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Superacid Catalysis of Light Hydrocarbon Conversion

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Report written by

Bruce C. Gates
Department of Chemical Engineering and Materials Science
University of California
Davis, CA 95616
telephone: (916) 752-3953
FAX: (916) 752-1031
Email: BCGATES@ucdavis.edu

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Executive Summary

Motivated by the goal of finding improved catalysts for low-temperature conversion of light alkanes into fuel components or precursors of fuel components, we have investigated sulfated zirconia and promoted sulfated zirconia for conversion of butane, propane, and ethane. Catalyst performance data for sulfated zirconia promoted with iron and manganese show that it is the most active noncorrosive, nonhalide catalyst known for n-butane isomerization, and it is an excellent candidate catalyst for new low-temperature n-butane isomerization processes to make isobutane, which can be converted by established technology into methyl t-butyl ether (MTBE).

In the conversion of n-butane at temperatures as low as room temperature, iron- and manganese-promoted sulfated zirconia is more than 90% selective for formation of isobutane. The additional products (propane and pentanes) result from disproportionation of n-butane.

The advantage of the high activity of iron- and manganese-promoted sulfated zirconia catalyst is offset by the disadvantage of a lack of stability. In operation for n-butane isomerization in a flow reactor, this catalyst is deactivated rapidly, losing most of its initial activity within a few hours. However, the catalyst can be regenerated successfully at least seven times by treatment in air at 500°C.

Various transition metals have been found to work as promoters of sulfated zirconia for n-butane isomerization. The combination of iron and manganese is the best known combination of promoters yet discovered. Manganese is the single promoter giving the most active catalyst initially, but the manganese-promoted catalyst rapidly loses activity in operation in a flow reactor. Iron is not as effective a promoter as manganese initially, but iron-promoted sulfated zirconia retains its activity longer in the flow reactor operation than manganese-promoted sulfated zirconia.

The iron- and manganese-promoted sulfated zirconia is also a catalyst for conversion of propane and of ethane. Ethane is converted into ethylene and butanes in the presence of the iron- and manganese-promoted sulfated zirconia; propane is also converted into butane, among other products. However, the activities of the catalyst for

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these reactions are orders of magnitude less than the activity for *n*-butane conversion, and there is no evidence that the catalyst would be of practical value for conversion of alkanes lighter than butane.

The product distribution data for ethane and propane conversion provide new insights into the nature of the catalyst and its acidity. These data suggest the involvement of Olah superacid chemistry, whereby the catalyst protonates the alkane itself, giving carbonium ions (as transition states). The mechanism of protonation of the alkane may also pertain to the conversion of butane, but there is good evidence that the butane conversion also proceeds via alkene intermediates by conventional mechanisms of carbenium ion formation and rearrangement.

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Prefatory note: organization of this report

The following report consists of a brief initial section that is a summary of the objectives of the work, the methods used, the major results, and a discussion and conclusions. This section is followed by appendices that include detailed statements of the major segments of the work, identified by the titles of the appendices, which are shown above in the Table of Contents. Comments in the initial section guide the reader to the appendices for more details. Still more details are available in the publications resulting from this work, which are listed in Appendix E.

II. Project/Contract Objectives

The principal goal of the research was to investigate promoted sulfated zirconia catalysts for conversion of light alkanes, with emphasis on butane isomerization. The specific tasks were as stated in the following subsections.

A. *Construction of a flow reactor system for catalyst testing.* A once-through plug flow reactor system was designed and constructed to fit on a mobile cart to fit in a walk-in fume hood. The gist of the design is as follows: The reactor is a quartz tube surrounded by an electrical heater and connected to a temperature controller. There is a thermocouple well in the reactor, and the catalyst powder is held on a porous frit. There are separate feed lines for hydrocarbon gas (e.g., n-butane), inert gas (N_2), and H_2. Each gas line is equipped with a mass flow controller. The line for hydrocarbon is heat traced and temperature controlled to prevent condensation. Liquid flows from a metering pump to a vaporizer for mixing with gases. Pressure transducers are be incorporated upstream and downstream of the reactor. Upstream of the reactor there are traps for removal of impurities from the feed. The product line (heat traced and temperature controlled) is connected to the heated gas sampling valve of a gas chromatograph for on-line product analysis. The gas chromatograph is equipped with a data analysis system and a flame ionization detector and a thermal conductivity detector.

B. *Preparation of catalysts.* Catalysts were prepared by standard wet inorganic chemistry methods followed by drying and calcining. For example, sulfated zirconia was modified by incorporation of iron, added as a salt, followed by drying and calcining. Details of the preparation of the most active catalyst are stated below. Details are given in Appendices A, B, and C.

C. *Catalyst testing.* The flow reactor system was used to test the catalysts for light hydrocarbon conversion. The reactor was operated in nearly plug flow and nearly isothermally at temperatures in the range 25 to 400°C. Conversions were often low and differential for the determination of precise reaction rates. Partial pressures of the hydrocarbon reactant (e.g., *n*-butane) were varied by mixing it with inert gas (N_2). Products will also be introduced into the feeds, for example, isobutane with *n*-butane, to allow experimental determination of equilibria in the catalytic reactions. All catalysts were tested in preliminary experiments, and the results were used to guide the preparation of more active and stable catalysts. Approximately 20 catalysts were tested. Catalyst deactivation was measured in long experiments (up to about 10 days) with continuous operation. In these experiments, the conversion of the reactant and the conversion to the various products will be monitored periodically for the length of the run.

Details are given in Appendices A, B, and C.

D. *Evaluation of catalyst performance data.* The data were reduced to determine conversions and, from differential conversions, rates of isomerization, disproportionation, and cracking of butane; details are given in Appendices A and B. Similar data were obtained for the reactions of propane and of ethane, with details given in Appendices C and D. Activities of the catalysts were determined as reaction rates. Rates and conversions were measured as a function of time in stream in the flow reactor operating at constant temperature and pressure to provide a measure of the catalyst break-in and deactivation. Furthermore, catalysts were regenerated in the reactor by treatment in air, and conversions were measured as a function of time on stream to provide

evidence of catalyst regenerability. The most thorough data were recorded for the catalyst showing the most favorable combination of activity and stability, namely, Fe- and Mn-promoted sulfated zirconia.

E. *Determination of catalyst properties.* Physical properties of catalysts, including surface areas and compositions, were measured with standard methods. Areas were measured with the BET methods by nitrogen adsorption; chemical analyses were determined by inductively coupled plasma analysis. Electron spin resonance spectra of some catalysts were measured.

III. Introduction: Background and Motivation

Environmental concerns are forcing the replacement of aromatic hydrocarbons in gasoline with high-octane-number branched paraffins and oxygenated compounds such as MTBE. The ether is produced from methanol and isobutylene. There is established technology for production of isobutylene from isobutane by catalytic dehydrogenation, but there is a pressing need for improved processes to convert *n*-butane into isobutane; these should operate *at low temperatures,* because low temperatures favor the production of the branched product.

Alkane isomerization reactions are catalyzed industrially today at low temperatures by very strong acids such as aluminum chloride supported on alumina. But the aluminum chloride-containing catalysts are corrosive and environmentally challenging; they are being phased out. Alternatively, hydroisomerization is catalyzed by zeolite-supported metals at high temperatures, but high temperatures do not favor branched products at equilibrium, and these processes are thus inherently limited.

Therefore there is a clear need for improved catalysts and processes for the isomerization of *n*-butane and other straight-chain alkanes. The improved catalysts must be highly active to operate at low temperatures. Because the butane isomerization reaction is catalyzed by acids and because they must be highly active, the best candidate catalysts appear to be extremely strong acids. For environmental reasons, they also need to be noncorrosive and easy to handle.

Consequently, researchers have sought for solid acids that are noncorrosive and active enough to catalyze isomerization of paraffins at low temperatures. The catalyst investigated in this research is evidently the best known candidate for the *n*-butane isomerization process. The catalyst is new, having been reported in only several patents and one publication (C.-Y. Hsu, C. R. Heimbuch, C. T. Armes, and B. C. Gates, *J. Chem. Soc., Chem. Commun.* **1992**, 1645) prior to this research project; almost nothing had been reported about the nature and performance of this and related catalysts; in particular, hardly any quantitative results were available.

Thus our goals were to investigate this class of catalyst for light alkane conversion by measuring its performance in a flow reactor; part of the goal was to understand the activity, selectivity, and regenerability of the catalyst and its acidity and glean information about the mechanisms of light alkane reactions in the presence of this catalyst.

IV. Technical Strategy

The plan was to evaluate a family of promoted sulfated zirconia catalysts for butane isomerization in preliminary experiments. The data characterizing the catalysts were used as a basis for identifying those with the best combination of activity and stability, and, after the initial testing, one catalyst was identified for the most detailed experiments. This catalyst was Fe- and Mn-promoted sulfated zirconia, the preparation of which is stated below. The data provide a preliminary basis for evaluation of this catalyst as a candidate for large-scale conversion of butane.

V. Experimental Apparatus and Procedure

A. *Catalyst testing.* Catalysts were tested in a once-through flow reactor, with on-line analysis of the products by gas chromatography. The experiments were challenging because the catalytic activities typically increased with time on stream and then decreased. Conversion data illustrating the results of the catalyst testing are summarized below, with details given for *n*-butane conversion in Appendix A.

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B. *Catalyst preparation.* The best catalyst was prepared as follows: The Fe- and Mn-promoted sulfated zirconia was prepared by stepwise incipient wetness impregnation. The starting material was sulfated zirconium hydroxide supplied by Magnesium Elektron, Inc., where it was determined by combustion analysis that the sulfur content of the material was 3.7 wt% SO_3 (based on the mass of the solid). Sulfated zirconium hydroxide (125.5 g) was first impregnated with 43 mL of a 0.62-M solution of iron (III) nitrate nonahydrate (Aldrich, 98 %) in an amount corresponding to 0.34 mL of solution per gram of zirconium hydroxide. The resulting material was dried in an oven at 120°C for 5 h. It was then impregnated with 43 mL of a 0.21-M solution of manganese (II) nitrate hexahydrate (Aldrich, 98 %) and dried as described above. It was then calcined in static air as the temperature was raised at a rate of 3°C/min from 20 to 650°C in a muffle furnace and held at this temperature for 3 h. The weight percentages of iron, manganese, and sulfur in the catalyst were 1.0, 0.5, and 1.8 %, respectively, as determined by inductively coupled plasma emission spectroscopy. The catalyst was rust colored.

Details of the catalyst preparation, including those for catalysts other than Fe- and Mn-promoted sulfated zirconia, are given in Appendix B.

C. *Surface areas and pore volumes.* These were measured with standard methods; the surface area were determined with the BET method. A typical surface area was 100 m^2/g.

D. *Catalyst compositions.* These were determined by inductively coupled plasma analysis.

E. *Electron spin resonance spectra.* These were determined with standard methods.

VI. Data Reduction, Interpretation, and Analysis

Conversions in flow reactor experiments were determined from the product analyses in the conventional way. It was essential that the reactor operate as an

isothermal plug-flow reactor; and it was designed to meet these criteria. Often, conversions were low to allow elucidation of product distributions that were simple enough to allow determination of initial rates of reaction and initial reaction networks. When the conversions were high, the mass balances were checked; in contrast, when the conversions were low, the mass balances were not a good check, as it was not possible to determine the disappearance of reactants accurately from the analytical data for the reactants. In the latter case, conversions were determined from product analyses.

Initial conversions, characterizing the fresh catalysts, were determined by extrapolating the conversion vs. time on stream data to zero time on stream. The extrapolations were not always straightforward, and sometimes rather large errors characterized the estimates of initial conversions. The initial conversions were used to determine the initial rates by the assumption of differential conversion. Differential
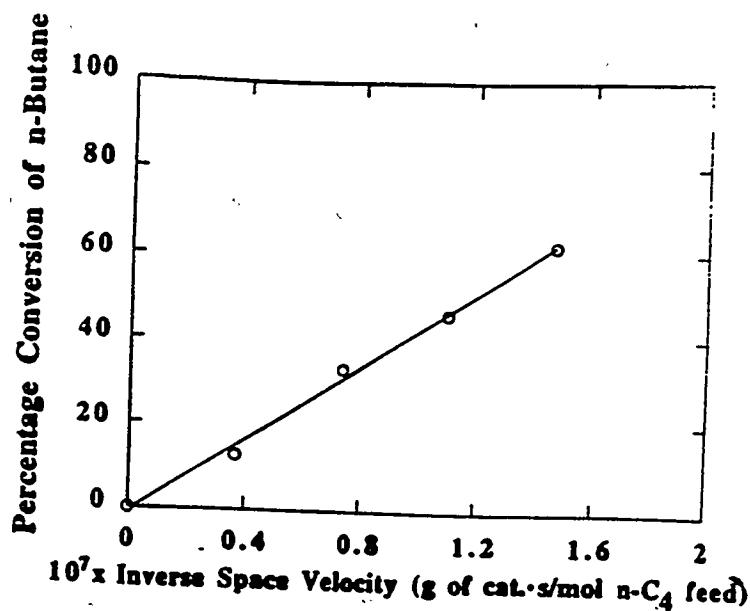
Fig. 1. Differential conversion of *n*-butane in a flow reactor at 75°C. The catalyst was Fe- and Mn-promoted sulfated zirconia.

conversions were determined experimentally from linear plots of conversion vs. inverse space velocity (which passed through the origin); such a plot is illustrated in Fig. 1.

Catalyst deactivation was indicated by the decline in conversion with time on stream, but the issues were complicated because there was typically an induction period of increasing rate preceding the decline in activity that is associated with catalyst deactivation; typical data are shown in Fig. 2, and more data are included in Appendix A.

Catalyst regeneration was carried out by treatment of the catalyst in a stream of flowing air at elevated temperature, and after this treatment, the catalyst was tested again under the same conditions as before. This procedure was repeated numerous times to determine the regenerability of the catalyst.

VII. Results

A. *Demonstration of successful reactor operation in* n-*butane conversion*. Carbon mass balances calculated from product analyses and feed flow rates demonstrated the high quality of the data in n-butane conversion. The carbon balances closed within ±
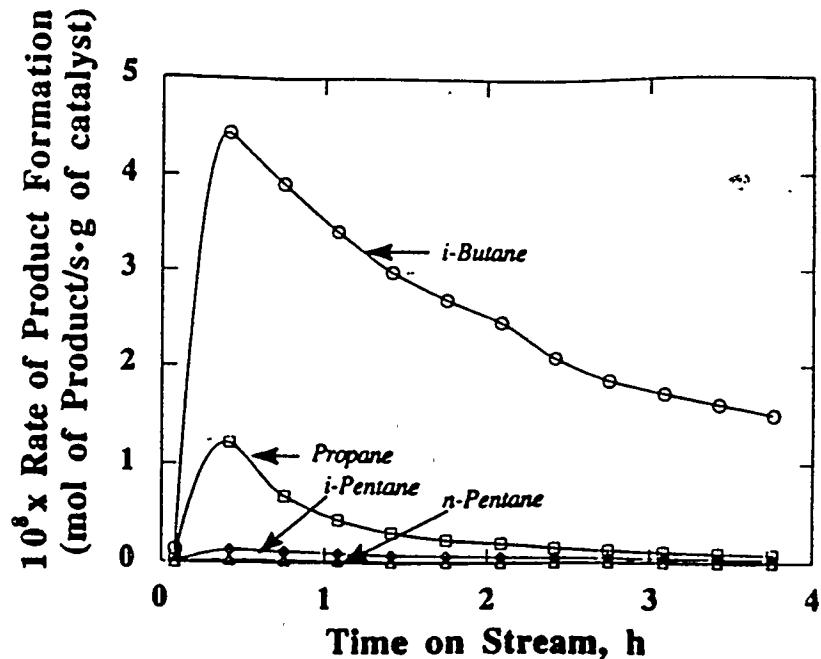
Fig. 2. Approximate rates of product formation from n-butane in a flow reactor at 100°C. The data demonstrate the typical induction period followed by catalyst deactivation. The catalyst was Fe- and Mn-promoted sulfated zirconia.

10% and in many instances within ± 5%. In the absence of a catalyst, no conversion of *n*-butane was observed.

B. n-*Butane conversion--the reaction network*. In the presence of Fe- and Mn-promoted sulfated zirconia catalyst, propane, isobutane, *n*-pentane, and isopentane (with traces of methane, ethane, and hexanes) were observed as products (Fig. 2). The selectivity for formation of isobutane from *n*-butane was greater than 85% for conversions less than 60%. At times on stream < 1 h, the carbon balance closed within ±10%, and at longer times on stream this balance closed within ± 5%.

The simplest product distribution is consistent with a reaction network including only isomerization and stoichiometric disproportionation. At the lowest reaction temperature, 40°C, the C_3/C_5 molar ratio after the break-in period was nearly the stoichiometric ratio of unity for disproportionation, namely, 1.1, with an estimated experimental error of about ± 5%.

The data for *n*-butane conversion at various temperatures demonstrate that the reactions occurring were isomerization and disproportionation at the lower temperatures (< 225 °C) and these with cracking at the higher temperatures.

The following classification summarizes the reactions observed, except for formation of carbonaceous deposits:

Low temp. 25 to 225°C	Intermediate temp. 225 to 275°C	High temp. 350 to 450°C
isomerization + dispropor-tionation	disproportionation + isomerization + cracking	cracking + isomerization

Further details are given in Appendix A.

The observation of disproportionation products suggests that a C_8 intermediate might have formed. According to this proposal, both the isomerization and disproportionation products could be formed from the C_8 intermediate. Reactions

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involving C_8 intermediates might be energetically favored over monomolecular isomerization because they would be expected to involve secondary and tertiary carbenium ions, whereas the monomolecular isomerization of *n*-butane requires the formation of a primary carbenium ion, which is highly unstable.

Fe- and Mn-promoted sulfated zirconia is an active catalysts for the cracking of *n*-butane. At low *n*-butane partial pressures, primary cracking products, methane and ethane, were observed at temperatures as low as 225°C. The observation of these products along with an ethane/ethylene molar ratio of 1 at 450°C is consistent with cracking occurring by a Haag-Dessau carbonium ion cracking (protolytic cracking) mechanism, whereby the catalyst protonates the alkane directly (giving a transition state carbonium ion). High concentrations of propane in the product indicate that cracking via a classical carbenium ion mechanism also occurs. These issues are addressed more fully in Appendix A.

