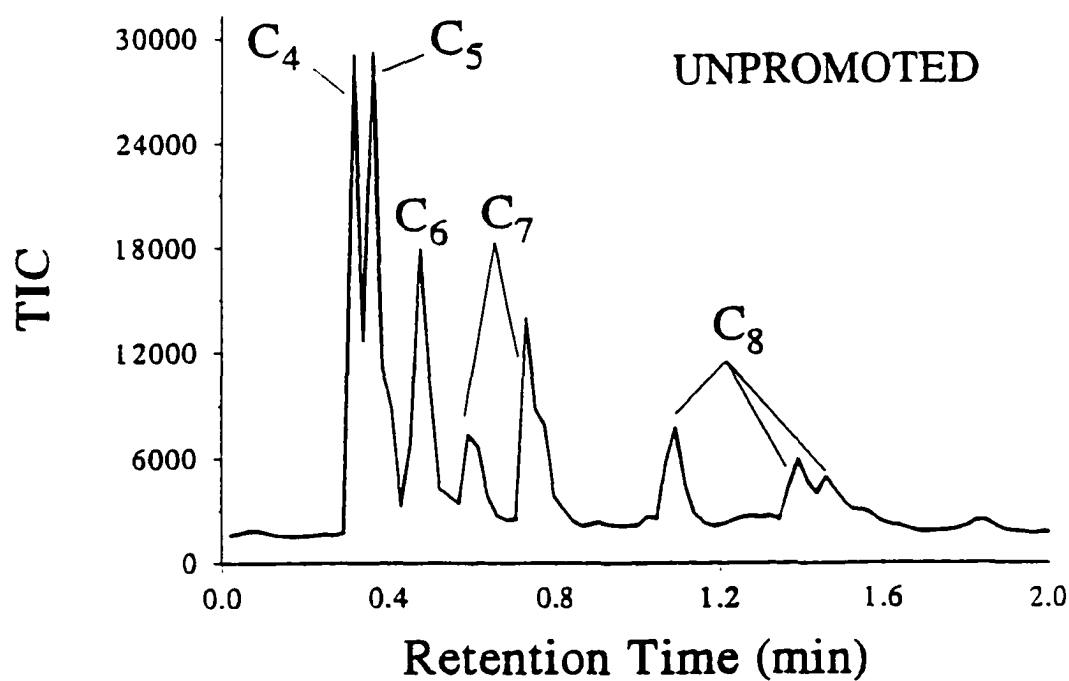


Figure 6.4 TG-GC/MS chromatograms obtained at 220 °C

catalyst temperature had reached 220°C. Chromatographic peaks in Figure 6.4 labeled C_n denote saturated hydrocarbons with n carbon atoms and peaks labeled by C_n^{*} denote corresponding unsaturated hydrocarbons.

Table 6.2 lists the relative yields of volatile products detected in the TPD-GC/MS chromatograms shown in Figure 6.4.

Table 6.2 Volatile Product Relative Yields at 220°C

Volatile Species	Unpromoted Catalyst (%)	Fe Promoted Catalyst (%)
C ₄ H ₈	---	30.9 ^a
C ₄ H ₁₀	9.6	---
C ₅ H ₁₀	7.2	24.4
C ₅ H ₁₂	19.8	2.2
C ₆ H ₁₂	---	15.2
C ₆ H ₁₄	16.4	4.5
C ₇ H ₁₄	1.9	8.1
C ₇ H ₁₆	15.4	7.4
C ₈ H ₁₆	1.3	1.4
C ₈ H ₁₈	16.1	5.4
C ₉ H ₂₀	8.4	---

^aComputed as the percentage of the GC/MS chromatogram integrated total ion current.

Relative yields were calculated by integrating the total ion current under chromatographic peaks representing isomeric species, adding peak areas for isomers with the same number

of carbon atoms, and dividing this integrated total ion current by the integrated total ion current determined for the entire chromatogram. Curve fitting was employed to obtain chromatographic peak area estimates for severely overlapping elutions. Nearly 86% of the volatile products detected at 220°C for the unpromoted catalyst sample were saturated hydrocarbons. In contrast, less than 20% of the volatile products detected at 220°C for the 4.0% Fe promoted catalyst were saturated hydrocarbons. Butene evolution was responsible for about 31% of the products evolved from the 4.0% Fe promoted catalyst at 220°C but was not detected in the TPD-GC/MS chromatogram obtained for the unpromoted catalyst at this temperature. Instead, isobutane was the only C₄ product detected at 220°C on SZ-2.

Reactions of C₄ carbenium ions formed by Brönsted acid protonation of butene with gas phase butene can produce C₈ carbenium ions. These C₈ carbenium ions may react further with butene to form larger carbenium ions, crack to form species smaller than C₈, abstract hydrides from neighboring surface species to form saturated C₈ species, or deprotonate to form C₈H₁₆. Volatile C₈H₁₆ species were detected during TPD-GC/MS analyses for both unpromoted and Fe promoted catalysts and are represented in Figure 6.5 by m/z 112 (C₈H₁₆ molecular ion) mass-selected ion chromatograms for the unpromoted and 4.0% Fe promoted catalyst samples. Like the total ion current TPD-GC/MS chromatograms, the m/z 112 mass-selected ion chromatograms indicate that more species yielding m/z 112 were evolved from Fe promoted catalysts than from the unpromoted catalyst at low catalyst sample temperatures. Several chromatographic elutions having mass spectra containing m/z 112 were detected for both catalyst samples.