C. *Role of promoters in* n-*butane conversion.* First-row transition metals were tested in a flow reactor as promoters of sulfated zirconia for the isomerization of *n*-butane at 100°C and 0.005 atm *n*-butane partial pressure. The activity of each of the sulfated zirconia samples increased through a maximum and then decreased with time on stream (Fig. 3). In order of increasing activity measured at the maximum, the effect of the promoters increased from right to left in the periodic table: zinc, nickel, cobalt, iron, and manganese. Iron and manganese increased the activity by 2-3 orders of magnitude. The causes of the promoter action are not elucidated; the promoters may play noncatalytic. roles as initiators. The product distribution data show that reactions accompanying isomerization and disproportionation are more important with some promoters (e.g., iron) than others (e.g., zinc). To apply this catalyst or a related catalyst industrially, it seems very likely to be necessary to reduce the rate of deactivation substantially and/or to regenerate the catalyst through many cycles.

Additional results giving evidence of the various promoters are summarized in Appendix B.
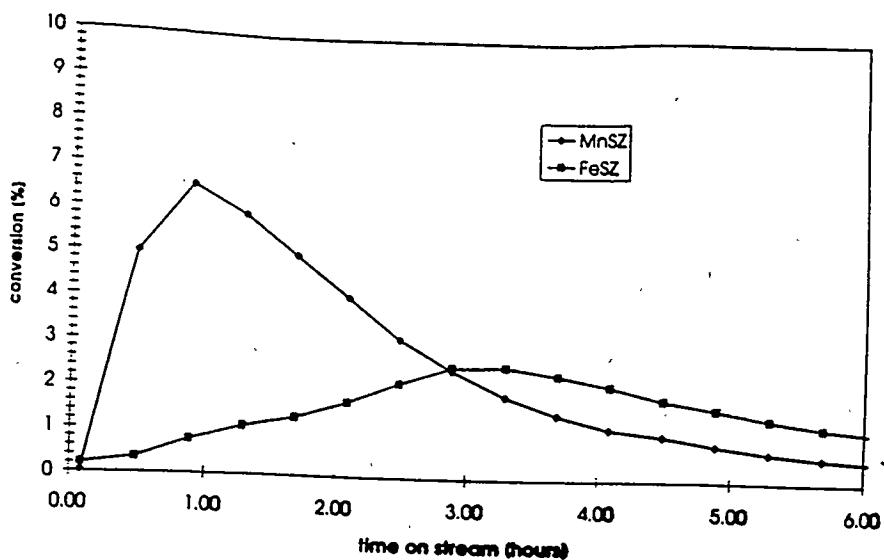
Fig. 3. Effects of Fe and Mn as promoters of *n*-butane isomerization in a flow reactor at 100°C. The term MnSZ refers to Mn-promoted sulfated zirconia, and the term FeSZ refers to Fe-promoted sulfated zirconia.

D. *Effects of feed impurities in* n-*butane conversion*. The effects of impurities in *n*-butane feed (alkenes and/or isobutane) are significant; they lead to an improvement in catalytic activity. These observations are inferred to be of practical importance; they indicate the benefit of the impurities in increasing butane conversion.

E. *Catalyst regeneration after use for* n-*butane conversion*. The data demonstrate that the iron- and manganese-promoted catalyst can be regenerated at least seven times with negligible loss of activity (within the experimental error).

F. *Structural evidence of the iron and manganese promoters*. The ESR spectra of Fe- and Mn-promoted sulfated zirconia, Fe-only-promoted sulfated zirconia, and Mn-only-promoted sulfated zirconia show that the Fe-only-promoted sample contained only relatively little Fe, and that much of the iron was present as Fe^{2+}. The data also lead to the conclusion that the contribution of the Fe species to the ESR spectrum of the Fe- and Mn-promoted sulfated zirconia is small. The shape of the spectrum characterizing the Mn-only-promoted sample suggests the presence of Mn^{2+}

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species that are closely associated with other Mn^{2+} species (a hyperfine structure consisting of six peaks, instead, is characteristic of isolated Mn^{2+} species).

The spectrum of Fe- and Mn-promoted sulfated zirconia is not satisfactorily represented by the appropriately weighted combination of spectra of the Fe-only-promoted catalyst and Mn-only-promoted catalyst. The difference spectrum (with a hyperfine structure of six peaks) suggests the presence of isolated Mn^{2+} species (this difference spectrum is nearly the same as that of the standard sample containing only Mn^{2+}). A comparison of observed and simulated spectra for the Fe- and Mn-promoted sulfated zirconia indicates that the experimental results can be simulated well on the basis of the assumption that the sample contained two different Mn^{2+} species, one isolated, and one closely associated with other Mn^{2+} species.

The ESR results show that (1) the effects of the iron and the manganese are not simply additive (this statement pertains to the structures; whether it pertains to the catalytic functions is still not resolved) and (2) the isolated Mn^{2+} species are associated with the greatest promoter effects.

The ESR results are only preliminary, no further ESR results are available.

G. *Propane conversion*. Iron- and manganese-promoted sulfated zirconia is a catalyst for the conversion of propane, but the rate of conversion of propane is much less than the rate of conversion of butane. Whereas this catalyst appears to be a good candidate for practical, industrial conversion of butane, it appears to lack sufficient activity for practical conversion of propane. Perhaps more active catalysts will be useful for propane conversion. The propane conversion data reported here provide excellent insights into the chemistry of the catalytic conversions; they are consistent with the inference that the catalyst is a superacid and that the chemistry is analogous to that determined in superacid solutions by G. A. Olah, who was awarded the Nobel Prize in chemistry for his work.

The catalyst was tested for conversion of propane at 1 atm, 200-300°C and propane partial pressures in the range of 0.01-0.05 atm. At 250°C, catalysis was

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demonstrated, as the number of propane molecules converted was at least 1 per sulfate group after 16 days of operation in a continuos flow reactor. Propane was converted in high yield to butanes, but the conversions were low, for example being only a fraction of a percent at a space velocity of 9.1×10^{-7} mol/(g of catalyst $\cdot$ s) and 250°C. Coke formation was rapid. The observation of butanes, pentanes, and methane as products is consistent with Olah superacid chemistry, whereby propane is first protonated by a very strong acid to form a carbonium ion. The carbonium ion then decomposes into methane and an ethyl cation which undergoes oligocondensation reactions with propane to form higher molecular weight alkanes. The results are consistent with the identification of iron- and manganese-promoted sulfated zirconia as a superacid.

Details of the propane conversion are given in Appendix C.

H. *Ethane conversion*. Ethane reacts in the presence of Fe- and Mn-promoted sulfated zirconia to form n-butane, ethylene, methane, and H_2 at temperatures 200°C. The data indicate autocatalysis with carbocation intermediates as in superacid solution chemistry, but the reactions are more than an order of magnitude slower than those of propane under the same conditions. The product distribution data indicate Olah chemistry, whereby the catalyst initially protonates the ethane (Fig. 4).

Presuming that the carbocation chemistry inferred here for ethane conversion in the presence of Fe- and Mn-promoted sulfated zirconia also pertains to n-butane isomerization catalyzed by Fe- and Mn-promoted sulfated zirconia, we suggest that the initial increase in conversion of butane in a flow reactor can be attributed to build-up of $C_4H_9^+$, which reacts with n-butane to form $C_8H_{19}^+$, which rearranges and splits into 2-methylpropane + $C_4H_9^+$. In contrast, others have proposed a classical bifunctional carbenium ion mechanism for n-butane isomerization catalyzed by Fe- and Mn-promoted sulfated zirconia, whereby $C_4H_9^+$ reacts with butene (formed by butane dehydrogenation) to give $C_8H_{17}^+$, which undergoes β-scission to form $C_4H_9^+$ and 2-methyl-1-propylene, with subsequent hydrogen transfer giving 2-methylpropane; correspondingly, some

authors have concluded that acidic sites in Fe- and Mn-promoted sulfated zirconia were only moderately strong.

The oligocondensation (giving butane) observed in the ethane reaction with this catalyst was not observed with USY zeolite replacing it, although ethylene was formed in comparable amounts with each material, provided that the space velocity was adjusted to give comparable ethane conversions. Furthermore, no evidence of autocatalysis was observed with USY zeolite; ethane conversion decreased monotonically with time on stream. Thus, in ethane conversion with USY zeolite, there is no evidence of the classical bifunctional carbenium ion mechanism for butane formation.

Consequently, we infer that butane formation from ethane in the presence of Fe- and Mn-promoted sulfated zirconia proceeds via a mechanism different from the classical bifunctional mechanism. Rather, carbocation chemistry analogous to that occurring in superacid solutions accounts for butane formation from ethane. The implication is that FMSZ incorporates extremely strong acidic sites. To reconcile this inference with the observation that the acidic groups in Fe- and Mn-promoted sulfated zirconia are only moderately strong, we postulate that the strongest acid groups constitute only a small minority that were not observed in reported spectroscopic experiments.
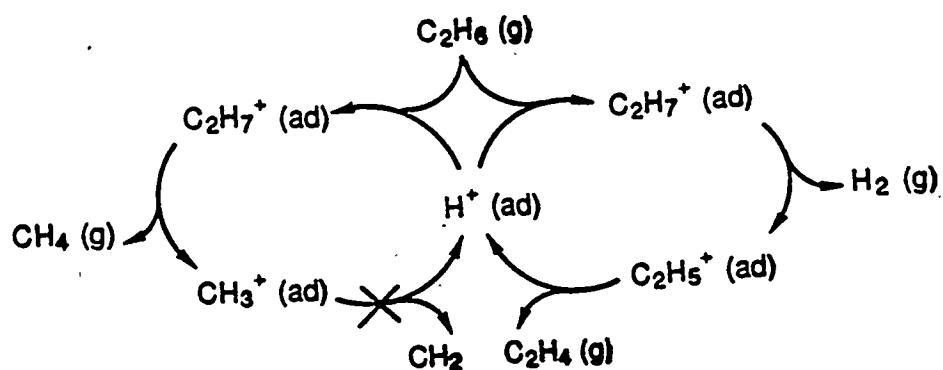
Fig. 4. Catalytic cycle suggested for ethane conversion involving Olah chemistry. The reactant was ethane and the catalyst Fe- and Mn-promoted sulfated zirconia.

The inference that the ethane conversion in the presence of Fe- and Mn-promoted sulfated zirconia proceeds via routes analogous to carbocation superacid chemistry does not exclude the possibility of butane isomerization proceeding (perhaps simultaneously) via the classical carbenium ion route.

Details of the ethane conversion are given in Appendix D.

I. *A compensation effect in cracking catalyzed by Fe- and Mn-promoted sulfated zirconia: evidence of reaction proceeding via protonated alkanes.* Low conversions of propane, *n*-butane, and 2,2-dimethylpropane were measured with each reactant in the presence of iron- and manganese-promoted sulfated zirconia in a once-through plug flow reactor at 1 atm, 202-500°C, and reactant partial pressures of 0.00025, 0.0025, and 0.01 atm. Rates of the reactions (overall conversion of propane, of *n*-butane, and of 2,2-dimethylpropane; formation of methane from each of the three reactants; formation of ethylene from propane and from *n*-butane; and formation of ethane from *n*-butane) were determined by extrapolating the declining conversions to zero time on stream. The apparent activation energies and pre-exponential factors characterizing each of the reactions inferred to proceed via a carbonium ion transition state falls near a straight line on a compensation effect plot. The plot (Fig. 5) is suggested to represent the family of reactions proceeding via protolytic cracking and carbonium ion transition states.
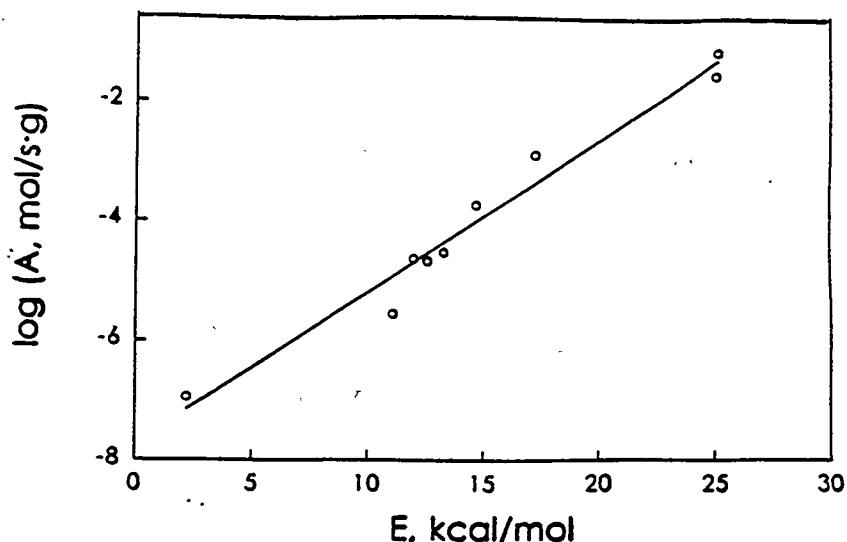
Fig. 5. Compensation effect: linear dependence of the log of the preexponential factor A on the activation energy E for alkane cracking reactions believed to proceed via protolytic cracking.

VIII. Discussion

The most important practical results of the work summarized in this report are those demonstrating the activity, selectivity, and regenerability of the Fe- and Mn-promoted sulfated zirconia catalyst for isomerization of n-butane. This reaction is important as a step in the conversion of n-butane into methyl-*tert*-butyl ether, an important clean-burning high-octane-number gasoline component and the chemical with the highest rate of production increase in the preceding decade.

The Fe- and Mn-promoted sulfated zirconia catalyst is the best of those tested in this work and the most active nonhalide catalyst known for this reaction. Besides the advantages of high activity and selectivity, it has the advantage of being noncorrosive, in contrast to a currently applied n-butane isomerization catalyst, the oxide-supported halide, aluminum chloride. The high activity of the Fe- and Mn-promoted sulfated zirconia catalyst suggests the feasibility of operation of processes for n-butane isomerization at low temperatures (less than 100°C), and this is important because the equilibrium conversion of n-butane to isobutane increases with decreasing temperature. Thus a highly active catalyst offers the prospect of higher conversions than a less active catalyst that would have to operated at higher temperatures to give satisfactory rates of reaction.

The results demonstrate that the catalyst undergoes rapid deactivation in continuous operation in a flow reactor, which would be the likely mode of operation in a large-scale process. Thus, in practice, the catalyst would have to be regenerated so that it could be used repeatedly. The results of this work show that the catalyst can be regenerated by treatment in air; it was regenerated as many as seven times, with the activity of the regenerated catalyst being indistinguishable from that of the fresh catalyst.

The promoters Fe and Mn work better in the catalyst than either Fe or Mn separately. Mn is associated with the initially high activity of the Fe- and Mn-promoted sulfated zirconia catalyst, and Fe is associated with a lower rate of catalyst deactivation than was observed with Mn separately.

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Fe- and Mn-promoted sulfated zirconia also catalyzes the conversion of propane and of ethane to form both lower- and higher-molecular-weight products (e.g., methane and butane from ethane). These reactions are typically at least one to two orders of magnitude slower than n-butane isomerization, and there seems to be no likelihood of their practical application with this catalyst. However, the product distribution data observed for ethane and propane conversion indicate the involvement of Olah superacid chemistry, whereby the catalyst protonates the alkane itself, giving carbonium ions (as transition states). This observation implies that the Fe- and Mn-promoted sulfated zirconia catalyst is an extraordinarily strong acid and that the acidic properties are important in determining the catalytic properties. Thus the observations of catalyst performance in conversion of propane and of ethane indicate that catalyst acidity is an important criterion for catalyst characterization and that catalytic activity for reactions including n-butane isomerization may be related to catalyst acidity.

IX. Conclusions

The Fe- and Mn-promoted sulfated zirconia catalyst is the most active noncorrosive, nonhalide solid acid known. It behaves like an extremely strong acid, catalyzing the isomerization of n-butane even at room temperature. The promoters Fe and Mn, predominantly present in the divalent states, are best used in combination with each other. The great advantage of the catalyst is its high activity, which allows low-temperature operation and the attendant benefit of the high equilibrium conversion to isobutane that is achievable at low temperatures. The major disadvantage of the catalyst is that it undergoes rapid deactivation in operation. However, the catalyst is easily regenerated by treatment in air at high temperatures.

This catalyst has excellent potential for commercial application; it is a candidate for application in the technology of manufacture of environmentally acceptable gasoline. It is anticipated that stabilizers in the catalyst and/or feed will be needed for such applications to become economical.

The work summarized here is the first thorough and quantitative investigation of the Fe- and Mn-promoted sulfated zirconia catalyst. But this work is only a start. More

needs to be learned about catalyst deactivation and stabilization; about the kinetics of the isomerization reaction and side reactions; about process economics; and about the application of catalysts related to Fe- and Mn-promoted sulfated zirconia for isomerization of alkanes other than butane and for alkylation (e.g., isobutane-propylene alkylation).

Low-Temperature Reactions of *n*-Butane Catalyzed by Iron- and Manganese-Promoted Sulfated Zirconia

Abstract

A catalyst was prepared by addition of iron and manganese to sulfated zirconium hydroxide followed by calcination. The catalyst was tested for *n*-butane conversion in a packed-bed flow reactor at temperatures of 40 to 225°C with the reactant partial pressure in the range of 0.0025-0.01 atm. The predominant catalytic reaction was *n*-butane isomerization, and this was accompanied at 40°C by near stoichiometric disproportionation. The C_3/C_5 molar ratio was generally greater than 1, consistent with conversion of the secondary C_5 products. As the temperature increased, the selectivity for isomerization decreased and that for disproportionation increased. In a typical experiment the activity of the catalyst increased for about 1 h on stream and then declined rapidly. The rate maxima as a function of time on stream were taken as a measure of the initial activity of the catalyst. For example, the approximate rate of isomerization of *n*-butane at the maximum was 4.3×10^{-8} mol/(g of catalyst · s) with a feed *n*-butane partial pressure of 0.0025 atm at 75°C. With a feed *n*-butane partial pressure of 0.005 atm at 40°C and a conversion of 11%, the molar ratio of propane to *i*-butane was 0.03, and with the same feed composition at 100°C, this ratio at a conversion of 50% was 0.1. The iron- and manganese-promoted solid catalyst is potentially of value for practical low-temperature paraffin isomerization accompanied by disproportionation of *n*-butane.