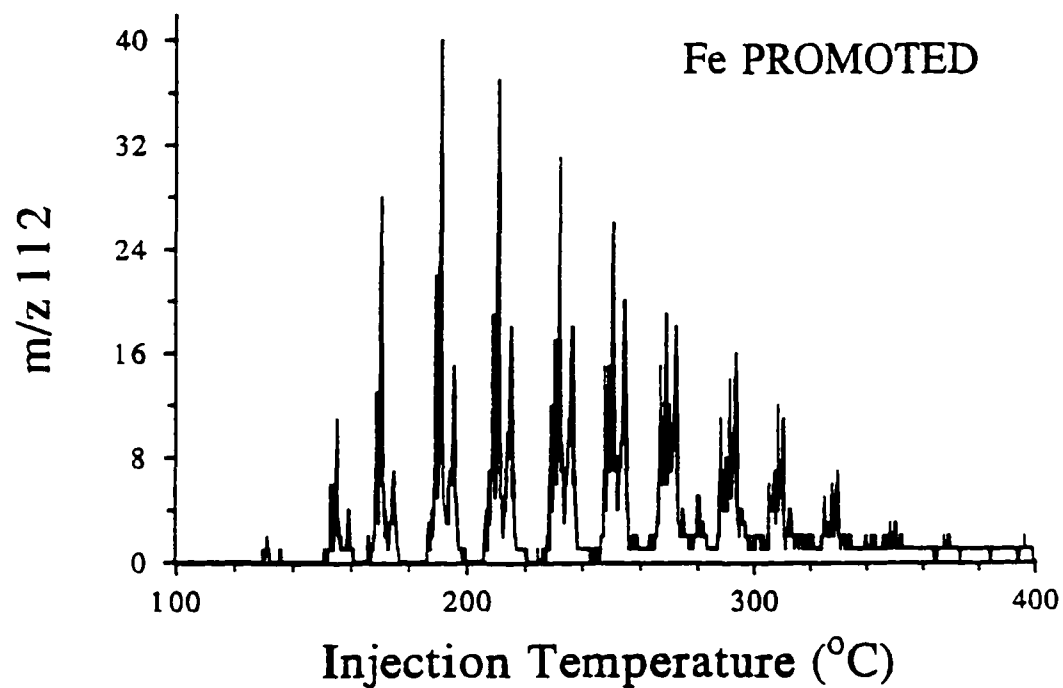
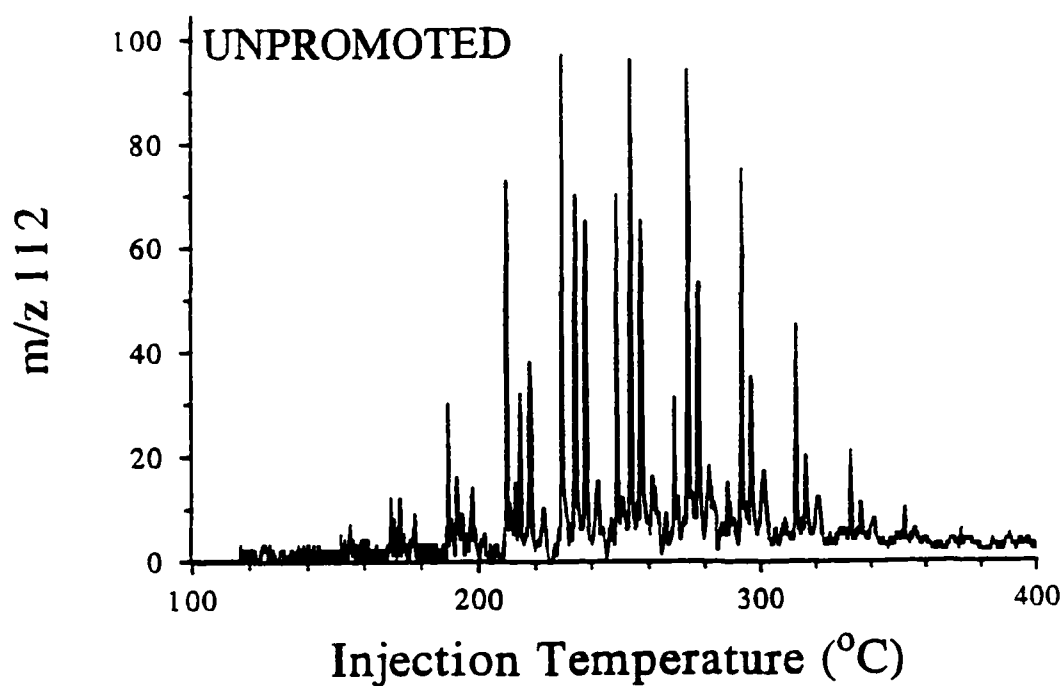


Figure 6.5 TG-GC/MS m/z 112 ion signal chromatograms

However, differences in retention times for species yielding m/z 112 shown in Figure 6.5 indicate that the species that yielded m/z 112 for the unpromoted catalyst were not the same as those that yielded m/z 112 for the 4.0% Fe promoted catalyst sample. This is consistent with the great disparity in the volatile product slates for these two catalysts (Table 6.2). Inspection of mass spectra for the chromatographic elutions containing m/z 112 in Figure 6.5 revealed that some of the m/z 112 mass-selected chromatographic peaks represented C_8H_{16} molecular ions but that others resulted from fragmentation of volatile species that had molecular weights larger than 112. In fact, only two of the elutions in the m/z 112 mass-selected chromatogram for the unpromoted catalyst and three of the elutions in the m/z 112 mass-selected chromatogram for the 4.0% Fe promoted catalyst sample represented C_8H_{16} molecular ions. Table 6.2 shows that the relative yields of total C_8H_{16} volatile products were similar for the unpromoted and 4.0% Fe promoted catalysts. Figure 6.6 shows m/z 112 containing mass spectra obtained by TG-GC/MS analysis during 1-butene TPD from unpromoted (Figure 6.6(a)) and 4% Fe promoted (Figure 6.6(b)) sulfated zirconias. Mass spectra obtained for the two C_8H_{16} species evolved from the unpromoted catalyst were consistent with dimethyl cyclohexane structures. In contrast, mass spectra for the three C_8H_{16} species evolved from the 4.0% Fe promoted catalyst were consistent with C_8 olefin isomers.