Introduction

Environmental concerns are leading to the replacement of aromatic hydrocarbons in gasoline with high-octane-number branched paraffins and oxygenated compounds such as methyl *t*-butyl ether. The ether is produced from methanol and isobutylene, and the

latter can be formed from *n*-butane by isomerization followed by dehydrogenation. Paraffin isomerization reactions are catalyzed by very strong acids such as aluminum chloride supported on alumina. The aluminum chloride-containing catalysts are corrosive, and their disposal is expensive. Alternatively, hydroisomerization is catalyzed by zeolite-supported metals at high temperatures, but high temperatures do not favor branched products at equilibrium.

Thus there is a need for improved catalysts and processes for the isomerization of *n*-butane and other straight-chain paraffins. Consequently, researchers have sought for solid acids that are noncorrosive and active enough to catalyze isomerization of paraffins at low temperatures. For example, sulfated zirconia catalyzes isomerization of *n*-butane at temperatures as low as 25°C (*1*). The addition of iron and manganese promoters has been reported to increase the activity of sulfated zirconia for *n*-butane isomerization by three orders of magnitude (*2*). Although the high activity of this catalyst is now established (*2, 3*), the reaction network is not known, and the mechanism has not been investigated.

Two pathways for acid-catalyzed *n*-butane isomerization have been proposed: (1) Branching rearrangement of carbenium ions formed by hydride abstraction by Lewis acids (*4, 5*); the rearrangement proceeds via a substituted protonated cyclopropane intermediate. (2) Formation of C_8 carbenium ion intermediates and subsequent cracking; this latter mechanism implies the simultaneous formation of isomerization and disproportionation products (*6*). Evidence indicating a substituted protonated cyclopropane intermediate is limited to low-temperature reactions in solution. Evidence for a C_8 intermediate was obtained with H-mordenite-catalyzed reaction of *n*-butane at 350°C; disproportionation and isomerization products were observed, but the disproportionation was not stoichiometric.

The goal of the research reported here was to investigate the low-temperature reactions of *n*-butane catalyzed by iron- and manganese-promoted sulfated zirconia. *n*-

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Butane was chosen as the reactant because it (1) gives a simple product distribution; (2) is relatively unreactive, being a good probe of the most strongly acidic catalysts (7); and (3) is a potentially valuable source of isobutane.

Experimental Methods

Materials

Gases were supplied by Liquid Carbonic. The diluent was N_2 (99.998 %); the feed, consisting of 1.0 mol% n-butane in N_2, was found by gas chromatography to contain less than 0.0002 mol% i-butane.

Catalyst Preparation

The iron- and manganese-promoted sulfated zirconia was prepared by incipient wetness impregnation. The starting material was sulfated zirconium hydroxide supplied by Magnesium Elektron, Inc., where it was determined by combustion analysis that the sulfur content of the material gave 3.7 wt% SO_3 (based on the mass of the solid). Sulfated zirconium hydroxide (125.5 g) was first impregnated with 43 mL of a 0.62-M solution of iron (III) nitrate nonahydrate (Aldrich, 98 %) in an amount corresponding to 0.34 mL of solution per gram of zirconium hydroxide. The resulting material was dried in an oven at 120°C for 5 h. It was then impregnated with 43 mL of a 0.21-M solution of manganese (II) nitrate hexahydrate (Aldrich, 98 %) and dried as described above. It was then calcined in static air as the temperature was raised at a rate of 2.7°C/min from 20 to 500°C and held at this temperature for 3 h. The weight percentages of iron, manganese, and sulfur in the catalyst were 1.0, 0.5, and 1.8 %, respectively, as determined by inductively coupled plasma emission spectroscopy. The catalyst was rust colored.

Catalytic Reaction Experiments

Before each reaction experiment, the catalyst in flowing N_2 [30 mL(NTP)/min] was heated from 20 to 450°C at a rate of 7.1°C/min, and the temperature was then held at 450°C for 1.5 h. After this pretreatment, the catalyst was cooled to the desired reaction temperature in N_2 flowing at 30 mL/min.

Reactions were carried out in a straight quartz tube with an inside diameter of 1.3 cm; the finely ground catalyst particles were supported on a porous frit. Typically, 1.5 g of catalyst was used for each experiment, except when the space velocity was varied by changing the mass of catalyst. Temperature was measured with a thermocouple placed in a quartz well located near the center of the catalyst bed. Reactions were carried out in the temperature range of 40 to 225°C, and temperature was controlled within ± 1°C. The gas flow rates were maintained by mass flow controllers (Brooks) with an accuracy of ± 1 mL/min. The *n*-butane inlet partial pressure was varied from 0.0025 to 0.01 atm by mixing the 1% *n*-butane stream with N_2 to maintain a constant total volumetric flow rate of 80 mL(NTP)/min. All the reactions were carried out at atmospheric pressure.

The reaction products were analyzed with an online gas chromatograph (GC) equipped with a flame ionization detector (Hewlett-Packard 5890A, Series II). The hydrocarbons were separated in a 0.53 mm x 50 m KCl/Al_2O_3 column (Chrompack). The first injection was made after 5 min on stream, and the subsequent injections were made every 20 min. Response factors and retention times of the hydrocarbons were determined with known samples from Scott Specialty Gases.

Results

In the absence of a catalyst, no conversion of *n*-butane was observed. In the presence of the promoted sulfated zirconia catalyst, propane, *i*-butane, *n*-pentane, and *i*-pentane (with traces of methane, ethane, and hexanes) were observed as products in the temperature range 40 to 225°C. The selectivity for formation of *i*-butane from *n*-butane

was greater than 85% for conversions less than 60%. At times on stream < 1 h, the carbon balance closed within ±10%, and at longer times on stream this balance closed within ± 5%.

The n-butane conversion as a function of time on stream is shown in Fig. A1 for the temperature range 40 to 100°C. The plots are characterized by two distinct regimes, represented as a break-in period followed by a deactivation period. At the lowest reaction temperature (40°C), the conversion of n-butane was still increasing even after 4 h on stream. In contrast, at 75°C and at 100°C, the maximum conversion was observed after less than 1 h. At 75°C, the maximum conversion of n-butane was observed at approximately the same time on stream when the inverse space varied from 7.33 x 10^6 to 1.47 x 10^7 (g of catalyst · s)/mol of n-butane; however, the maximum shifted to longer times on stream when the contact time decreased to 3.66 x 10^6 (g of catalyst · s)/mol of n-butane (Fig. A1).

A linear correlation was observed between the maximum n-butane conversion observed in each experiment carried out at temperatures in the range 40-100°C and the inverse space velocity, as illustrated by the data of Fig. 1. Thus the data demonstrate that these conversions are differential and determine reaction rates. However, catalyst deactivation was so fast at the higher temperatures that the maxima in conversion vs. inverse space velocity plots could not be discerned. Thus, the data at these higher temperatures do not determine the maximum conversions. Rates at these higher temperatures were calculated from conversions < 30% on the basis of the assumption that the conversions were still differential; these rates all represent the performance of the partially deactivated catalysts.

Rates of formation of the various products at 100°C are summarized Fig. 2. No other products were observed except for traces of methane and ethane and occasionally hexanes. For example, at 75°C the approximate rate of isomerization of n-butane (calculated from the conversion to i-butane) at the maximum as a function of time on

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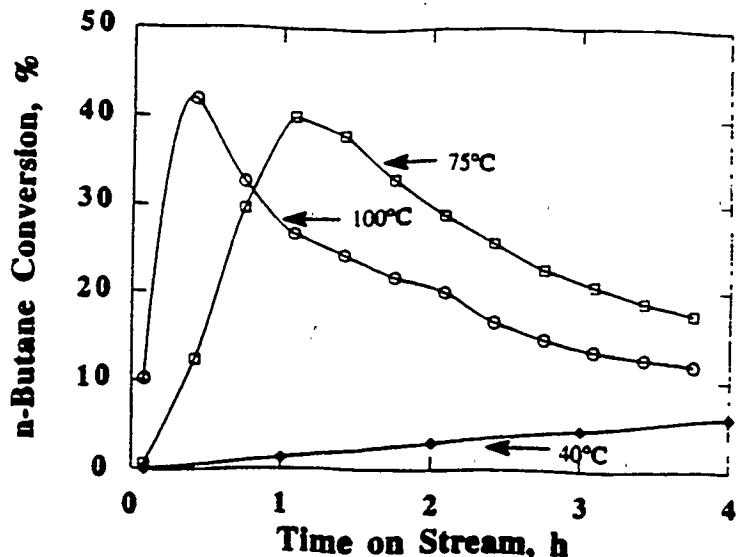
Fig. A1. Effect of reaction temperature on *n*-butane conversion catalyzed by Fe- and Mn-promoted sulfated zirconia. Feed *n*-butane partial pressure = 0.0025 atm at 75°C and 100°C and 0.005 atm at 40°C. Total feed flow rate = 80 mL(NTP)/min. Catalyst mass = 1.5 g.

stream was 4.3 x 10^{-8} mol/(g of catalyst · s) with a feed *n*-butane partial pressure of 0.0025 atm. Maxima in the rates of formation of each of the following products were observed as a function of time on stream at temperatures < 150°C, provided that the partial pressure of *n*-butane in the feed was < 0.005 atm: propane, *i*-butane, *n*-pentane, and *i*-pentane; these results are illustrated in Fig. 2.

Because of the break-in period, it was not possible to extrapolate these rates accurately to zero time on stream. Thus the values of the rates at the maxima are taken as the best available measures of the initial reaction rates (i.e., those characterizing the undeactivated catalyst).

The predominant product was isobutane, and thus it is concluded that the principal reaction was isomerization of *n*-butane. The observation of propane and pentanes suggests that disproportionation also occurred.

The molar ratio of C_3 to C_5 approached a value of approximately 1.10 ± 0.05 at the lowest temperature investigated (40°C), after about 25 h onstream (Fig. A2). Thus
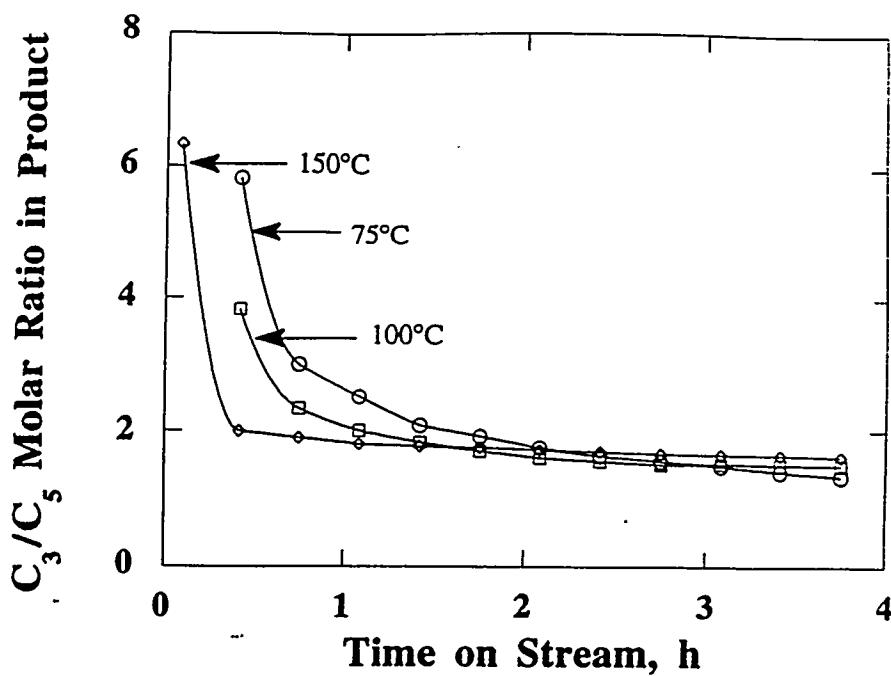
Fig. A2. Effect of temperature on the C_3/C_5 molar ratio in the products of *n*-butane conversion. Feed *n*-butane partial pressure = 0.0025 atm. Total feed flow rate = 80 mL(NTP)/min. Catalyst mass = 1.5 g.

these data suggest that stoichiometric disproportionation and isomerization were virtually the only catalytic reactions taking place under these conditions. However, this simple result was not generally observed. Typically, the molar C_3/C_5 ratio was greater than unity. For example, after 3 h on stream at temperatures of 75 to 150°C, the ratio was in the range of approximately 1.5-1.7. The samples taken at the shortest times on stream (0.08 h) were characterized by an absence of C_5 products, which suggests that these were held up in the catalyst bed. During the first hour on stream at temperatures from 75 to 150°C, the C_3/C_5 ratio decreased by a factor of 3-4. Variation of space velocity did not lead to significant changes in this ratio (Fig. A3), which suggests that the products were primary.

At short times on stream, greater than stoichiometric C_3/C_5 ratios were observed at all temperatures. With increasing temperature, the C_3/C_5 molar ratio increased as shown in Table A1.

The ratio of C_3 to *i*-C_4 in the product is taken as an approximate measure of the selectivity for disproportionation relative to isomerization of *n*-butane. For example, with

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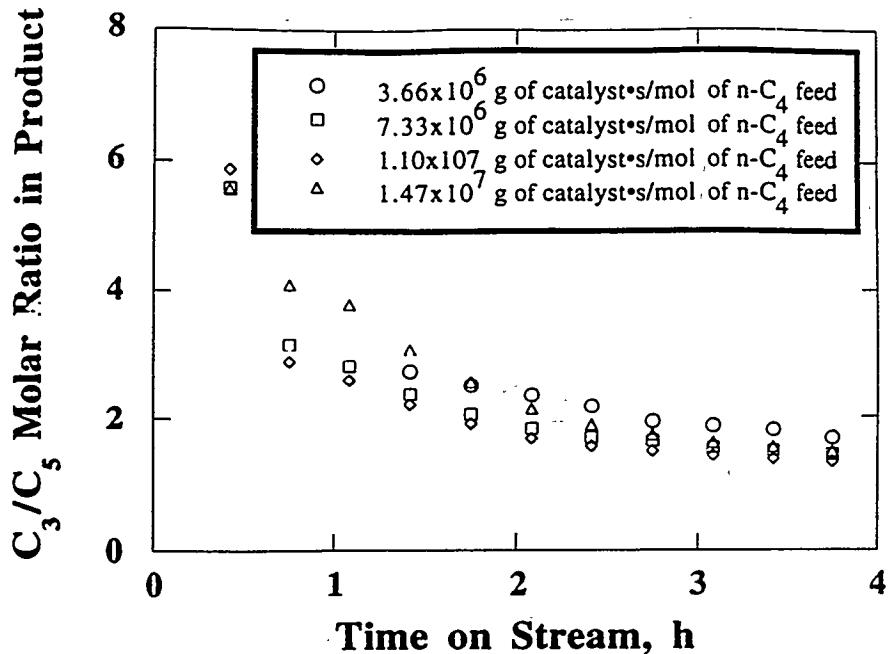
Fig. A3. Influence of inverse space velocity on C_3/C_5 molar ratio. Feed n-butane partial pressure = 0.0025 atm. Total feed flow rate = 80 mL(NTP)/min.

a feed n-butane partial pressure of 0.005 atm at 40°C and a conversion of 11%, the molar ratio of propane to i-butane was 0.03, and with the same feed composition at 100°C, this ratio at a conversion of 50% was 0.1. This ratio varied with reaction temperature and time on stream. The maxima in the C_3/i-C_4 ratios were observed at times on stream corresponding to the maxima in n-butane conversion at the lower temperatures, i.e., those at which the maxima could be observed (Fig. A4). The C_3/i-C_4 ratio increased with increasing temperature in the range of feed n-butane partial pressures of 0.0025 to 0.01 atm. The C_3/i-C_4 ratio was higher the lower the inlet n-butane partial pressure at a given reaction temperature.