Oligomeric carbenium ions can abstract hydrides from neighboring adsorbates to form volatile hydrocarbons. Volatile C_8H_{18} hydrocarbons formed after $C_8H_{17}^+$ hydride abstraction were detected during TPD-GC/MS analyses of both unpromoted and Fe promoted catalysts. However, as Table 6.2 shows, the relative yield of volatile C_8H_{18}

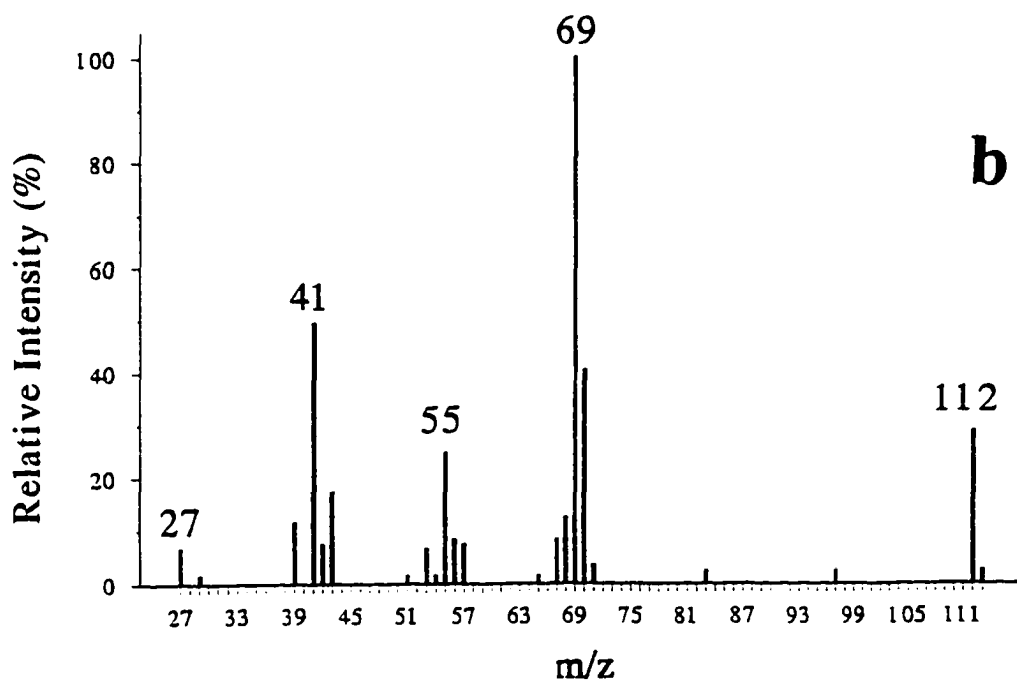
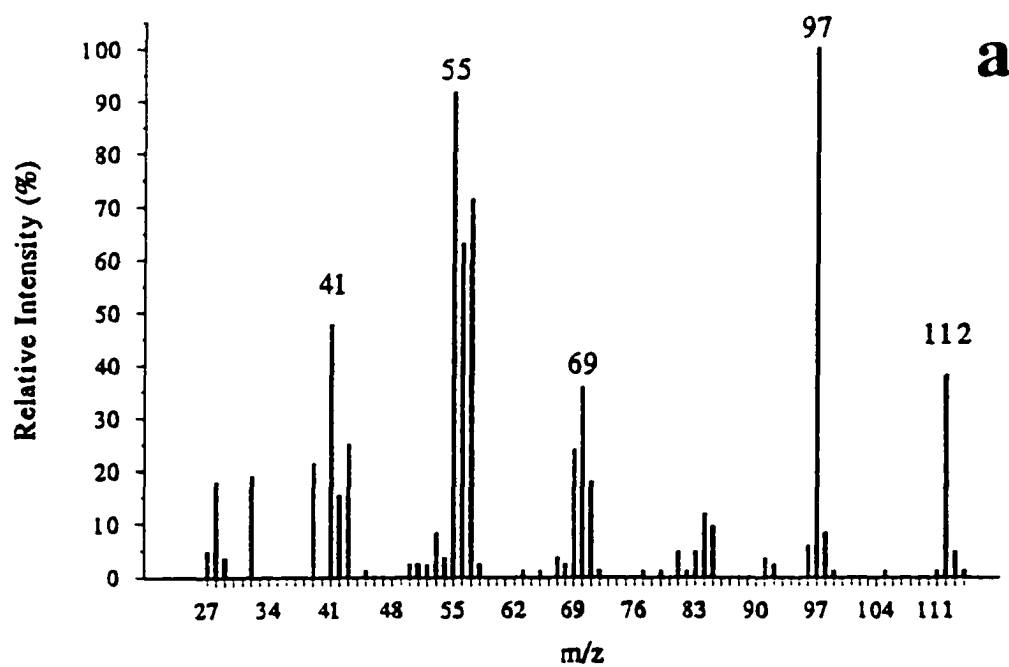
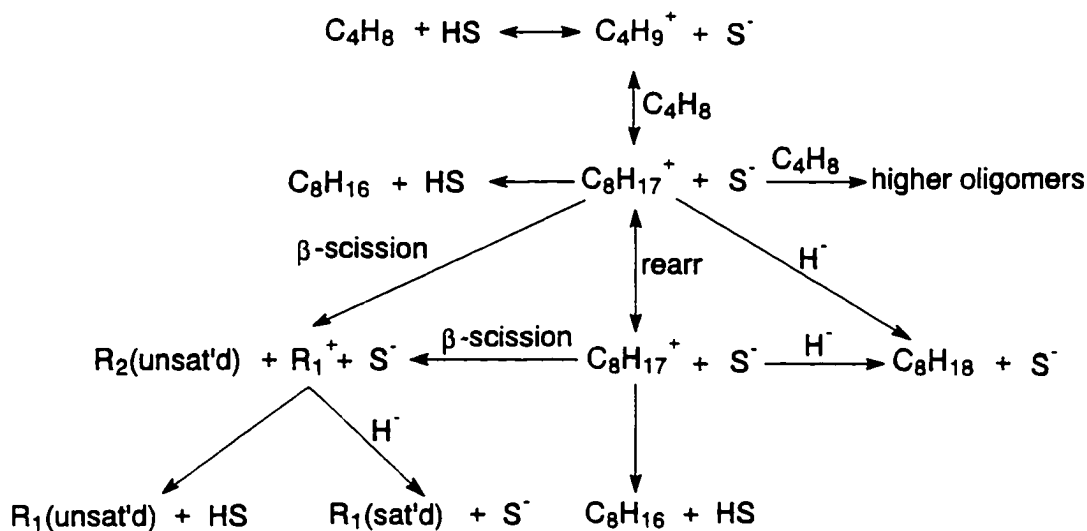