The product C_3/i-C_4 ratios were at least an order of magnitude smaller than the equilibrium ratios (Table A2). The product i-C_5/n-C_5 ratios observed at different feed n-butane partial pressures in the range of 0.0025 to 0.01 atm remained nearly constant with respect to time on stream. However, as shown in Table A3, this ratio decreased as the temperature was increased from 100 to 225°C. The observed product i-C_5/n-C_5 ratios
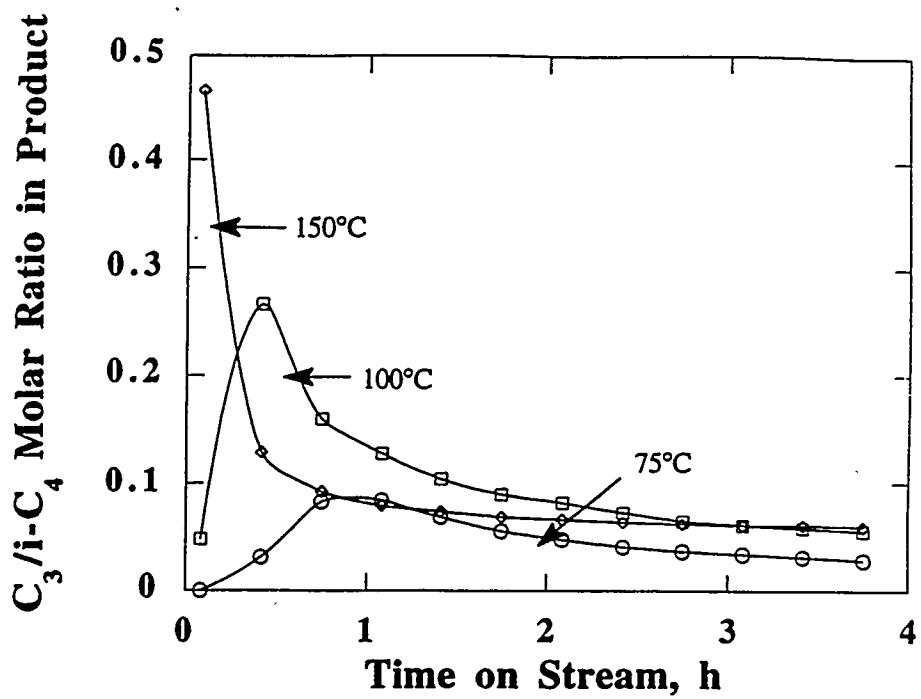
Fig. A4. Influence of reaction temperature on the selectivity of *n*-butane conversion to C_3 and *i*-C_4. Feed *n*-butane partial pressure = 0.0025 atm. Total feed flow rate = 80 mL/min. Catalyst mass = 1.5 g.
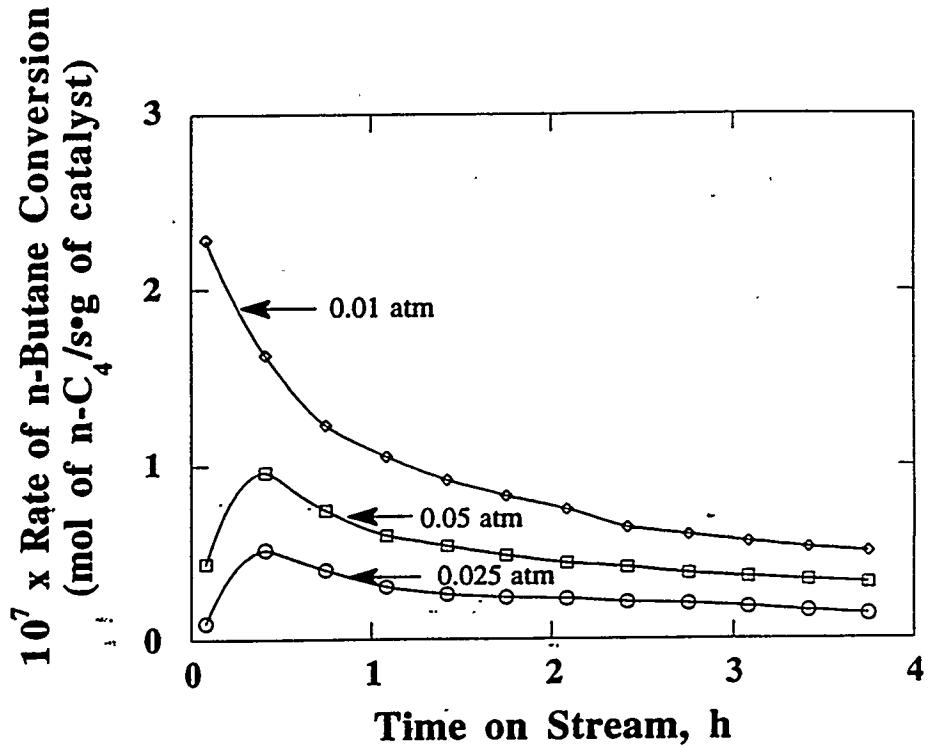
Fig. A5. Effect of *n*-butane feed partial pressure on the overall reaction rate. Total feed flow rate = 80 mL(NTP)/min. Temperature = 100°C. Catalyst mass = 1.5 g.

Table A1. Effect of Temperature on the Product C_3/C_5 Ratio.[a]

Temperature (°C)	Conversion of n-butane (%)	Molar C_3/C_5 ratio
40	5	1.10
75	17	1.19
100	19	1.24
150	11	1.36

[a] Feed: n-butane at a partial pressure of 0.005 atm.
Mass of catalyst = 1.5 g.
Total feed flow rate = 80 mL(NTP)/min.

Table A2. Comparison of C_3/i-C_4 Ratios with equilibrium Values. [a]

				Molar C_3/i-C_4 Ratio		
				Observed		Calculated[b]
Temperature, °C	Feed n-Butane Partial Pressure, atm	Percentage Conversion of n-butane at maximum	after 4 h	maximum	after 4 h	
75	0.0025	49	24	0.08 0.045		0.69
75	0.005	52	22	0.1	0.02	0.69
75	0.01	25	8	-	0.02	0.69
100	0.0025	49	9	0.15 0.045		0.79
100	0.005	53	15	0.16 0.023		0.79
100	0.01	46	9	-	0.021	0.79
150	0.0025	37	9	0.12 0.047		1.13
150	0.05	59	8	-	0.035	1.13
150	0.01	57	13	-	0.03	1.13

Mass of catalyst = 1.5 g, Total Feed Flow Rate = 80 mL(NTP)/min.

[b] Equilibrium values were calculated from thermochemical data in the "CRC Handbook of Chemistry and Physics," 65th Edition, CRC Press, Boca Raton, 1984, assuming that the following reactions occurred:

n-$C_4H_{10} = i$-C_4H_{10}

$2n$-$C_4H_{10} = C_3H_8 + n$-C_5H_{12}

$2n$-$C_4H_{10} = C_3H_8 + i$-C_5H_{12}
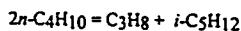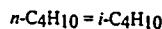
Table A3. Comparison of measured i-C_5/n-C_5 Ratios with Thermochemical Values.[a]

	i-C_5/n-C_5	
Temperature, °C	Experimental Value	Equilibrium Value[b]
75	6.0	5.9
100	5.1	4.5
150	3.9	3.8
225	3.0	2.8

[a] The i-C_5/n-C_5 ratio was approximately independent of the feed n-butane partial pressure.

Mass of catalyst = 1.5 g.

Total Feed Flow Rate = 80 mL(NTP)/min.

[b] Equilibrium values were derived as stated in Table A2.

were approximately equal to the equilibrium ratios calculated from thermochemical data. (Table A3).

Conversions of n-butane to i-butane were always less than the equilibrium conversions when they were estimated from thermochemical data simply on the basis on the isomerization equilibrium. However, when the equilibrium compositions were estimated for the combination of isomerization and disproportionation reactions, the conversions to i-butane were sometimes in excess of equilibrium. We lack sufficient data to model the reaction kinetics incorporating the equilibria.

As shown in Fig. A5, as the n-butane feed partial pressure increased, the rate of reaction increased, indicating the positive order of the reaction. Fig. A5 also gives an indication of the rates of deactivation. Catalyst deactivation was least at the lowest n-butane partial pressure.

Discussion

Comparison with Literature

The data show that conversion of n-butane catalyzed by iron- and manganese-promoted sulfated zirconia at 40°C gives propane, isobutane, and pentanes as the principal products, along with traces of methane, ethane, and hexanes. By far the predominant product was the isomerization product, isobutane. The same principal product has been observed for n-butane conversion catalyzed by unpromoted sulfated zirconia at 25°C; it was formed along with propane and traces of isopentane (1). In the presence of a H-mordenite catalyst at 400°C, n-butane was also converted into isobutane and propane along with some C_5 products, methane, and ethane. When unpromoted sulfated zirconia was used as a catalyst for n-butane conversion at 300°C, a high selectivity to isobutane was observed, with only trace amounts of other products being formed (8). Thus the general pattern indicates n-butane isomerization accompanied by

formation of higher- and lower-molecular-weight products. The differences from one solid acid catalyst to another evidently reflect their different activities, and presumably their different acid strengths.

The activity of the promoted sulfated zirconia catalyst is higher than those of the other solid acid catalysts. Our results show that at 100°C, conversions as high as approximately 60% were observed at a space velocity of 9×10^{-8} mol/(g of catalyst · s). For comparison, the equilibrium conversion in the isomerization reaction was approximately 72%. The reactivity of n-butane is lower than that of higher-molecular-weight paraffins, and the observation of its conversion in the presence of the promoted sulfated zirconia at low temperatures confirms the identification of this catalyst as a superacid (2, 9).

Hsu et al. (2) reported the first characterization of the promoted sulfated zirconia catalyst, investigating n-butane isomerization under approximately the same conditions as ours, but with a higher feed n-butane partial pressure (e.g., 0.58 atm). These authors estimated rates of the isomerization reaction by extrapolating conversions to zero time on stream to approximate the performance of the fresh catalyst. Zarkalis (10) investigated a catalyst similar to that of Hsu et al. and estimated activities of the fresh catalyst from the maximum rates measured as a function of time on stream (as in this work). In the work of Hsu et al. and that of Zarkalis, liquid n-butane was used as a feed which was vaporized before introduction into the flow reactor. In the work reported here, the butane was fed as a gas, and the n-butane partial pressures were typically 1-2 orders of magnitude lower than those used by Hsu et al. and Zarkalis. Thus, the rates reported by these workers are not directly comparable to the rates reported here. A rough comparison based on extrapolation of Zarkalis' data shows an order of magnitude agreement with our data. The catalytic reaction results reported here are also similar to the results of Jatia et al. (3), who did not include estimates of reaction rates. We conclude that our results are in

satisfactory agreement with the published results for iron- and manganese-promoted sulfated zirconia.

Reaction Network

The simplest product distribution observed in this work is consistent with a reaction network including only isomerization and stoichiometric disproportionation. At the lowest reaction temperature, 40°C, the C_3/C_5 molar ratio after the break-in period was nearly the stoichiometric ratio of unity for disproportionation, namely, 1.1 (Table A1), with an estimated experimental error of about ± 5%. The only other demonstration of a nearly stoichiometric paraffin disproportionation reaction was reported for *n*-butane conversion catalyzed by aluminum chloride supported on sulfonic acid resin at 100°C; the principal reaction was isomerization, which was much faster than disproportionation (5).

The observation of disproportionation products suggests that a C_8 intermediate might have formed. This same suggestion was made by Bearez *et al.* (5, 6, 11), who proposed a bimolecular pathway for *i*-butane conversions catalyzed by H-mordenite at about 350°C. According to their proposal, both the isomerization and disproportionation products could be formed from the C_8 intermediate. Reactions involving C_8 intermediates might be energetically favored over monomolecular isomerization because they would be expected to involve secondary and tertiary carbenium ions, whereas the monomolecular isomerization of *n*-butane requires the formation of a primary carbenium ion, which is highly unstable (4).

The product distributions at the higher temperatures show that the reaction network must in general be more complex than just isomerization and disproportionation. The observed C_3/C_5 molar ratios were always greater than 1, suggesting the further reaction of C_5 products, which undergo cracking more readily than smaller paraffins (12). The results are not sufficient to demonstrate the stoichiometry of the cracking; they

are consistent with the possible formation of C_9 intermediates. Cracking of a C_9 intermediate would give C_3 and C_6 products, among others, and trace amounts of C_6 products were observed. A C_9 intermediate would be formed only from secondary products of *n*-butane conversion, and therefore it is expected that the concentrations of these species were much lower than those of primary products. Thus the reaction network is approximated as follows:

Low temp. 25 to 225°C	Intermediate temp. 225 to 275°C	High temp. 350 to 450°C
isomerization + dispropor-tionation	disproportionation + isomerization + cracking	cracking + isomerization

The data show that the secondary reactions become less important in determining the product distribution as the temperature is decreased (Table A1). Thus, the results suggest that the highly active solid superacid could be a practically useful catalyst for isomerization, which would be accompanied by disproportionation. It could be advantageous to operate at low temperatures to minimize the secondary reactions and to favor the branched isomerization products.

Catalyst Break-in and Deactivation

The performance of the catalyst as a function of time on stream in the flow reactor is consistent with an induction period followed by a period of deactivation (Fig. A1). The deactivation is fast, and any application of the catalyst would be likely to require frequent regeneration. The rapid deactivation is consistent with the report of Hsu *et al.* (2), and those of Zarkalis (10) and Jatia *et al.* (3), who also observed the break-in period. The deactivation rate increased markedly with temperature, and deactivation was so fast at the higher temperatures (>100°C) that the induction period could no longer be observed. We infer that the catalysts used at these higher temperatures were substantially deactivated

before the first product samples were taken. Because of the rapid deactivation, the data seem to indicate that the conversion of n-butane decreases with increasing reaction temperature in the range of 150-225°C; however, these data (not shown) are disguised by the deactivation.

The rate of deactivation also increased with increasing n-butane partial pressure in the feed (Fig. A5). At low partial pressures of n-butane, the reaction rate increased slightly with temperature, whereas, at higher n-butane partial pressures, the measured rate appeared to decrease with increasing temperature. Again, the data were disguised by catalyst deactivation. At a given temperature, the maximum reaction rate (observed at the end of the break-in period) increased with inlet n-butane partial pressure in the range from 0.0025 to 0.01 atm, consistent with the order of reaction in n-butane being greater than zero.

Deactivated catalysts have been regenerated by treatment in air (2, 3, 13). The treatments lead to removal of carbonaceous deposits and may reoxidize sulfur on the surface (13, 14). Platinum has been incorporated into sulfated zirconia catalysts to reduce the rate of deactivation (15). Hydrogen in the feed may be dissociated on the Pt and spill over onto the acidic surface and react with precursors of carbonaceous deposits that cause deactivation. However, sulfated zirconia catalysts incorporating Pt that were tested for n-hexane conversion in the presence of H_2 at 6.5 atm and 200°C nevertheless underwent rapid deactivation (16).

The cause of the break-in period is not known. It appears unlikely that the break-in is a consequence of holdup in the reactor, because as inverse space velocity was varied in the range of 7.3×10^6 to 1.5×10^7 (g of catalyst · s)/mol of n-butane, the time of the maximum did not change. At the lowest inverse space velocity [3.7×10^6 (g of catalyst · s)/mol], the maximum was shifted to 1.75 h. This shift to a longer time on stream with a smaller inverse space velocity demonstrates that the maximum should not be attributed to a holdup of material in the catalyst bed, as the opposite trend would be expected if the

holdup were dominant. It is possible that the break-in may be an indication of a change in the chemical properties of the catalyst, such as the oxidation state of the sulfur or other components present in the promoted sulfated zirconia. The break-in period might also be related to the formation of an intermediate in the reaction pathway.

Conclusions

1. Iron- and manganese-promoted sulfated zirconia is a superacid that catalyzes n-butane isomerization and disproportionation at temperatures in the range of 40°C to 225°C.

2. The predominant reaction was isomerization with the rate of isomerization being 4.2×10^{-8} mol/(s · g of catalyst) with a feed n-butane partial pressure of 0.0025 atm at 75°C.

3. Under the same conditions the rate of formation of propane was 1.2×10^{-9} mol/(s · g of catalyst).

4. As the temperature increased, the selectivity for isomerization decreased and that for disproportionation increased.

5. Following an initial break-in period of about an hour, the catalyst underwent rapid deactivation.

6. The C_5 disproportionation products were partially converted to lower-molecular-weight products; the C_3/C_5 ratio increased with increasing temperature.

7. The solid superacid catalyst is potentially valuable for practical low-temperature paraffin isomerization accompanied by disproportionation of n-butane.

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Manganese, Iron, Cobalt, Nickel, and Zinc as Promoters of Sulfated Zirconia for *n*-Butane Isomerization

Abstract

First-row transition metals were tested in a flow reactor as promoters of sulfated zirconia for the isomerization of *n*-butane at 100°C and 0.005 atm *n*-butane partial pressure. The activity of each of the sulfated zirconia samples increased through a maximum and then decreased with time on stream. In order of increasing activity measured at the maximum, the effect of the promoters increased from right to left in the periodic table: zinc, nickel, cobalt, iron, and manganese. Iron and manganese increased the activity by 2-3 orders of magnitude. The causes of the promoter action are not elucidated; the promoters may play noncatalytic roles as initiators.

Introduction

Sulfated zirconia based materials have attracted interest as solid acids for low-temperature alkane isomerization. Iron- and manganese-promoted sulfated zirconia allows the conversion of *n*-butane even at room temperature [1-6]. The activity is 2-3 orders of magnitude greater than that of sulfated zirconia [1]. However, after a period of increasing conversion, the activity rapidly declines [2].

Metals other than iron and manganese are also promoters of sulfated zirconia [7-9], with the iron-manganese combination being the best yet reported among the first-row transition metals. Jatia et al. [5] found iron to be an order-of-magnitude better promoter than manganese, whereas Resasco et al. [10] found that manganese alone was not a promoter, although iron was. The combination was found by each group to be better than iron alone. Resasco et al. [10] suggested that manganese affects the dispersion of the iron

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species. Adeeva et al. [4] hypothesized that the isomerization of butane proceeds through a bimolecular mechanism involving C_8 intermediates formed from butenes and C_4 carbenium ions; the promoting effect of the transition metal oxides could thus involve their activity as butane dehydrogenation catalysts. The formation of C_8 intermediates was confirmed by results of ^{13}C tracer experiments showing a binomial ^{13}C distribution in the product. Wan et al. [6] suggested that butenes result from dehydrogenation of butane by redox active iron oxy sites.

There is little literature on the characterization of iron- and manganese-promoted sulfated zirconia [11, 12]. According to Coelho et al. [13], nickel showed a promoting effect comparable to that of iron and manganese; others have also observed promotion by nickel [14].

As the roles of the first-row transition metal promoters for *n*-butane isomerization are not well documented, our goals were to compare manganese, iron, cobalt, nickel, and zinc as promoters of sulfated zirconia for *n*-butane isomerization and to compare the promotion by iron and manganese separately with the promotion by the combination of the two.

Experimental methods

Sample preparation and surface area measurement

The materials used in the sample preparations were the following: sulfated zirconium hydroxide (3.4 wt% SO_3, Magnesium Elektron, Inc., XZO-682/01); iron(III) nitrate nonahydrate (Aldrich, 98%); manganese(II) nitrate (Aldrich, 98%); cobalt(II) nitrate hexahydrate (Aldrich, 99.999%); nickel(II) nitrate hexahydrate (Strem, 99.9985%); and zinc(II) nitrate hexahydrate (Sigma, 98%).

The composition of each sample was chosen to provide a basis for comparison with that of the previously reported iron- and manganese-promoted sulfated zirconia [1, 2, 15]; containing approximately 1.5 wt% iron and 0.5 wt% manganese, corresponding to

a total metal content of 360 (µmol of promoter metal)/(g of sample). All samples thus contained the same number of promoter atoms per unit mass, which corresponds to approximately 2 wt% of the promoter metal in each.

The sulfated zirconium hydroxide was dried for at least 24 h at 115°C. The samples were prepared from it by incipient wetness impregnation [2]. Each sample was calcined for 3 h at 650°C in a muffle furnace with the temperature ramped at a rate of 3 °C/min.

BET surface areas of the samples were measured with an Advanced Scientific Designs RXM-100 adsorption/reaction/characterization system after pretreatment at 100°C for 1 h in vacuum.

Catalytic testing

Each sample was tested in a once-through quartz flow reactor at atmospheric pressure with on-line product analysis by gas chromatography and flame ionization detection [2]. The powders were pretreated in N_2 flowing at 35 ml(NTP)/min. The temperature was ramped from room temperature to 450°C within 1 h and held at 450°C for 1.5 h. Each sample was cooled to reaction temperature in flowing N_2. The feed to the reactor was a mixture of 1 mol% *n*-butane in N_2 (Liquid Carbonic, <5 ppm isobutane) and N_2 (Liquid Carbonic, 99.999%). The following reaction conditions were used: temperature, 100°C; feed *n*-butane partial pressure, 0.005 atm (with the balance being N_2); pressure, 1 atm; sample mass, 1.0 g; total feed flow rate, 80 ml(NTP)/min. Iron-promoted and manganese-promoted sulfated zirconia were also tested at 50°C and 0.01 atm *n*-butane partial pressure.

Results

A list of the samples and their BET surface areas is given in Table B1 with the colors before and after calcination.

Table B1. Colors of the samples and BET surface areas after calcination.

Sample	Color		BET surface area, m^2/g
	prior to calcination	after calcination	
Sulfated zirconia (SZ)	white	white	100[a]
Manganese-promoted (MnSZ)	light pink	blue-gray	70
Iron-promoted (FeSZ)	ochre	ochre/rust	80
Cobalt-promoted (CoSZ)	pink/purple	pale purple	60
Nickel-promoted (NiSZ)	light green	pale purple/gray	65
Zinc-promoted (ZnSZ)	white	white	50

[a]Data from Magnesium Elektron, Inc.

Terms used to represent the sample performance include the following: Normalized conversion to a gas-phase product is defined as (concentration of individual gas-phase product x number of carbon atoms in individual product)/(4 x *n*-butane concentration in feed). The conversion to gas-phase products is taken to be the sum of the conversions to the individual products. Selectivity to a product is defined as (100 x number of moles of the gas-phase product)/(number of moles of all the gas-phase products).

The reproducibility of the conversions was typically ±15% for a particular sample. The performance was sensitive to the preparation conditions in ways that are not yet resolved, and the activity of a sample sometimes differed as much as twofold from one preparation to the next. The performance of some samples changed so rapidly during the first few minutes on stream that only imprecise data could be obtained to characterize the initial performance. Nonetheless, the differences in performance from one promoted sulfated zirconia to another are large enough to distinguish them clearly.
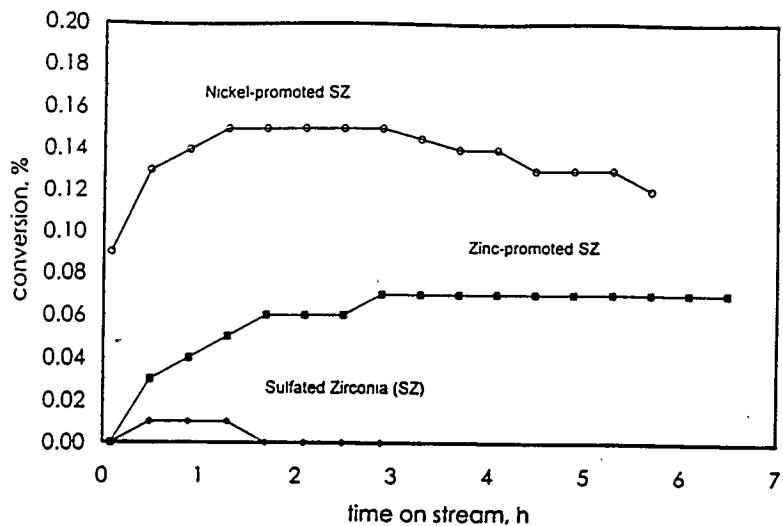
Fig. B1. *n*-Butane conversion in a flow reactor in the presence of sulfated zirconia (SZ) (sample mass, 1.5 g); zinc-promoted sulfated zirconia (1 g); and nickel-promoted sulfated zirconia (1 g). Temperature, 100°C; *n*-butane partial pressure, 0.005 atm; total feed flow rate, 80 ml (NTP)/min.

The conversion observed in the presence of unpromoted sulfated zirconia was low relative to that observed for the promoted samples (Fig. B1), and isobutane was the only gas-phase product observed at the low conversions investigated in these experiments. The presence of nickel in the sample led to only a modest increase in activity (Fig. B1), and again only isobutane was observed in the product stream; the maximum conversion was observed between 1 and 2.5 h on stream. Like nickel, zinc led to a modest increase in the activity (Fig. B1), with the gas-phase product being isobutane and the changes with time on stream being small.

The performance of cobalt-promoted sulfated zirconia was characterized by an initial steady increase in activity (Fig. B2), with the conversion reaching 1% after an induction period of about 20 h and then declining. Propane and pentanes were sometimes observed as side products, but the selectivity for isobutane was always >95%.

Manganese-promoted sulfated zirconia was characterized by a high initial activity, with conversions up to 15-20% at about 5 min on stream (Fig. B3). Besides isobutane,
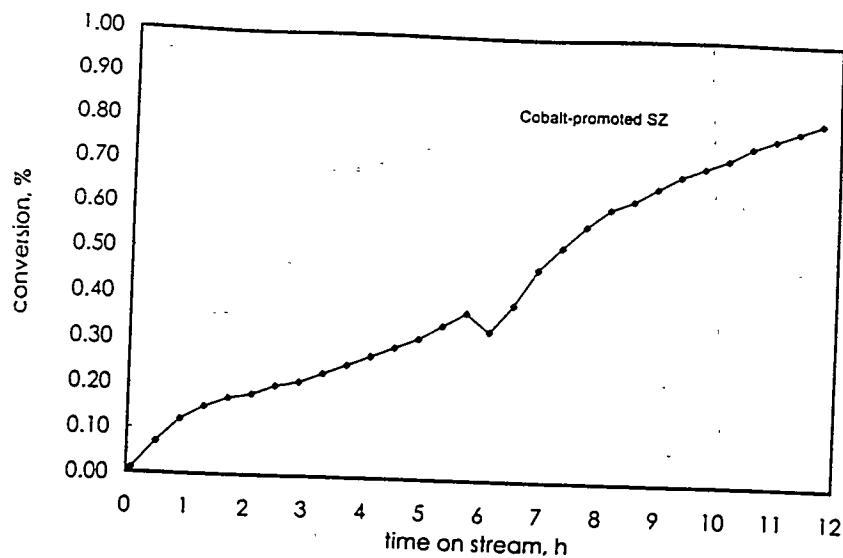
Fig. B2. *n*-Butane conversion in a flow reactor in the presence of cobalt-promoted sulfated zirconia (sample mass, 1 g). Temperature, 100°C; *n*-butane partial pressure, 0.005 atm; total feed flow rate, 80 ml (NTP)/min.
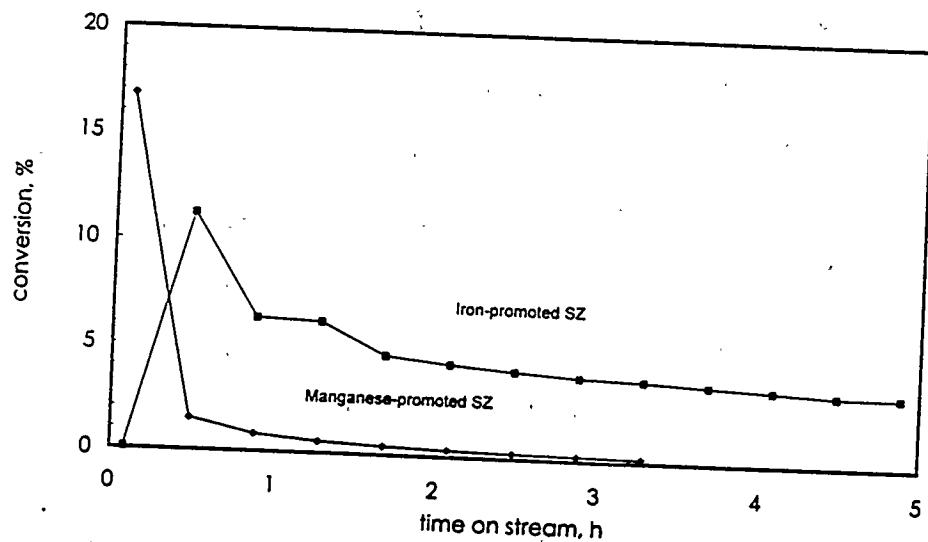
Fig. B3. *n*-Butane conversion in a flow reactor in the presence of iron-promoted sulfated zirconia (sample mass, 1 g) and manganese-promoted sulfated zirconia (1 g). Temperature, 100°C; *n*-butane partial pressure, 0.005 atm; total feed flow rate, 80 ml (NTP)/min.

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the predominant product (formed with a selectivity >80% after 5 min on stream and >95% after 30 min on stream), propane and pentanes were also observed, along with traces of methane after 5 min on stream. Within 30 min, the activity declined to conversions <2%. Propane and pentanes were observed for about 1 h, and at longer times on stream the selectivity for isobutane was 100%. At 50°C when the reaction was conducted at a 0.01 atm *n*-butane partial pressure, an induction period of about 1 h was observed, with a maximum conversion between 5 and 10% (Fig. B4). The relative decrease in activity after the maximum conversion was far less than that observed at 100°C. Propane and pentanes were observed in the product stream for several hours, but the selectivity to isobutane was always >95%.

The performance of the iron-promoted sulfated zirconia at 100°C was characterized by an induction period with a steeply increasing rate (Fig. B3). The conversion reached its maximum of about 10% within the first hour on stream. After the initial sharp decrease in activity, a slow decline in activity was observed. The products were isobutane (selectivity >85%), propane, and pentanes. The performance at 50°C (Fig. B4) was similar to that at 100°C.

Discussion

The data show that zinc and nickel have only modest effects as promoters; cobalt has a significant effect, giving more than an order of magnitude increase in activity; and iron and manganese increase the activity by two or three orders of magnitude. Even the largely deactivated iron- and manganese-promoted sulfated zirconia is much more active than the other promoted sulfated zirconias at their maximum activities. Notwithstanding the large differences in activity, the selectivities for the formation of the detectable products were similar for all investigated samples.
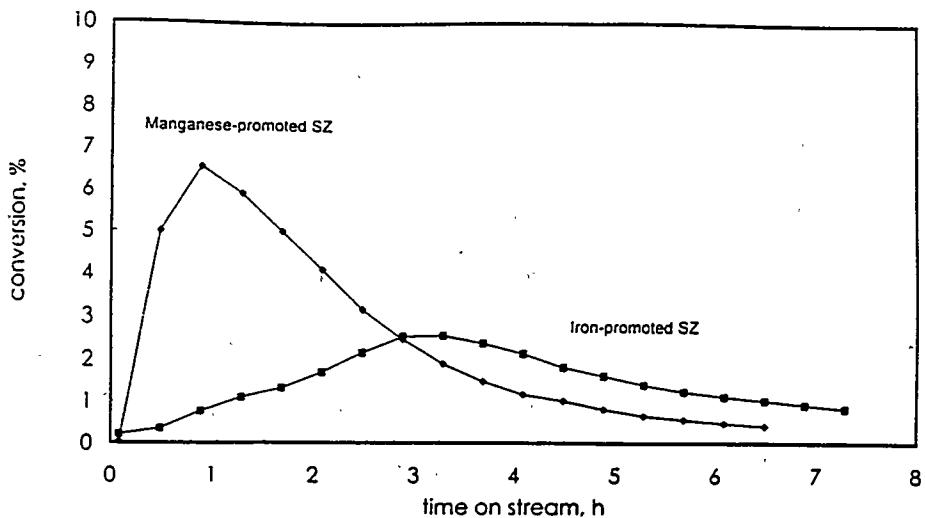
Fig. B4. *n*-Butane conversion in a flow reactor in the presence of iron-promoted sulfated zirconia (sample mass, 1 g) and manganese-promoted sulfated zirconia (1 g). Temperature, 50°C; *n*-butane partial pressure, 0.01 atm; total feed flow rate, 80 ml (NTP)/min.

The activities of the promoted sulfated zirconias do not correlate with the BET surface areas, and thus we infer that there are distinct chemical effects of the different promoters. However, the data are not sufficient to determine whether the promoters are differently dispersed in the various promoted sulfated zirconias.

Although the activities differ significantly from one promoted sulfated zirconia to another, the reaction profiles were all found to be characterized by an induction period of increasing conversion followed by a declining conversion. The more active the sample, the shorter was each stage of operation; the induction period characteristic of the manganese-promoted sulfated zirconia was observed only at 50°C (Fig. B4) and was presumably too short to observe at 100°C.

Thus our data do not agree with the result of Coelho et al. [13] and Resasco et al. [10] that manganese alone without iron is not a promoter; their reactions were conducted at 100°C and at much higher *n*-butane partial pressures than ours, i.e., 0.25 atm. Since the manganese-promoted sulfated zirconia is rapidly deactivated even at 0.005 atm *n*-butane partial pressure, we suggest that the conversion might have rapidly dropped to so low a value as to become immeasurable under Coelho's conditions.

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Nickel was found to enhance the catalytic activity for n-butane conversion only modestly, which also seemingly contradicts the results of Coelho et al. [13]. Their samples contained 8 wt% sulfur and up to 1% nickel, and their test conditions were different from ours, as they applied a much higher n-butane partial pressure, the mole fraction of n-butane in the feed being 0.25. The promotion effect of nickel observed by Coelho et al. [13] was roughly the same as what they observed for the iron-manganese combination (although they did not regard their data as a basis for quantitative comparisons of promoters). The difference between their results and ours suggests a strong dependence of promoter effects on reaction and/or sample preparation conditions; we reemphasize the importance of accounting for deactivation in comparisons of promoters. Thus although our results confirm that iron and manganese are the best promoters with regard to maximum activity known for sulfated zirconia, the conclusion should be restricted to catalysts containing about 2 wt% promoter and 4 wt% sulfate operated under conditions of our experiments.

The conversion profiles were used to estimate roughly the number of turnovers per promoter atom in each promoted catalyst by integration to determine the number of moles of n-butane that were converted to gas-phase products over the time on stream, assuming that each promoter atom might be a potential site (Table B2). This calculation does not account for promoter atoms that are inaccessible because of poor dispersion.

The number of turnovers per manganese promoter atom was about unity at 100°C, and the catalytic activity had declined to almost zero by the end of the experiment (Fig. B3). The comparable values shown for the other catalysts in Table B2 are less than unity (although the catalysts still had measurable activities when the experiments were terminated).

Table B2. Number of molecules *n*-butane converted per number of promoter atoms present in the sample integrated over time on stream

Sample	Temperature, °C	Time on stream, h	Mol of *n*-butane converted to gas-phase products per mol of promoter metal
MnSZ	50	6.5	0.96
FeSZ	50	7.5	0.64
MnSZ	100	3.5	0.15
FeSZ	100	5.0	0.67

Thus the data raise the question of whether first-row transition metal promoters may be playing noncatalytic roles. These metals might be initiators rather than catalysts, consistent with the proposal [4] that butane is dehydrogenated in association with the metal to give butene.

Conclusions

The first-row transition metals manganese, iron, cobalt, nickel, and zinc are all promoters of sulfated zirconia for the isomerization of *n*-butane in a flow reactor at 100°C and 0.005 atm *n*-butane partial pressure. Promoter contents of approximately 2 wt%, introduced by incipient wetness impregnation lead to increased reaction rates but barely affect the selectivity. Zinc and nickel have only modest effects as promoters; cobalt has a significant effect, giving more than an order of magnitude increase in activity; and iron and manganese increase the activity by two or three orders of magnitude. The promoter effects are short lived. The causes of the promoter action are not elucidated; the promoters may play noncatalytic roles as initiators.