Figure 6.6 Representative mass spectra corresponding to chromatographic peaks in Figure 6.5 for (a) unpromoted and (b) 4% Fe promoted catalysts

species evolved from the unpromoted catalyst was about three times that for the 4.0% Fe promoted catalyst. As shown in Figure 6.7, mass-selected chromatograms for m/z 114 were similar for both catalysts and contained two chromatographic peaks. Inspection of TPD-GC/MS mass spectra indicated that m/z 114 was the molecular ion in the mass spectra obtained for each of these elutions (Figure 6.7c). Retention times and mass spectra for each of the C_8H_{18} species evolved from unpromoted (Figure 6.7a) and Fe promoted (Figure 6.7b) catalysts were similar, suggesting that the same two species were evolved from both catalysts. In contrast to the C_8H_{16} evolution temperature profiles, the catalyst temperature at which C_8H_{18} evolution maximized was higher for the 4.0 % Fe promoted catalyst (260°C) than for the unpromoted catalyst (220°C).

The volatile products detected during TPD-GC/MS analysis of Fe promoted catalysts can be explained by the following reaction scheme:



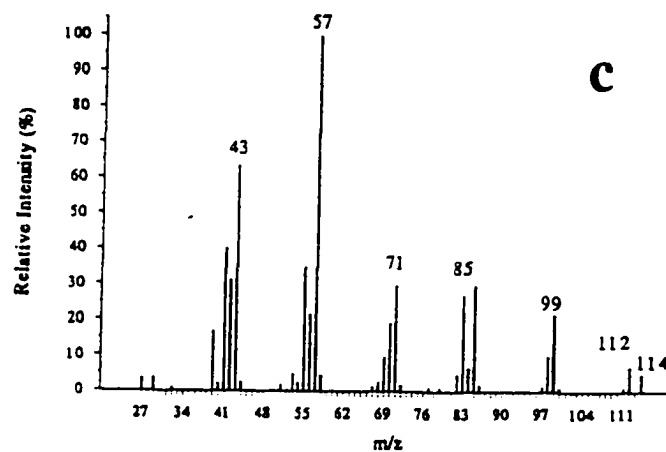
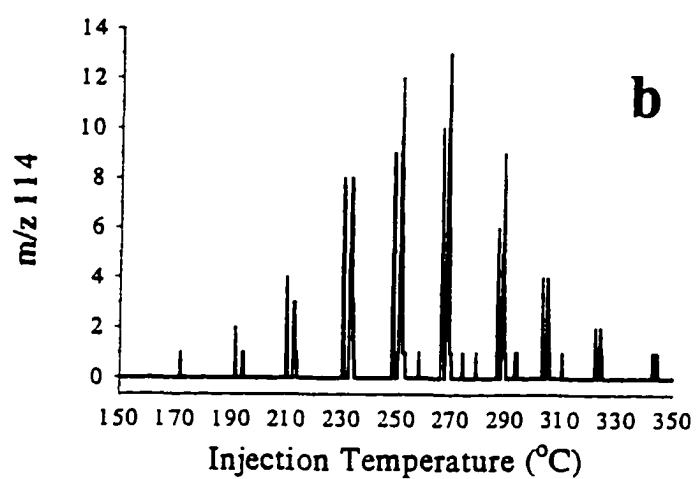
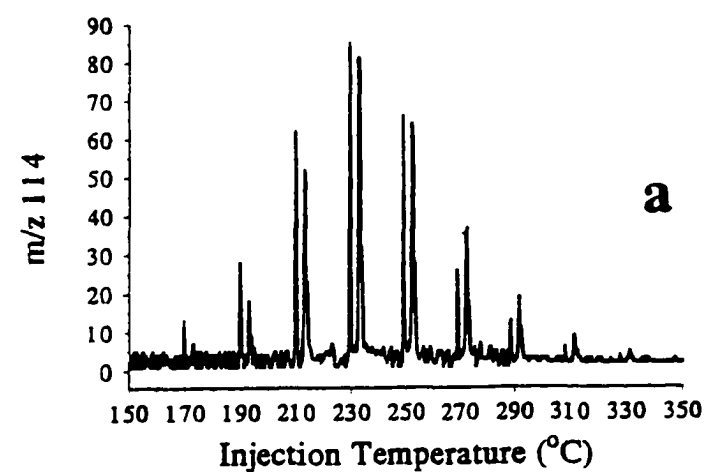
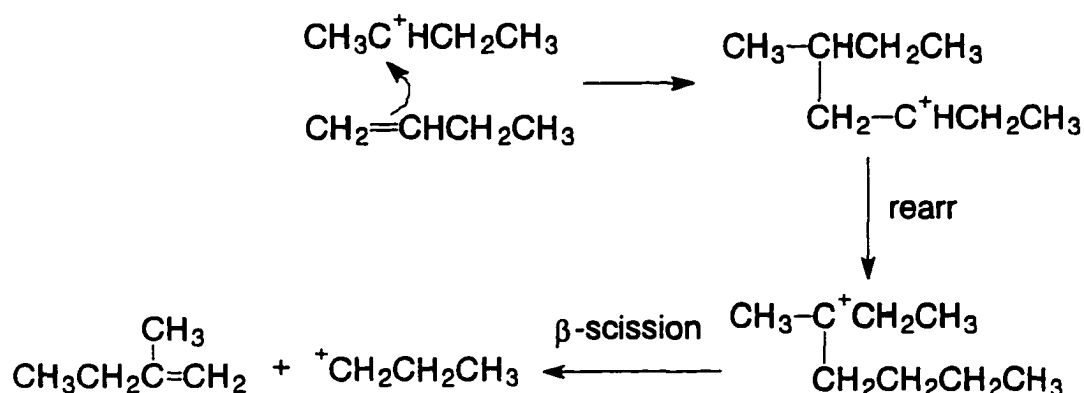


Figure 6.7 TG-GC/MS m/z 114 ion signal chromatograms for (a) unpromoted catalyst (b) 4% Fe promoted catalyst, and (c) representative mass spectrum

In this reaction scheme, C_4H_8 represents 1-butene, HS denotes a Brönsted acid site on the catalyst surface and S^- is its conjugate base. One source of butenes detected by TPD-GC/MS analysis of Fe promoted catalysts may have been deprotonation of $C_4H_9^+$ species when thermal energy due to sample heating exceeded the interaction energy between the carbenium ion and the catalyst surface. In addition, reactions of 1-butene with $C_4H_9^+$ carbenium ions to form $C_8H_{17}^+$ must have occurred to produce the detected volatile products that were larger than C_4 . Initially formed $C_8H_{17}^+$ carbenium ions may rearrange, react with additional 1-butene to form larger carbenium ions, or may be converted to volatile products by: deprotonation to regenerate HS Brönsted acid sites and form C_8H_{16} species, hydride abstraction from neighboring adsorbates to form C_8H_{18} species, or by β -scission to produce unsaturated products and smaller carbenium ions. These smaller carbenium ions may desorb as olefins or abstract hydrides and desorb as saturated hydrocarbons. The selectivity for unsaturated volatile products and the relatively low yields of C_8H_{16} and C_8H_{18} detected by TPD-GC/MS analysis of Fe promoted catalysts (Table 6.2) suggest that $C_8H_{17}^+$ β -scission was a dominant process and that carbenium ions formed by β -scission desorbed primarily as olefins when iron was present in sulfated zirconia catalysts. The large yield of butenes evolved from Fe promoted catalysts may have resulted from a combination of $C_4H_9^+$ deprotonation and oligomer carbenium ion β -scission. The TPD-GC/MS chromatogram in Figure 6.4(b) and volatile species yields contained in Table 6.2 show that C_5H_{10} species were also evolved from the 4.0% Fe promoted catalyst in relatively large yields. C_5H_{10} can readily

be formed from $C_8H_{17}^+$ carbenium ions after they rearrange to form tertiary cations:

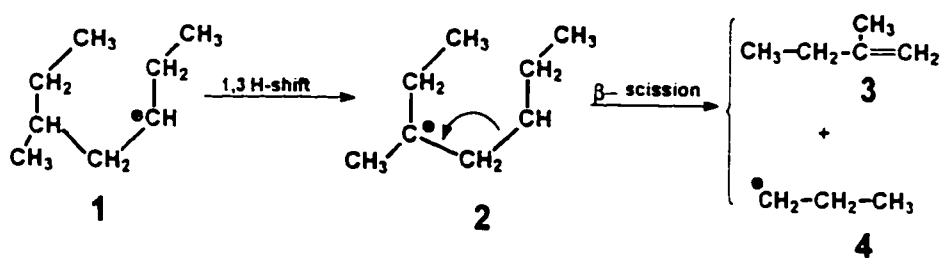


This should be a significant reaction path due to the increased stability of the tertiary cation intermediate compared to the secondary cation initially formed.

In contrast to the adsorbed 1-butene TPD-GC/MS results obtained for Fe promoted catalysts, unsaturated species were not the primary volatile products for the unpromoted catalyst and butenes were only detected at relatively low catalyst temperatures. The lack of a substantial yield of butenes suggests that $C_4H_9^+$ was not present in significant amounts on the unpromoted catalyst. Instead, oligomeric carbenium ions were more likely the dominant species on the surface of the unpromoted catalyst. The fact that 8.4% of the chromatogram total ion current measured by TPD-GC/MS for the unpromoted catalyst at 220°C corresponded to saturated C_9 hydrocarbons (Table 6.2) suggests that surface concentrations of oligomeric carbenium ions that were larger than C_8 were significant on the unpromoted catalyst. Furthermore, the facts that the amount of butene that was adsorbed by the unpromoted catalyst was almost twice the number of