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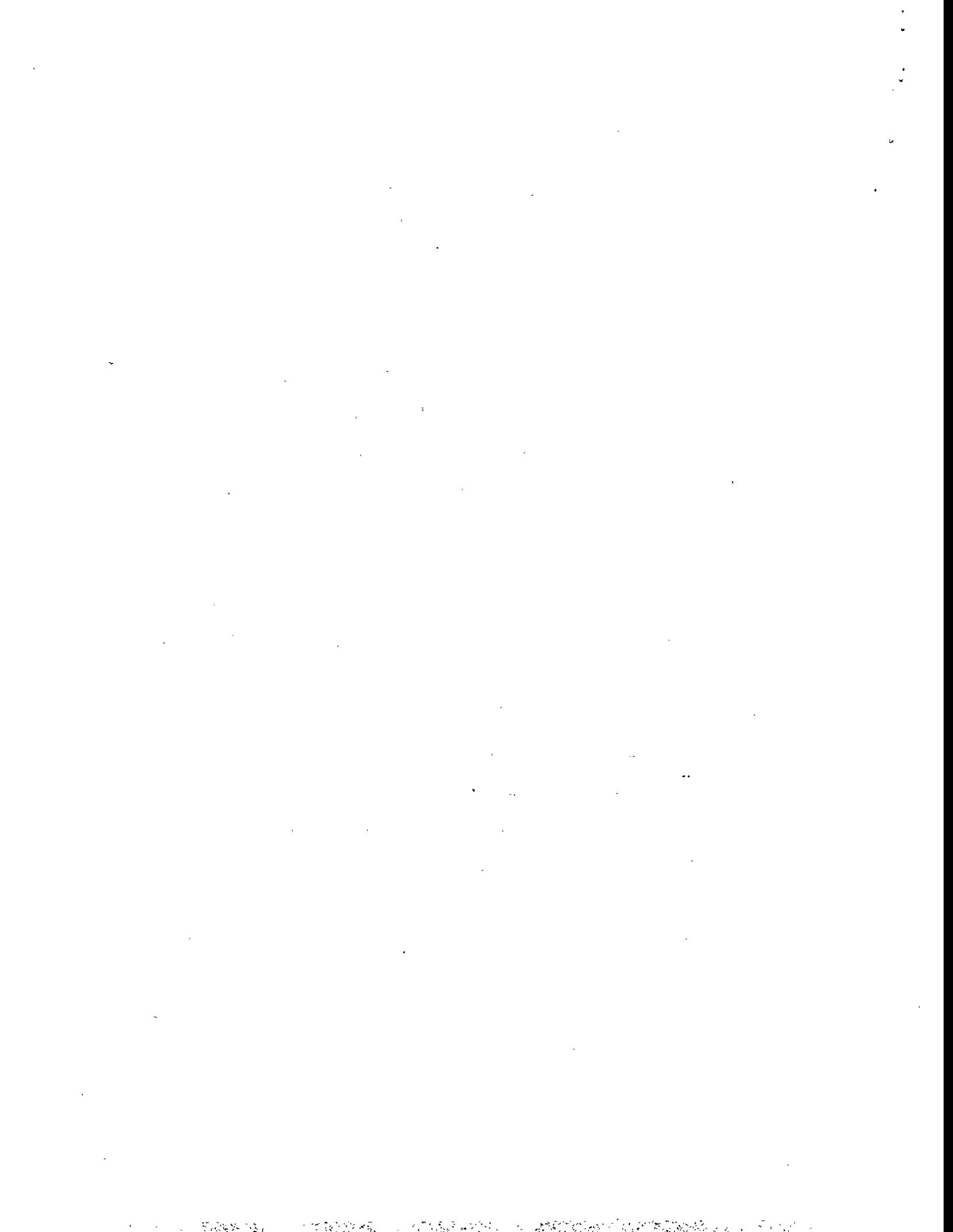
APPENDIX C

Propane Conversion in the Presence of Iron- and Manganese-Promoted Sulfated Zirconia: Evidence of Olah Carbocation Chemistry

Abstract

Solid acid catalysts, namely, sulfated zirconia, iron- and manganese-promoted sulfated zirconia, and USY zeolite, were tested for conversion of propane at 1 atm, 200-450°C, and propane partial pressures in the range of 0.01-0.05 atm. Both promoted and unpromoted sulfated zirconia were found to be active for conversion of propane into butanes, pentanes, methane, ethane, ethylene, and propylene in the temperature range of 200-350°C, but catalyst deactivation was rapid. At the higher temperatures, only cracking and dehydrogenation products were observed. In contrast to the zirconia-supported catalysts, USY zeolite was observed to convert propane (into propylene, methane, and ethylene) only at temperatures ^{3}400°C. The initial (5 min on stream) rates of propane conversion in the presence of iron- and manganese-promoted sulfated zirconia, sulfated zirconia, and USY zeolite at 450°C and 0.01 atm propane partial pressure were 3.3 x 10^{-8}, 0.3 x 10^{-8}, and 0.06 x 10^{-8} mol/(s · g), respectively. The product distributions in the temperature range 200-450°C are those of acid-base catalysis, being similar to what has been observed in superacid solution chemistry at temperatures <0°C. If propane conversion at 450°C can be considered as a probe of acid strength of the catalyst, then the activity comparison suggests that the promoted sulfated zirconia is a stronger acid than sulfated zirconia, which is a stronger acid than USY zeolite.

Introduction

Solid acids at high temperatures catalyze the conversion of propane into both higher- and lower-molecular-weight products, namely H_2, paraffins, olefins, and aromatics. The zeolite HZSM-5 at temperatures >350°C catalyzes propane cracking and dehydrogenation (1-3). About half of the converted propane was transformed into C_4 and C_5 paraffins in the presence of this catalyst at 450°C; the selectivity for these paraffins decreased with increasing temperature as more aromatics were formed (1). Kwak *et al.* (2) observed that methane and ethylene were produced in equimolar amounts in the limit of zero conversion of propane at 530°C, consistent with cracking proceeding through a protonated propane intermediate and in agreement with Olah superacid solution chemistry whereby the liquid acid protonates the paraffin (4-6).

Very strong solid acids activate propane at temperatures <200°C (7, 8). In the presence of SbF_5 supported on SiO_2-Al_2O_3, propane was converted into methane (the principal product) and ethane in a recirculation reactor at room temperature (7). Sulfated zirconia incorporating dispersed Pt catalyzed the formation of methane, ethane, butanes, and traces of pentanes in a pulse reactor at 150°C (8).

Similarly, propane was converted in the presence of iron- and manganese-promoted sulfated zirconia; butanes were the predominant products along with pentanes and methane at 200°C (9). These results indicate that cracking of propane in the presence of very strong acids occurs at temperatures much lower than those used conventionally for paraffin cracking. The product distribution data are qualitatively in agreement with superacid chemistry, suggesting that the reactions are initiated by protonation of propane to form carbonium ions which collapse into methane and ethyl cations or into H_2 and *s*-propyl cations, followed by secondary reactions of the carbocations with propane.

Sulfated zirconia and related catalysts have drawn attention because of their extraordinarily high activities for paraffin isomerization and the prospect that they might be useful for isomerization of *n*-butane into isobutane at low temperatures, whereby thermodynamics favors the valuable branched product. Iron- and manganese-promoted

sulfated zirconia catalyzes this reaction two to three orders of magnitude faster than sulfated zirconia at 28°C (10), but the roles of the iron and manganese are still not clarified.

Notwithstanding the high activity of the promoted sulfated zirconia for butane isomerization at temperatures <100°C, it has been demonstrated that the rates of *n*-butane cracking and neopentane cracking at 5 min time on stream catalyzed by iron- and manganese-promoted sulfated zirconia at 450°C are not much higher than those of the respective reactions catalyzed by unpromoted sulfated zirconia and zeolites (11, 12).

Here we extend the investigation of the promoted sulfated zirconia to a less reactive paraffin, propane. The goals of this research were to compare the catalytic properties of iron- and manganese-promoted sulfated zirconia with those of unpromoted sulfated zirconia and USY zeolite for propane conversion over a wide temperature range.

Experimental

Catalysts

Unpromoted sulfated zirconia was prepared by calcination of sulfated zirconium hydroxide (Magnesium Elektron, Inc.) at 500°C in a quartz tube with once-through flow. Rust-colored promoted sulfated zirconia containing approximately 1 wt% Fe, 0.5 wt% Mn, and 1.8 wt% sulfur was prepared from sulfated zirconium hydroxide, as described elsewhere (13). The BET surface areas of the unpromoted and promoted sulfated zirconia were 100 and 90 m^2/g respectively (as measured by Magnesium Elektron, Inc.). USY zeolite (Si/Al atomic ratio 8.9, surface area 800 m^2/g, determined by the Davison Division of W. R. Grace and Co.) was supplied by W. R. Grace and Co..

The pore size distribution measurements of the zirconia-supported catalysts were conducted with an RXM-100 instrument (Advanced Scientific Designs, Inc.). Nitrogen adsorption at liquid nitrogen temperature was used to make the measurements. Data were analyzed with the BJH method. Both the unpromoted and promoted sulfated zirconia

were found to have a pore volume of roughly 0.2 mL(NTP)/g. The pore radius for these two catalysts was determined to be in the range of 10-100 Å; the average pore radius of each sample was about 20 Å.

Catalytic Reaction Experiments

The catalyst pretreatment and experimental equipment are described elsewhere (12). Gas mixtures were fed to a once-through plug flow reactor containing the catalyst powder. The feed stream contained propane, either 1 mol% (containing 0.002 mol% ethane, Liquid Carbonic) or 5 mol% (containing 0.01 mol% ethane and traces of butanes, Matheson) in N_2 carrier gas. The 5 mol% propane stream was also diluted with N_2 to yield a 2.5 mol% feed. The reaction conditions were as follows: temperature, 200-450°C; pressure, 1 atm; mass of catalyst, 0.05-2.0 g; inverse space velocity, $(0.1-10) \times 10^6$ (g · s)/(mol of propane fed); propane partial pressure, 0.01, 0025, or 0.05 atm; and run length, 4 h to 16 days. Most experiments were done with an inverse space velocity of 1×10^6 (g · s)/(mol of propane fed).

Thermogravimetric Analysis

Thermogravimetric analysis (TGA) of some used catalysts was carried out with a Du Pont 951 TGA instrument. The experiments were done with a sweep gas of air at a flow rate of 100 mL(NTP)/min, with the sample temperature ramped from room temperature to 500°C at a rate of 20°C/min; a typical sample mass was 20 mg.

Results

Definitions used in Data Analysis

Propane conversion and selectivity are defined as follows (9): normalized conversion of propane to each of the individual gas-phase products (containing n carbon atoms) is defined as (n x number of moles of product)/(3 x number of moles of propane

fed); normalized selectivity for formation of an individual product is defined as (normalized conversion to gas-phase product)/(propane conversion to gas-phase products). Propane conversion is defined as the sum of the individual gas-phase product conversions.

Catalytic Activities

If it is (arbitrarily) assumed that the number of active sites is equal to the number of sulfate groups on the promoted sulfated zirconia, then the number of turnovers to gas phase products per site calculated from the data at temperatures >350°C was >1 after 8 h of operation in the flow reactor. However, to achieve one turnover per site at 250°C, the reaction experiment had to be continued for 16 days. The number of turnovers per site was about 0.1 at 200°C after 5 days of operation. The data taken at temperatures <350°C therefore could represent noncatalytic reactions. In the temperature range of 350-450°C, the reactions were catalytic.

At a propane partial pressure of 0.05 atm, both the unpromoted sulfated zirconia and the iron- and manganese-promoted sulfated zirconia were active for propane conversion at temperatures ³200°C. In contrast, the lowest temperature at which conversion was observed for USY zeolite was 400°C. The gas-phase products formed from propane in the presence of either promoted or unpromoted sulfated zirconia at 200°C were methane, butanes (the predominant product), and pentanes. The conversion of propane at 200°C increased with time on stream for the promoted sulfated zirconia, followed by a period of declining conversion (Fig. C1). In contrast, the conversion in the presence of the unpromoted sulfated zirconia remained approximately constant during the first 4 h of operation in the flow reactor (Fig. C1).

In the temperature range 250-350°C, ethane, ethylene, and propylene were observed as products in addition to those stated above. The propane conversion to gas-
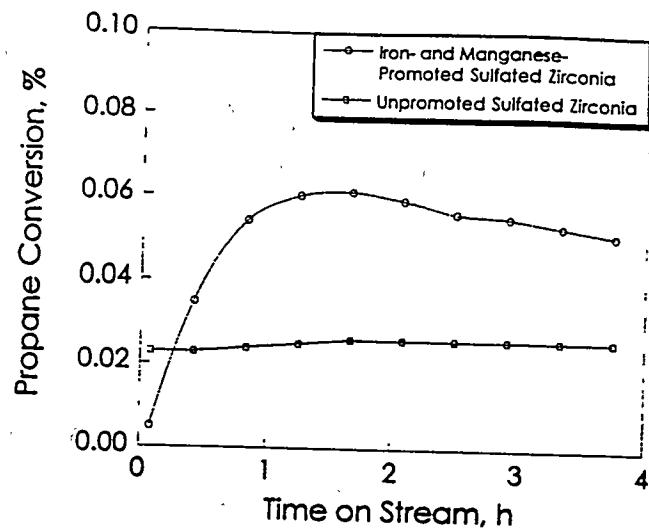
Fig. C1. Conversion of propane to gas-phase products at 200°C in the presence of iron- and manganese-promoted sulfated zirconia and unpromoted sulfated zirconia. Feed propane partial pressure, 0.05 atm; total feed flow rate, 40 mL(NTP)/min; catalyst mass, 2.0 g.

phase products declined with time on stream. The selectivities for formation of butanes and pentanes decreased with increasing temperature at a given conversion. Butanes and pentanes were not observed at temperatures >350°C.

At 450°C, the initial (5 min on stream) activity measured by the conversion observed for the promoted sulfated zirconia was an order of magnitude greater than that observed for the unpromoted sulfated zirconia and two orders of magnitude greater than that observed for USY zeolite.

Product Distributions

The conversion (represented as the highest observed as a function of time on stream in each experiment) and selectivity at 200, 350, and 450°C are shown in Tables C1, C2, and C3, respectively; data are presented for the unpromoted sulfated zirconia, the promoted sulfated zirconia, and USY zeolite. At 200 and at 350°C, the activity of the

Table C1. Comparison of activity[a] and selectivity for propane reaction[b] at 200°C in the presence of Fe- and Mn-promoted sulfated zirconia, and unpromoted sulfated zirconia.

Catalyst	Fe- and Mn-promoted sulfated zirconia	Sulfated zirconia
	Propane conversion, %	
	0.06 ± 0.01	0.03 ± 0.01
	Normalized selectivity, %	
Product:		
methane	2.4	6.6
isobutane	56.4	51.6
n-butane	34.6	31.1
isopentane	6.6	10.7

[a]The data were taken at the highest conversion of each run; the times on stream were 1.5 h for Fe- and Mn-promoted sulfated zirconia and 3 h for unpromoted sulfated zirconia, respectively.

[b]Mass of catalyst, 2 g; feed propane partial pressure, 0.05 atm; total feed flow rate, 40 mL(NTP)/min.

Table C2. Comparison of initial[a] activity and selectivity for propane reaction[b] at 350°C in the presence of Fe- and Mn-promoted sulfated zirconia, and unpromoted sulfated zirconia.

Catalyst	Fe- and Mn-promoted sulfated zirconia	Sulfated zirconia
	Propane conversion, %	
	0.75 ± 0.05	0.35 ± 0.05
	Normalized selectivity, %	
Product:		
methane	43.2	48.3
ethane	4.3	2.6
ethylene	43.7	36.1
propylene	8.2	12.4
isobutane	0	0
n-butane	0.6	0.6

[a]The data were taken at 5 min on stream.

[b]Mass of catalyst, 1 g; feed propane partial pressure, 0.01 atm; total feed flow rate, 40 mL(NTP)/min.

Table C3.   Comparison of initial[a] activity and selectivity for propane reaction[b] at
450°C in the presence of Fe- and Mn-promoted sulfated zirconia, and
unpromoted sulfated zirconia, and USY-zeolite.

Catalyst	Fe- and Mn-promoted sulfated zirconia	Sulfated zirconia	USY zeolite
	Propane conversion, %		
	6.2 ± 0.2	0.56 ± 0.02	0.11 ± 0.02
	Normalized selectivity, %		
Product:			
methane	44.8	50.9	9.8
ethane	3.2	0	0
ethylene	48.8	36.6	22.3
propylene	3.2	12.5	67.9

[a]The data were taken at 5 min on stream.

[b]Mass of catalyst, 1 g; feed propane partial pressure, 0.01 atm; total feed flow rate,
80 mL(NTP)/min for Fe- and Mn-promoted sulfated zirconia, 40 mL(NTP)/min
for USY zeolite.

promoted sulfated zirconia was about twice that of the unpromoted sulfated zirconia, as measured by the conversions (Tables C1 and C2); the product distributions were about the same for the two catalysts. The principal products observed for the two zirconia-supported catalysts (conversion >0.3%) were methane and ethylene at 350 and at 450°C, whereas more than half of the propane converted in the presence of USY zeolite gave propylene at 450°C.

The normalized selectivities for the formation of methane, ethane, ethylene, and propylene as a function of time on stream for the promoted sulfated zirconia at 450°C are shown in Fig. C2. Methane and ethylene were the principal products at the shorter times on stream (<1 h), and the normalized selectivity to propylene increased to more than 90% after 3 h on stream; similar behavior was observed for the unpromoted sulfated zirconia. The product distribution observed for USY zeolite at 450°C did not vary substantially during the course of reaction; the normalized selectivity for the formation of propylene was always >60%.

The molar ratio of methane to ethylene in the gas-phase products for reaction in the presence of iron- and manganese-promoted sulfated zirconia at 250, 350, and 450°C

is shown as a function of conversion in Fig. C3. This ratio exceeded unity at all conversions but approached this value in the limit of zero conversion at each of the three temperatures. The slopes of the plots of this ratio versus propane conversion decreased with increasing temperature. The ratio was >3 when the propane conversion exceeded 0.1% at 250°C, but the ratio was <2 at 450°C, although the conversion was >6%.

The molar ratio of methane to propylene is compared in Fig. C4 with the ratio of methane to ethylene in the gas-phase products for reaction in the presence of iron- and manganese-promoted sulfated zirconia at 350°C. As the molar ratio of methane to ethylene approached 1 for conversions <0.2%, the molar ratio of methane to propylene approached a value of 2. At higher conversions, both ratios exceeded these limiting values.

The only hydrocarbon products observed in the gas phase at 350°C (5 min on stream) in the presence of the promoted sulfated zirconia at conversions <0.2% were methane, ethylene, and propylene; the normalized selectivities for the formation of these products were 22, 45, and 33%, respectively. However, ethane and butanes were also observed at propane conversions...

Carbonaceous Deposits

Because propane conversions were only a few percent at most, typically being about 0.3% at 250°C, the errors in the analysis for propane in the product stream were larger than the conversions, making impossible any realistic estimates of the selectivities for the formation of carbonaceous deposits from mass balance calculations. However, some information about the carbonaceous deposits was determined from the TGA data,
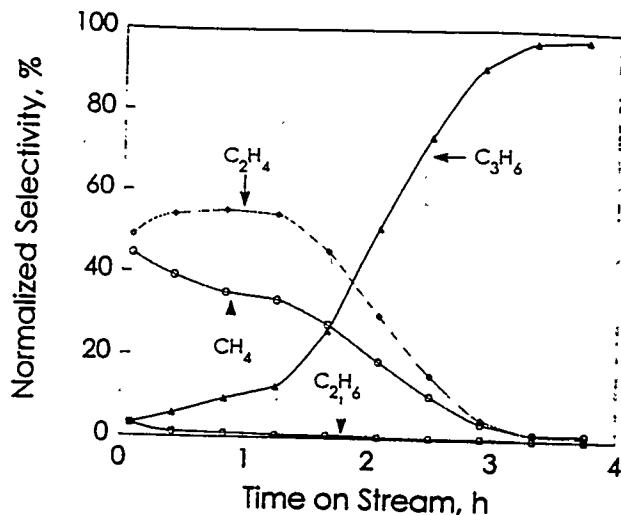
Fig. C2. Normalized selectivity for propane conversion in the presence of iron- and manganese-promoted sulfated zirconia at 450°C. Feed propane partial pressure, 0.01 atm; total feed flow rate, 80 mL(NTP)/min; catalyst mass, 1.0 g. The initial conversion after 5 min on stream was 6.6% and dropped to approximately 1% after 2 h of operation.

which show that, after operating iron- and manganese-supported sulfated zirconia for 16 days on stream at a temperature of 250°C, a propane partial pressure of 0.05 atm, and a space velocity of 1×10^{-6} mol/(s · g), the amount of carbonaceous deposit burned off at temperatures up to 500°C was about 2 wt% of the used promoted sulfated zirconia. Peaks appeared in the TGA patterns at about 200 and about 400°C; these were preceded by a water peak centered at about 90-100°C. However, these data are not sufficiently accurate to give a good estimate of the selectivity for carbonaceous deposit formation.