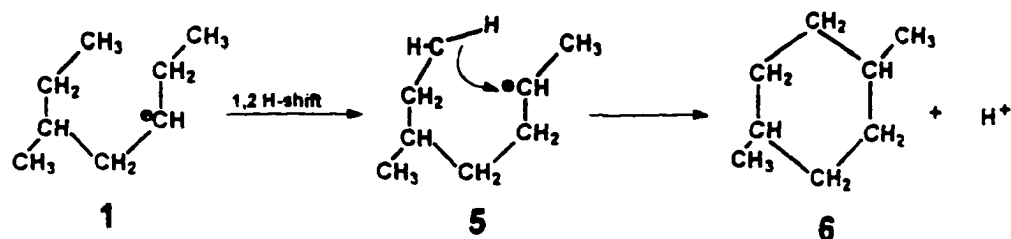
sulfate groups on the catalyst whereas the amounts of butene adsorbed on Fe promoted catalysts were about the same as the number of sulfate groups (Table 6.1) also suggest that larger oligomers were formed on the unpromoted catalyst than on the Fe promoted catalysts. Many of the saturated hydrocarbons that constituted most of the volatile products detected by TPD-GC/MS for the unpromoted catalyst likely resulted from β -scission of these large oligomeric carbenium ions. Apparently, the neutral unsaturated β -scission products from oligomer carbenium ions were too large to be volatile at the catalyst temperatures at which scission occurred. The carbenium ions also formed by these scissions subsequently reacted by hydride abstraction to form the detected saturated hydrocarbon products.

TG-GC/MS results suggest that $C_8H_{17}^+$ carbenium ions react differently on unpromoted and Fe promoted catalysts. Reactions of 1-butene with surface adsorbed $C_4H_9^+$ species would likely form the $C_8H_{17}^+$ species shown as species (1). Deprotonation of (1) would yield the C_8H_{16} unsaturated species detected by 1-butene TPD studies of the Fe promoted catalyst. In addition, if (1) rearranges to (2), β -scission would yield the unsaturated C_5 species detected from the Fe promoted catalyst(3):

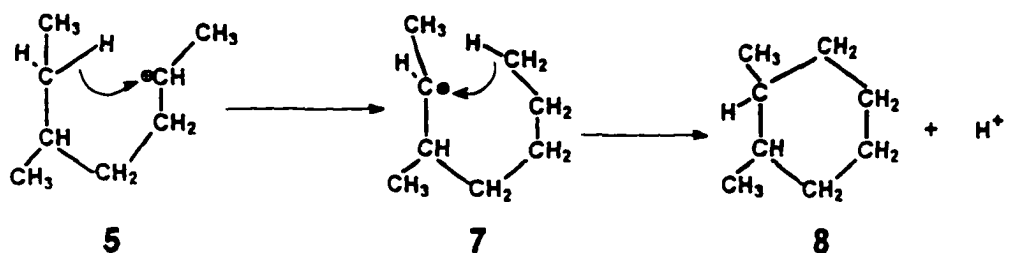


Alternatively, dimethylcyclohexanes evolved from the unpromoted catalyst may originate from (5), which can be produced by rearrangement of (1). 1,4-dimethylcyclohexane

could be produced directly from (5):



Rearrangement of (5) to (7) could produce 1,2-dimethylcyclohexane:



$\text{C}_8\text{H}_{17}^+$ carbenium ions have been proposed by Adeeva *et al* as reaction intermediates in the isomerization of *n*-butane to isobutane on Fe, Mn promoted sulfated zirconias[4]. In their mechanism, $\text{C}_8\text{H}_{17}^+$ carbenium ions crack by β -scission to form butene and $\text{t-C}_4\text{H}_9^+$, which subsequently abstracts a hydride to form isobutane. Results described here suggest that this process can readily occur with Fe promoted catalysts but is not favored on unpromoted catalysts due to competition from reactions leading to larger oligomeric carbenium ions. This may explain why the *n*-butane isomerization catalytic activities for unpromoted catalysts are so much lower than for metal promoted catalysts.

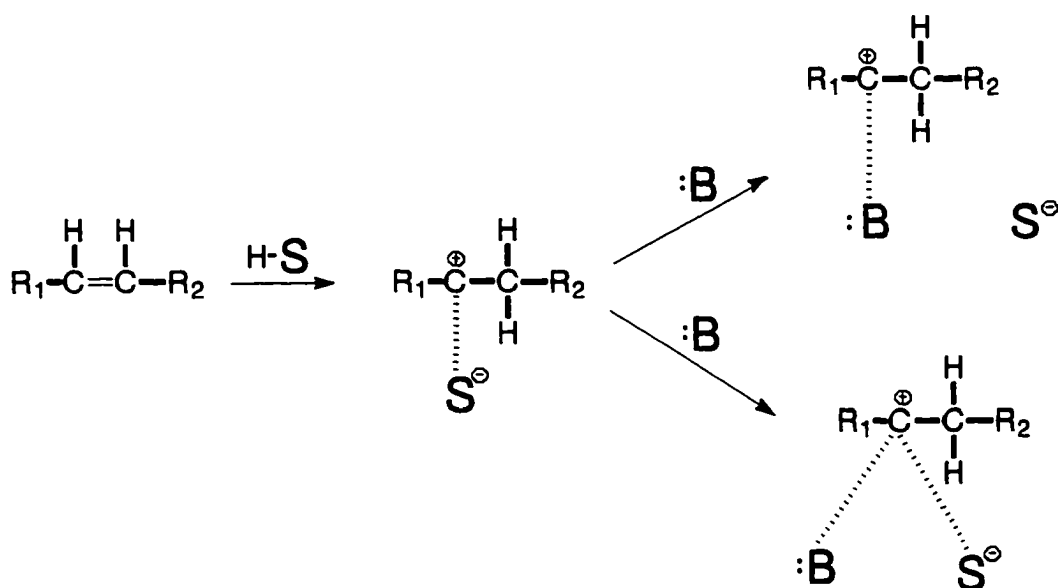
In the absence of iron promoter, TG-GC/MS results suggest that oligomeric carbenium ions formed on sulfated zirconia surfaces undergo β -scission followed by hydride abstraction to produce volatile saturated hydrocarbons that are released from the

surface when the catalyst is heated. This must necessarily lead to a decrease in the H/C ratio of species remaining on the catalyst surface. As a result, this carbenium ion behavior on unpromoted sulfated zirconia should quickly lead to char formation. Catalyst deactivation caused by rapid coking as a result of these surface reactions may also be a factor in the weaker catalytic activity for *n*-butane isomerization for unpromoted catalysts compared to metal promoted catalysts.

The dramatic differences in the reactivities of unpromoted and Fe promoted catalysts containing adsorbed 1-butene may be explained by differences in the Lewis acidity of surface carbenium ions. Comparing the reactions that occur on unpromoted and Fe promoted catalysts, carbenium ions formed on unpromoted catalysts react as if they are more Lewis acidic than those formed on Fe promoted catalysts. The observed increase in the tendency to form oligomers, cyclization of oligomeric carbenium ions to form dimethyl cyclohexanes, and the increased abundance of products formed by hydride abstraction (i.e. saturated hydrocarbons) on the unpromoted catalyst are all consistent with greater Lewis acidity for surface carbenium ions on the unpromoted catalyst compared to the Fe promoted catalysts. This apparent change in carbenium ion Lewis acidity undoubtedly results from perturbations of the catalyst surface caused by the iron promoter. Thus, one role of iron promoter in sulfated zirconia catalysts is to perturb the catalyst surface in a way that strengthens interactions between surface sites and carbenium ions and consequently decreases the Lewis acidity of surface carbenium ions. If carbenium ions interact primarily with negatively charged surface sites that are conjugate bases of Brønsted acids, then the iron promoter effectively increases the

basicity of these sites, which is equivalent to decreasing Brönsted acidity. This is inconsistent with previously described Brönsted acidity measurements in which no significant differences were found between unpromoted and transition metal promoted sulfated zirconias. However, a decrease in Brönsted acidity due to metal promoters is consistent with results of a study described by Venkatesh *et al* in which the acid catalyzed cracking of diphenylmethane to produce benzene was found to be significantly slower for a sulfated zirconia containing nickel compared to unpromoted sulfated zirconia^[25].

Alternatively, the effects of metal promoters may be summarized by the following scheme:



After forming on conjugate base sites, carbenium ions may migrate to Lewis base sites associated with promoter ($:B$) or interact simultaneously with conjugate base and Lewis

base sites. A stronger interaction between the carbenium ion and the surface reduces the Lewis acidity of the ion, which is reflected in its reactivity and the products detected by 1-butene TPD measurements. In conclusion, the volatile products detected during 1-butene TPD were indicative of the effect that the addition of metal promoters have on sulfated zirconia and 1-butene surface reactions demonstrated the differences among these catalysts.

6.4 General Conclusions

Questions concerning the nature of the acid site, acid strength distributions, and the roles of metal promoters in sulfated zirconia catalytic activity were examined during the work described in this dissertation. Based on infrared and thermogravimetry-mass spectrometry measurements, a structure for the sulfated zirconia active site was proposed. The proposed active site may be envisioned as consisting of a sulfur trioxide (SO_3) molecule inserted into the ZrO_2 crystal lattice surface. All sulfated zirconias calcined above 600°C were catalytically active for *n*-butane skeletal isomerization at 100°C . Therefore, sulfur-containing species were responsible for catalyst activity.

For *n*-butane isomerization, Ni, Fe, and Fe + Mn promoted sulfated zirconias were much more active than unpromoted catalysts. Analysis of conversion-time curves obtained during *n*-butane isomerization reactions revealed an induction period during which the reaction rate increased with time, followed by a period of decreasing activity. The presence of the induction period was consistent with accumulation of intermediates on metal promoted catalyst surfaces.

Adsorbed ammonia and pyridine infrared studies revealed Lewis and Brønsted acid sites on metal promoted and unpromoted sulfated zirconias. Adsorbed CO infrared measurements indicated that promoted and unpromoted sulfated zirconia had similar Lewis acid site strengths. Differences in Brønsted and Lewis acid site densities were found for catalysts with different metal promoter compositions. However, these

differences could not be correlated with the enhanced catalytic activity obtained when Fe, Ni, and Fe+Mn were incorporated into sulfated zirconia.

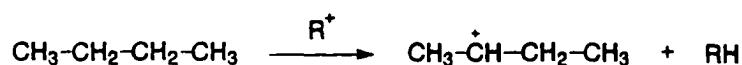
The conventional TPD method of using probe desorption temperatures to measure relative acid strengths was not applicable to sulfated zirconia because adsorbates decomposed before desorption. Benzene and pyridine TPD studies revealed that interactions between adsorbates and catalyst reduced catalyst decomposition temperatures. Interestingly, mass spectrometric ion signal temperature profiles for SO₂ evolution resulting from adsorbate-catalyst interactions could be correlated to catalyst activities for *n*-butane isomerization. For instance, during pyridine TPD, catalysts exhibited SO₂ ion signal temperature profiles with maxima at 590, 568, and 520°C for the Ni, Fe, and Fe+Mn promoted catalysts, respectively. Catalytic reactor studies indicated that the Ni-promoted catalyst was more active than the Fe-promoted catalyst at 100°C and that the Fe-promoted catalyst was more active than the Fe+Mn-promoted catalyst at the same temperature. Similar results were obtained when benzene was used as the adsorbate. However, during benzene TPD, two SO₂ evolutions were detected for metal promoted catalysts. The first SO₂ evolution maximized at 596, 557, and 544°C for catalysts containing Ni, Fe, and Fe+Mn, respectively. The second SO₂ evolution maximum occurred at about the same temperature as when no adsorbate was present. The two SO₂ evolutions are consistent with the presence of two sulfate environments, which is in agreement with recent Drago and Kob findings^[26]. For the unpromoted catalyst, SO₂ evolution maximized above 800°C with or without adsorbates, indicating that some catalyst-adsorbate interactions occurring on metal promoted catalysts do not exist for

unpromoted catalysts.