Kinetics

In an earlier report (9), we demonstrated that propane conversions < 0.5% were approximately differential, determining reaction rates directly. Because propane conversions were typically only a few percent or less in the present investigation, we assumed that they were also differential and used them to estimate rates. For example,
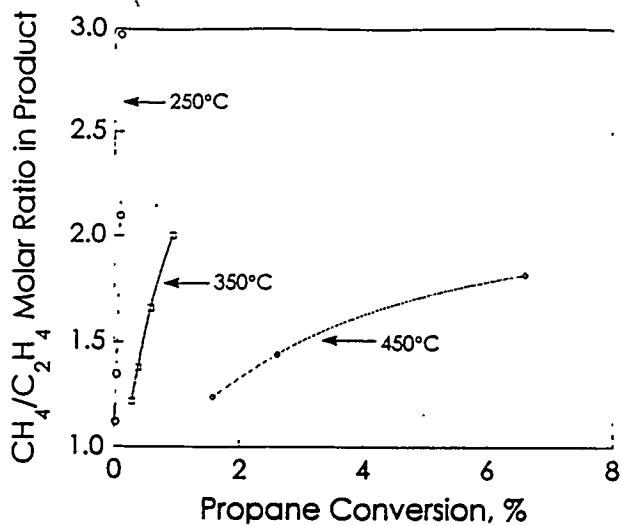
Fig. C3. Methane to ethylene molar ratio in the product of propane conversion in the presence of iron- and manganese-promoted sulfated zirconia at 250, 350, and 450°C. Feed partial pressure, 0.01 atm; total feed flow rate, 40-80 mL(NTP)/min. Catalyst mass, 1.0-2.0 g.

the initial (5 min on stream) rate of propane conversion to gas-phase products catalyzed by iron- and manganese-promoted sulfated zirconia at 450°C and a propane partial pressure of 0.01 atm was estimated to be 3.3×10^{-8} mol/(s · g); that for the conversion catalyzed by sulfated zirconia under the same conditions was 0.30×10^{-8} mol/(s · g); and that for the conversion catalyzed by USY zeolite under the same conditions was 0.06×10^{-8} mol/(s · g).

Plots of the rate of propane conversion to gas phase products versus propane partial pressure on logarithmic coordinates for reaction at temperatures of 250 and 350°C in the presence of the promoted sulfated zirconia are shown in Fig. C5. The reaction order in propane and the rate constant for the total conversion were determined to be 1.6 $\pm$ 0.1 and 2.3×10^{-7} mol/(s · g · atm$^{1.6}$), respectively, at 250°C, and 1.4 $\pm$ 0.1 and 1.7×10^{-6} mol/(s · g · atm$^{1.4}$), respectively, at 350°C. At a propane partial pressure of 0.01 atm, the temperature dependence of the rate (Fig. C6) indicates an apparent activation energy of 15 $\pm$ 1 kcal/mol.
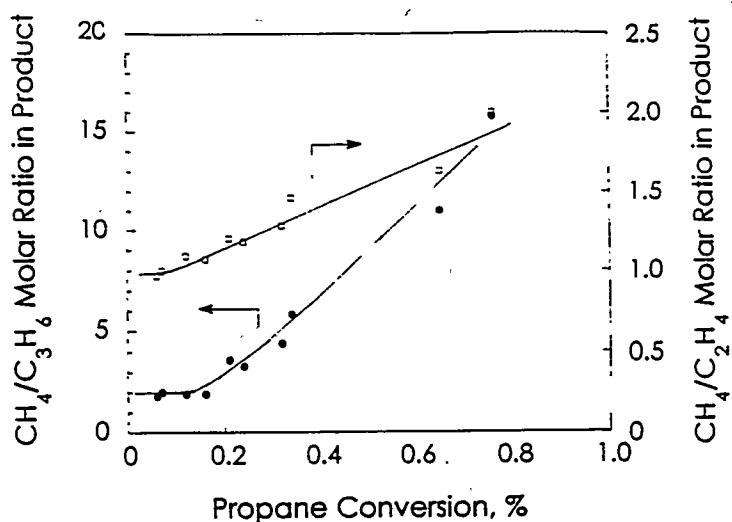
Fig. C4. Methane to propylene and methane to ethylene molar ratios in the products of propane conversion in the presence of iron- and manganese-promoted sulfated zirconia at 350°C. Feed partial pressure, 0.01 atm; total feed flow rate, 80 mL(NTP)/min; catalyst mass, 0.05-0.5 g.

Discussion

High-temperature (350-450°C) Reactions

At 350-450°C, the observed conversions of propane in the presence of the promoted sulfated zirconia were as high as 6%, and the reaction was clearly catalytic and not just stoichiometric. At these high temperatures, cracking and dehydrogenation are thermodynamically favorable. These reactions account for the observed gas-phase products, namely, methane, ethane, ethylene, and propylene. The products formed in the presence of unpromoted sulfated zirconia and USY zeolite at these temperatures are also consistent with cracking and dehydrogenation reactions.

The molar ratio of methane to ethylene, which approached 1 in the limit of zero conversion in the temperature range of 250-450°C when the conversion was carried out in the presence of promoted sulfated zirconia (Fig. C3), is consistent with a mechanism whereby propane is protonated by the catalyst to give penta-coordinated carbonium ions
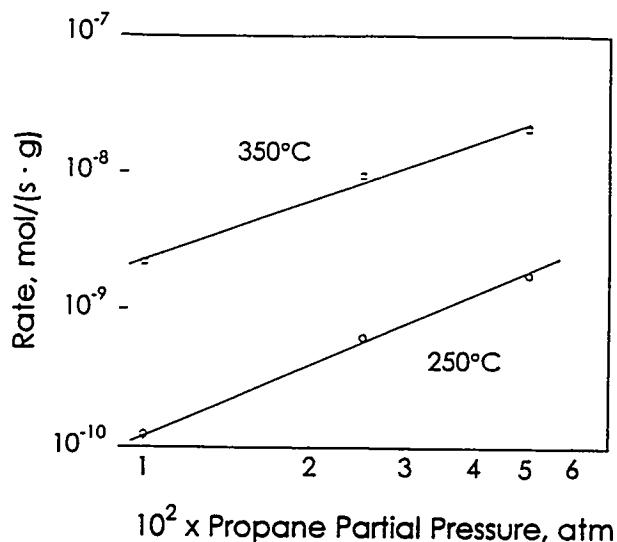
Fig. C5. Rate of propane conversion to gas-phase products in the presence of iron- and manganese-promoted sulfated zirconia. Total feed flow rate, 40 mL(NTP)/min; catalyst mass, 1.0 g.

(presumably transition states) that collapse into methane and ethyl cations (or into H_2 and s-propyl cations). According to this interpretation, the primary cracking products methane and ethylene (resulting from the carbonium ions) would form in equimolar amounts, consistent with the observations. Likewise, H_2 and propylene would be expected to form in equimolar amounts at the lowest conversions, but no attempts were made to analyze for H_2 during reactions. However, a few qualitative experiments with a thermal conductivity detector in the gas chromatograph showed the presence of H_2 as a reaction product.

The molar ratio of methane to propylene (a measure of the ratio of the rate of cracking to the rate of dehydrogenation) is approximately 2 at conversions <0.2% (Fig. C4), consistent with the distribution of cracking and dehydrogenation products formed from the carbonium ions, as illustrated in Fig. C7. In Fig. C7, reaction 1 represents the formation of the carbonium ions, and the dotted lines indicate schematically the patterns of collapse of the carbonium ions; there are three possibilities for cleavage, two of them

68
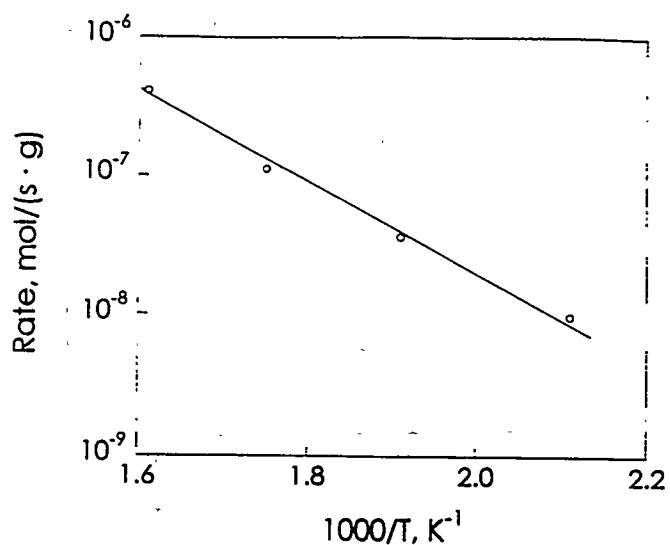
Fig. C6. Arrhenius plot for propane conversion to gas-phase products in the presence of iron- and manganese-promoted sulfated zirconia. Feed propane partial pressure, 0.1 atm; total feed flow rate, 40 mL(NTP)/min; catalyst mass, 1.0 g.

(reaction 2) leading to methane and ethyl cations, and one of them (reaction 3) leading to H_2 and s-propyl cations. The product distribution observed by Krannila *et al.* (14) for *n*-butane cracking catalyzed by HZSM-5 at 496°C suggests that each of the cleavage pathways indicated by the dotted lines in Fig. C7 is equally probable, but theoretical results (15) suggest that the relative rates of these two reactions could be temperature dependent. The data observed in this work for propane conversion catalyzed by the promoted sulfated zirconia are consistent with a simple statistical cleavage of the carbonium ions.

Although it was almost impossible to obtain data that allow a comparison of the catalysts used in this work at the same conversion and the same degree of deactivation, an approximate comparison can be made on the basis of data obtained initially (5 min on stream) and at particular conversions (although they represent reaction at different
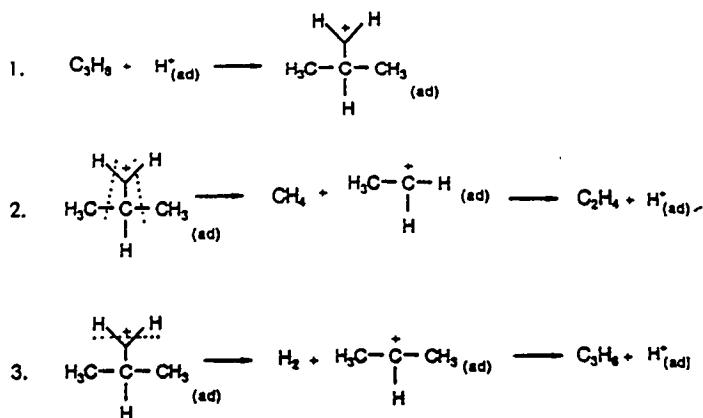
Fig. C7. Some steps postulated to occur in propane conversion in the presence of promoted sulfated zirconia, unpromoted sulfated zirconia, or USY-zeolite. The dotted lines indicate schematically the different pathways for collapse of carbonium ions. The carbonium ions can presumably be formed either by protonation of C-C bonds or C-H bonds, leading to reactions 2 and 3, respectively (although the schematic depictions do not distinguish between the two possibilities).

temperatures and space velocities). For example, at a propane conversion of 0.1%, the gas-phase products observed with the promoted sulfated zirconia (at 350°C) and USY zeolite (at 450°C) were methane, ethylene, and propylene only. The molar ratio of methane to ethylene was found to be approximately one for each catalyst; thus these data indicate a consistency from one catalyst to the other and a consistency with the chemistry shown in Fig. C7. However, the molar ratio of methane to propylene was found to be about 2 for the promoted catalyst (Fig. C4) and 0.5 for the zeolite (Table C3); thus, some of the product distribution data indicate differences between the catalysts.

Propane dehydrogenation is catalyzed not only by acids such as the zeolite HZSM-5 (at temperatures > 400°C) (1-3, 16), but also by HZSM-5 containing a separate dehydrogenation function such as Pt (2, 17), Ga (1, 2, 18, 19), or Fe (20). The initial selectivity for the formation of propylene from propane at low conversions increased by a factor of 2 or more upon addition of these components to the zeolite (20, 21). By

extension, one might infer from results such as these that the iron and/or manganese in the sulfated zirconia provided a dehydrogenation function in the catalyst; such a suggestion was made by Adeeva *et al.* (22).

If the suggestion of bifunctional catalysis were correct, then the initial selectivity for propylene formation observed with the promoted sulfated zirconia would be expected to be higher than that observed for the unpromoted sulfated zirconia or the zeolite at low conversions. In contrast to this expectation, the product distribution data show that the two zirconia-supported catalysts had roughly the same selectivity pattern over the whole range of investigated temperatures; the selectivity for formation of propylene observed for the promoted sulfated zirconia at 350°C (33%) was lower than that observed for USY zeolite at 450°C (68%) at a propane conversion of 0.1%. However, the activities observed for these two catalysts were significantly different from each other. Thus the matter of a possible dehydrogenation function associated with iron and manganese is not completely resolved; there is no evidence in the data presented here for a dehydrogenation function in the catalyst.

In the propane conversion catalyzed by iron- and manganese-promoted sulfated zirconia at 350°C, ethane was formed only at the shorter times on stream, when the conversions were >2%. Acid-catalyzed reactions of paraffins often include hydride transfer from paraffins to carbenium ions and/or oligomerization-cracking pathways (23, 24), giving paraffinic products. If ethane formed by hydride transfer, it would be expected at the high conversions but not necessarily at the low conversions, because the ethyl cations (formed in primary reactions, Fig. C7) give up protons readily to complete catalytic turnovers. These ethyl cations could then be converted into paraffins only in secondary reactions, which occur at higher conversion. Similarly, oligomerization-cracking cycles are also secondary processes, and they occur only when enough surface carbocations are formed on the catalyst surface. Thus the data are consistent with either of the above hypotheses.

At longer times on stream (greater than about 3 h), the promoted sulfated zirconia was partially deactivated, and propylene from dehydrogenation became the predominant product. It is not known why the selectivity changes during the course of reaction in the flow system. In contrast to the promoted sulfated zirconia, USY zeolite had roughly the same selectivity even after it had been operated for 4 h.

In summary, all the high-temperature reaction products are consistent with those expected for acid-catalyzed reactions. Thus the results are consistent with the hypothesis that the catalytic sites in the zirconia-supported catalysts are acidic; however, this statement does not rule out the possibility of another kind of catalytic site in these materials.

Low-temperature (200-250°C) Reactions

At the lower reaction temperatures (200-250°C), the observed conversions of propane to gas-phase products were low (<0.5%). The principal products after 1 h of operation were butanes, which implies that carbon-carbon bond forming reactions took place. Thus the data are consistent with the occurrence of reactions such as those that take place when propane is converted in a superacid solution, as reported by Olah *et al.* (6). Once the ethyl or *s*-propyl cations are formed (from the carbonium ions), they undergo further reactions with propane to form higher-molecular-weight hydrocarbons such as butanes and pentanes (6). Thus, the products of reaction of propane observed in this work are similar to those observed in the reaction of propane in superacid solutions (9). However, there are not enough data for a quantitative comparison of our results with those characterizing the solution reactions.

Mixtures of higher- (C_4 and C_5 aliphatic) and lower- (C_1 and C_2) molecular-weight products formed from propane have also been observed in a flow reactor with HZSM-5 catalyst, but at high temperatures, e.g., 450°C (1). Thus, the performance of the zirconia-supported catalysts at low temperatures (ca. 200-300°C) is comparable to that of

the zeolite HZSM-5 at high temperatures (ca. 450°C). Consistent with this comparison, USY zeolite was found to have negligible activity for propane conversion at temperatures <400°C under our experimental conditions. However, in contrast to the reported observations for HZSM-5 summarized in the introduction (1), methane, ethylene, and propylene (from cracking and dehydrogenation) were the only products observed in propane conversion catalyzed by USY zeolite at 450°C; no higher-molecular-weight products were observed.

Summary Comparison of Catalyst Performance for Various Reactants

A comparison of approximate rates of conversion of propane, *n*-butane, and neopentane catalyzed by promoted sulfated zirconia and zeolites is shown in Table C4. The data for the zeolites, which appear to be less strongly influenced by catalyst deactivation than the others, indicate that the reactivities of *n*-butane and neopentane at 450°C are about the same. Propane is two orders of magnitude less reactive than these compounds at 450°C. The data for promoted sulfated zirconia show that, in contrast to the reactivity pattern for the zeolites, propane is only one order of magnitude less reactive that *n*-butane or neopentane. The difference in the reactivity patterns from one catalyst to another may reflect different degrees of deactivation of the different catalysts. The zeolites underwent deactivation less rapidly than the promoted sulfated zirconia for reactions of *n*-butane and neopentane, and thus the data reported for the zeolites are more likely to represent intrinsic catalytic properties of fresh catalysts than those for the promoted sulfated zirconia.

The rates of catalyst deactivation were greater for the more strongly acidic promoted sulfated zirconia than for the less strongly acidic zeolites. The relatively slow deactivation of HZSM-5 is associated with the smallness of the pores (25). However, the different rates of deactivation of the catalysts may also be related to the catalyst acidities. It has been postulated (26) that the lifetimes of adsorbed carbocations or related

intermediates depend on the acid strength of the catalyst surface (and temperature); the stronger the acid (or the lower the temperature), the longer the lifetime. Thus the data are consistent with the hypothesis that deactivation is associated with blocking of strongly acidic surface sites once stable surface species such as t-butyl cations or structures equilibrated with them are formed during n-butane or neopentane reactions. These intermediates could then undergo oligomerization to form carbonaceous deposits. t-Butyl cations and related intermediates are expected to be less important for the reaction of propane at 450°C than for the reactions of n-butane or neopentane; thus deactivation of the promoted sulfated zirconia for propane conversion might be less severe than that for n-butane or neopentane conversion.

Table C4. Comparison of hydrocarbon reactivities in the presence of iron- and manganese-promoted sulfated zirconia and zeolites at 450°C.[a]

Reactant	Catalyst	$P_{reactant}$, atm	Approximate observed rate[b] of reaction, mol/(s · g)	Reaction rate[c] normalized to reactant partial pressure 0.01 atm, mol/(s · g)
n-butane	promoted sulfated zirconia	0.0025	1×10^{-7}	4×10^{-7}
neopentane	promoted sulfated zirconia	0.005	5×10^{-8}	1×10^{-7}
propane	promoted sulfated zirconia	0.01	3×10^{-8}	3×10^{-8}
n-butane	HZSM-5[d]	0.0025	1×10^{-8}	4×10^{-8}
neopentane	USY	0.005	6×10^{-9}	1×10^{-8}
propane	USY	0.01	6×10^{-10}	6×10^{-10}

[a]The data were taken at 5 min on stream.

[b]Rates of n-butane and neopentane reaction were calculated from the disappearance of the reactants, whereas rate of propane reaction was based upon the formation of gas-phase products only.

[c]Reaction rates were normalized to a reactant partial pressure 0.01 atm by assuming that orders of reaction in n-butane and in neopentane were 1.

[d]Values for n-butane conversion catalyzed by HZSM-5 were extrapolated from data of Krannila et al. (14).

It is also possible that because the reactivity of propane is less than the reactivities of *n*-butane and neopentane, the rate of catalyst deactivation would be less for propane conversion than for *n*-butane or neopentane conversion under similar experimental conditions.

The comparison of activities of the three catalysts for propane conversion stated in the Results section shows that the promoters increase the activity of the sulfated zirconia, which is more active than USY zeolite. Thus, if the propane conversion can be regarded as a reaction catalyzed by acidic groups alone, then the activity data imply that the acid strength decreases in the order promoted sulfated zirconia > sulfated zirconia > USY zeolite. However, as stated above, further work is needed to clarify the nature of the catalytic sites.

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APPENDIX D

Ethane conversion in the presence of Fe- and Mn-promoted sulfated ZrO$_2$: evidence of autocatalysis and oligocondensation chemistry

Abstract

Ethane reacts in the presence of Fe- and Mn-promoted sulfated ZrO$_2$ to form *n*-butane, ethylene, methane, and H$_2$ at temperatures ³ 200°C; the data indicate autocatalysis with carbocation intermediates as in superacid solution chemistry.

Light alkanes in liquid superacids react at temperatures 0°C, giving heavier hydrocarbons via carbenium ion and carbonium ion intermediates.[1] In the presence of Fe- and Mn-promoted sulfated zirconia, propane reacts similarly, being converted largely into butane at 200°C,[2] and *n*-butane is catalytically isomerized and disproportionated even at 25°C.[3, 4] The propane product distribution and the high catalytic activity for *n*-butane conversion suggest superacid chemistry.[1] Although Fe- and Mn-promoted sulfated zirconia was called a superacid,[5] the acid strength is still debated.[6,7] Our goal was to probe the acidic character of FMSZ (and, for comparison, acidic USY zeolite) by investigating its reactivity and catalytic activity with a relatively unreactive alkane (ethane).

Fe- and Mn-promoted sulfated zirconia,[4] containing approximately 1 wt% Fe, 0.5 wt% Mn, and 1.8 wt% S, was made by incipient wetness impregnation of sulfated Zr(OH)$_4$ with aqueous Fe(NO$_3$)$_3$ then aqueous Mn(NO$_3$)$_2$ and calcined in static air at 923 K. The BET surface area and pore volume were about 90 m^2/g and 0.2 mL(NTP)/g, respectively.

Ethane conversion was carried out in a once-through packed-bed flow reactor under the following conditions: temperature, 200-500°C; pressure, 101 kPa; ethane partial pressure, 5-20 kPa; mass Fe- and Mn-promoted sulfated zirconia, 0.5-1.5 g; feed

(ethane + N_2) flow rate, 10-80 mL(NTP)/min. The products were H_2, methane, ethylene, butane, and traces of aromatics; at 200°C they were predominantly n-butane and ethylene. n-Butane selectivity decreased from 30% (at 0.01% conversion) at 200°C to 10% (at 0.1% conversion) at 400 °C. In the temperature range 200-400°C, the conversion to n-butane, ethylene, and methane decreased with increasing time on stream. At temperatures > 400°C, the conversion into n-butane decreased monotonically with increasing time on stream, but the conversion to ethylene and to methane decreased and then increased with time on stream (suggesting autocatalysis), followed by another declining period (Fig. D1). The length of the first declining period for ethane conversion decreased with increasing temperature and ethane partial pressure. H_2 was observed only at temperatures >673 K; at 723 K, production of H_2 was characterized by a period of increasing conversion followed by a slow decline with time on stream.

At 450°C, 20 kPa ethane partial pressure, and 5.5¥10^{-6} mol/(s · g) space velocity, the number of ethane molecules converted/sulfate group was >1 after 18 h time on stream; ethane conversion was then catalytic. Catalysis was not demonstrated at lower temperatures. Initial ethane conversion rates were estimated by extrapolating conversions in the first declining period to zero time on stream. At 450°C and 20 kPa alkane partial pressure, the rate of ethane conversion in the presence of FMSZ [4¥10^{-8} mol/(s · g)] is lower than that of propane conversion [determined by extrapolating published data,[8] 4¥10^{-6} mol/(s · g)]. The products formed from ethane (or propane[2]) at 200°C are nearly the same as those reported[1] for reaction in superacid solution.

Adopting the analogy to superacid chemistry for the reactions in the presence of Fe- and Mn-promoted sulfated zirconia, we suggest reaction cycles whereby ethane is first protonated to form $C_2H_7^+$, which collapses to either H_2 and $C_2H_5^+$ or methane and CH_3^+ (Fig. D2A). Then $C_2H_5^+$ is deprotonated to give ethylene (CH_3^+ deprotonation is energetically unfavorable). The initial decrease in conversion with time on stream is
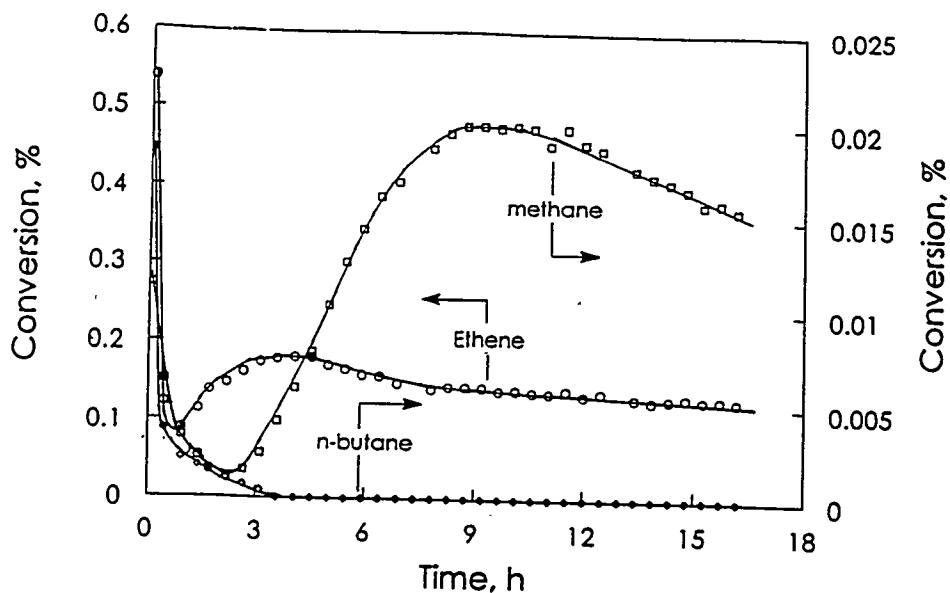
Fig. D1. Conversion of ethane to gas-phase hydrocarbons at 723 K in the presence of Fe- and Mn-promoted sulfated zirconia. Feed ethane partial pressure, 10 kPa; total feed flow rate, 40 mL(NTP)/min; mass of FMSZ, 1.0 g.

attributed to deactivation of acidic sites. Oligocondensation to give n-butane is inferred to proceed (Fig. D2B) as ethane combines with adsorbed $C_2H_5^+$ to form $C_4H_{11}^+$, which is deprotonated to give butane. Autocatalysis is postulated to set in as $C_2H_5^+$ and CH_3^+ (Fig. D2A) function as chain carriers (Fig. D2C). Thus, ethane is converted into ethylene, along with methane. The conversions to ethylene and to methane ultimately decrease with time on stream as the number of these chain carriers declines, e.g., because carbonaceous deposits form on Fe- and Mn-promoted sulfated zirconia.

This carbocation chemistry accounts for the ethane reactivity with Fe- and Mn-promoted sulfated zirconia, being consistent with Olah's results,[1] except that Olah did not observe autocatalysis, presumably because products were analyzed only following the batch reactor experiment. The behavior suggestive of autocatalysis in ethane conversion was not observed for propane[2] or n-butane.[4] The difference may be associated with the higher reactivities of propane and butane and the correspondingly shorter initial declining periods.

1. Initiation from the original acid site H^+

C_2H_6 (g)

$C_2H_7^+$ (ad) $C_2H_7^+$ (ad)

CH_4 (g) H^+ (ad) H_2 (g)

CH_3^+ (ad) $C_2H_5^+$ (ad)

CH_2 C_2H_4 (g)
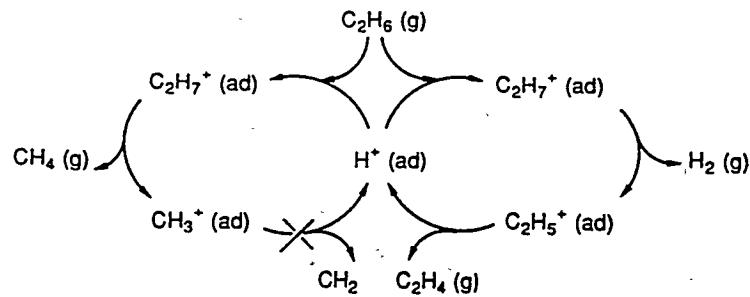
2. Autocatalysis with CH_3^+ and $C_2H_5^+$

CH_4 (g)

$C_2H_5^+$ (ad) C_2H_6 (g) $C_3H_9^+$ (ad)

C_2H_4 (g) $C_4H_{11}^+$ (ad) CH_3^+ (ad) H_2 (g)

$C_4H_9^+$ (ad) $C_3H_7^+$ (ad)

H_2 (g) C_2H_4 (g)

CH_4 (g)

3. Formation of butane

C_2H_6 (g) $C_2H_7^+$ (ad) H_2 (g)

H^+ (ad) $C_2H_5^+$ (ad)

$C_4H_{11}^+$ (ad)

C_4H_{10} (g) C_2H_6 (g)
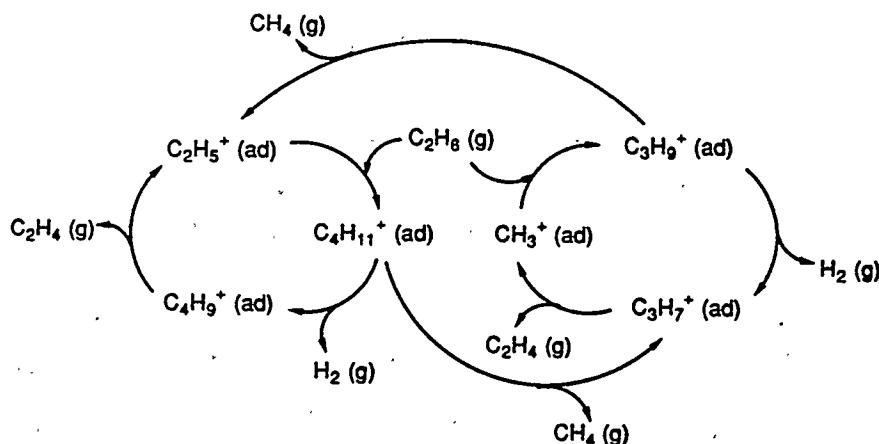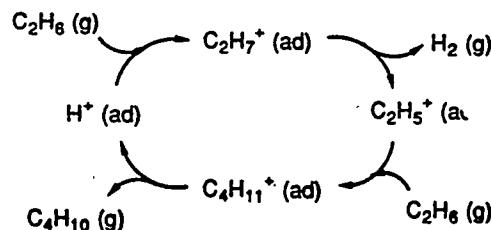
Fig. D2. Proposed reaction cycles for ethane conversion.

Presuming that the carbocation chemistry inferred here for ethane conversion in the presence of Fe- and Mn-promoted sulfated zirconia also pertains to *n*-butane isomerization catalyzed by Fe- and Mn-promoted sulfated zirconia, we suggest that the initial increase in conversion of butane in a flow reactor can be attributed to build-up of $C_4H_9^+$, which reacts with *n*-butane to form $C_8H_{19}^+$, which rearranges and splits into 2-methylpropane + $C_4H_9^+$. In contrast, Adeeva *et al.*[9] proposed a classical bifunctional

carbenium ion mechanism for *n*-butane isomerisation catalyzed by Fe- and Mn-promoted sulfated zirconia, whereby $C_4H_9^+$ reacts with butene (formed by butane dehydrogenation) to give $C_8H_{17}^+$, which undergoes b-scission to form $C_4H_9^+$ and 2-methyl-1-propene, with subsequent hydrogen transfer giving 2-methylpropane; correspondingly, Adeeva *et al.*[6] concluded that acidic sites in Fe- and Mn-promoted sulfated zirconia were only moderately strong.

The oligocondensation (giving butane) observed in the ethane reaction with Fe- and Mn-promoted sulfated zirconia was not observed with USY zeolite replacing Fe- and Mn-promoted sulfated zirconia, although ethylene was formed in comparable amounts with each material, provided that the space velocity was adjusted to give comparable ethane conversions. Furthermore, no evidence of autocatalysis was observed with USY zeolite; ethane conversion decreased monotonically with time on stream. Thus, in ethane conversion with USY zeolite, there is no evidence of the classical bifunctional carbenium ion mechanism for butane formation analogous to that postulated by Adeeva *et al.*[9] for butane isomerisation.

Consequently, we infer that butane formation from ethane in the presence of Fe- and Mn-promoted sulfated zirconia proceeds via a mechanism different from the classical bifunctional mechanism. Rather, carbocation chemistry analogous to that occurring in superacid solutions accounts for butane formation from ethane. The implication is that Fe- and Mn-promoted sulfated zirconia incorporates extremely strong acidic sites, consistent with Lin and Hsu's[5] postulate. To reconcile this inference with the observation[6] that the acidic groups in Fe- and Mn-promoted sulfated zirconia are only moderately strong, we postulate that the strongest acid groups constitute only a small minority that were not observed by Adeeva.

The inference that the ethane conversion in the presence of Fe- and Mn-promoted sulfated zirconia proceeds via routes analogous to carbocation superacid chemistry does

not exclude the possibility of butane isomerisation proceeding (perhaps simultaneously) via the classical carbenium ion route.

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APPENDIX E

Publications summarizing work done in this project

1. "Low-Temperature Superacid Catalysis: Reaction of *n*-Butane Catalyzed by Iron- and Manganese-Promoted Sulfated Zirconia, T. K. Cheung, J. L. d'Itri, and B. C. Gates, *Journal of Catalysis* **151**, 464 (1995).

2. "Cracking of *n*-Butane Catalyzed by Iron- and Manganese-promoted Sulfated Zirconia," T. K. Cheung, J. L. d'Itri, and B. C. Gates, *Journal of Catalysis*, **153**, 344 (1995).

3. "Propane Conversion in the Presence of Iron- and Manganese-Promoted Sulfated Zirconia: Evidence of Olah Superacid Chemistry," T.-K. Cheung, F. C. Lange, and B. C. Gates, *Catalysis Letters,* **34**, 351 (1995).

4. "Propane Conversion Catalyzed by Sulfated Zirconia, Iron- and Manganese-Promoted Sulfated Zirconia, and USY Zeolite," T.-K. Cheung, F. C. Lange, and B. C. Gates, *Journal of Catalysis*, **159**, 99 (1996).

5. "Manganese, Iron, Cobalt, Nickel, and Zinc as Promoters of Sulfated Zirconia for *n*-Butane Isomerization," F. C. Lange, T.-K. Cheung, and B. C. Gates, *Catalysis Letters*, **41**, 95 (1996).

6. "Ethane Conversion in the Presence of Fe- and Mn-Promoted Sulfated ZrO_2: Evidence of Autocatalysis and Oligocondensation Chemistry," T.-K. Cheung and B. C. Gates, *Chemical Communications*, **1996**, 1937.

7. "Solid-acid-catalyzed Alkane Cracking Mechanisms: Evidence from Reactions of Small Probe Molecules," F. C. Lange and B. C. Gates, *Topics in Catalysis*, in press, 1996.

8. "Hydrocarbon Reaction Mechanisms," D. S. Santilli and B. C. Gates, in *Handbook of Heterogeneous Catalysis* (G. Ertl, H. Knözinger, and J. Weitkamp, Eds.), VCH, in press.

9. "Protolytic Cracking of Low-Molecular-Weight Alkanes in the Presence of Fe- and Mn-promoted Sulfated Zirconia: Evidence of a Compensation Effect," T.-K. Cheung, F. C. Lange, J. L. d'Itri, and B. C. Gates, *Chemical Engineering Science*, submitted.