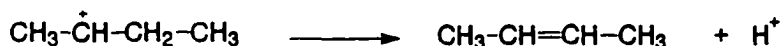
1-Butene TPD studies provided an insight into reactions that may be responsible for differences in reactivity between metal promoted and unpromoted catalysts. Volatile product distributions for promoted and unpromoted catalysts were consistent with 1-butene oligomerization followed by catalytic cracking of the oligomers. On metal promoted catalysts, 1-butene reactions produced more alkenes than alkanes. The formation of an alkene by deprotonation of carbocations on catalyst surfaces is less favored when adsorbate sites are strongly acidic^[27]. Carbocation deprotonation was apparently more favored on metal-promoted catalysts than on unpromoted catalysts. This suggests that adsorbate sites on metal promoted catalysts were of lower acidity than unpromoted catalyst adsorbate sites. This finding is consistent with a recent report by Drago and Kob that the acidity of metal promoted sulfated zirconia was lower than that of unpromoted sulfated zirconia^[26]. In contrast to metal promoted catalysts, 1-butene reactions on unpromoted catalysts produced predominantly alkanes. Alkane formation from 1-butene requires hydride abstraction, which is apparently more favored on unpromoted catalysts. It is suggested that one role of metal promoters is to alter the catalyst active site environment so that the electrophilic nature of adsorbed carbenium ions is diminished.

n-Butane isomerization may occur by intramolecular or bimolecular processes. The intramolecular path involves the formation of a cyclopropane intermediate that breaks to produce a thermodynamically unfavorable primary carbenium ion, which then rearranges to a $t\text{-C}_4^+$ ion^[28-30]. Hydride abstraction from a butane molecule subsequently

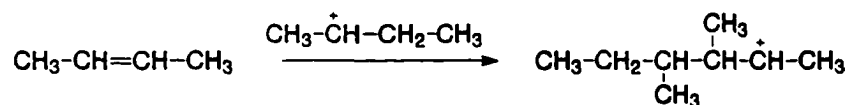
forms isobutane. From reactor studies of *n*-butane isomerization catalyzed by sulfated zirconias, a bimolecular mechanism is supported by the facts that C₃ and C₅ are produced in equimolar amounts and that the reaction order is 2 with respect to butane^[31]. The formation of a C₈ carbocation by alkylation of butene by a butyl carbocation has been proposed as the rate limiting step of the bimolecular process^[32]. The initial reaction in this mechanism is the formation of a carbenium ion (R⁺) at a surface acid site. R⁺ subsequently reacts with *n*-butane to form a C₄⁺ ion :



The C₄⁺ ion may then lose a proton to generate butene :

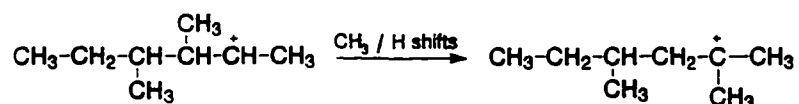


Reaction of C₄⁺ with butene forms a C₈ carbenium ion:

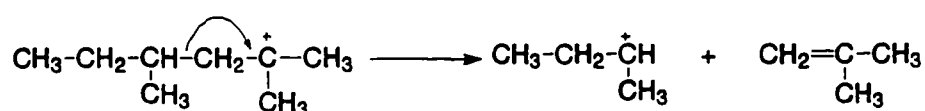


1-Butene TPD results described here suggest that C₈ carbenium ions form on both metal promoted and unpromoted sulfated zirconias. However, unpromoted sulfated zirconia catalyzes (more efficiently than metal promoted catalysts) additional oligomerization to yield carbenium ions larger than C₈ .

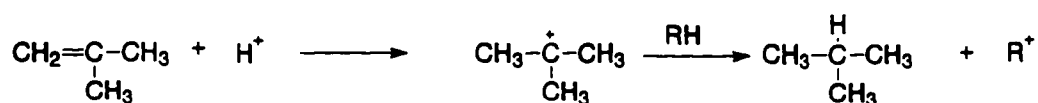
Rearrangements of C₈ carbenium ions by alkyl and hydrogen shifts generates more stable tertiary C₈ carbenium ions :



β-scission of the C₈ carbenium ion produces isobutene and a C₄ carbenium ion :



Protonation of isobutene forms t-C₄⁺ ions. Hydride abstractions by t-C₄⁺ ions yields isobutane and a carbenium ion (R⁺).



1-Butene TPD volatile product distributions suggested that unpromoted catalysts favored formation of large oligomers (> C₈) and that these reactions apparently competed with reactions yielding isobutane. This may be why unpromoted catalysts were less active than metal promoted catalysts for *n*-butane isomerization.

Because metal promoted sulfated zirconias show very high catalytic activity for hydrocarbon isomerization, alkylation, and cracking at low temperatures, industrial use of these catalysts as a replacement for presently used liquid acid catalysts remains very

attractive. However, *n*-butane isomerization reactor studies indicated that the catalysts were prone to rapid deactivation due to formation of carbonaceous residues. The fact that deactivated catalysts cannot be regenerated to obtain their original activity is a problem that must be addressed. Clearly, more work in this area is warranted before metal promoted sulfated zirconia can be effectively used in industry.

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