

ACTIVATION OF LIGHT ALKANES IN THE PRESENCE OF Fe- AND Mn-PROMOTED SULFATED ZIRCONIA

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ABSTRACT

A strong solid acid prepared by impregnation of sulfated zirconium hydroxide with iron nitrate and manganese nitrate was tested for conversion of *n*-butane, propane, and ethane in a packed bed flow reactor at 40–450°C. At 40°C, the predominant reaction of *n*-butane was catalytic isomerization (with disproportionation). Propane and ethane reacted at 200°C, each of these alkanes being converted predominantly into butanes. The occurrence of *n*-butane isomerization at temperatures <200°C suggests that the catalyst is strongly acidic, and the observations of butane formation from propane and from ethane are consistent with chemistry analogous to superacidic solution chemistry, but not to the exclusion of conventional strong-acid catalysis. The catalyst appears to offer good prospects for low-temperature butane conversion, although it deactivates rapidly. If acid catalysis were to be applied for propane and ethane conversion, more active catalysts would be needed.

INTRODUCTION

Environmental concerns are leading to the replacement of aromatic hydrocarbons in gasoline by branched alkanes and oxygenated compounds such as methyl *tert*-butyl ether. The ether is produced from the reaction of methanol with isobutylene, and the latter can be formed from *n*-butane by isomerization followed by dehydrogenation. Alkane isomerization reactions are catalyzed by very strong acids such as aluminum chloride supported on alumina, which has the disadvantages of being corrosive and expensive to dispose of. Thus, there is a need for improved catalysts and processes for the isomerization of *n*-butane and other straight-chain alkanes. Propane and ethane, which are present in natural gas, could also in prospect be converted by acid catalysis, giving valuable higher-molecular-weight hydrocarbons and liquid fuels (1), but practical catalysts for such conversions are lacking.

Researchers have long been searching for strong solid acids that are noncorrosive and active enough to activate light alkanes at low temperatures. A good candidate is sulfated zirconia, which catalyzes isomerization of *n*-butane at temperatures as low as 25°C (2). The addition of iron and manganese promoters increases the activity of sulfated zirconia for *n*-butane isomerization by three orders of magnitude (3). The discovery of such a highly active acidic catalyst has provided a good opportunity to explore the reactions of light alkanes at low temperatures. Our goals were to investigate the reactivities of ethane, propane, and *n*-butane with iron- and manganese-promoted sulfated zirconia (FMSZ), emphasizing low conversions to allow investigation of the reactivities of these alkanes under conditions of the simplest possible chemistry. Here we summarize new and published results for reactions of these alkanes with FMSZ and, for comparison, with zeolites.

EXPERIMENTAL

FMSZ was prepared by stepwise incipient wetness impregnation from sulfated zirconium hydroxide (Magnesium Elektron, Inc.) that was impregnated with iron and manganese nitrate solutions. The impregnated material was calcined at 650°C. The weight percentages of iron, manganese, and sulfur in the catalyst were determined to be 1, 0.5, and 1.8 %, respectively.

Before each reaction experiment, the FMSZ in flowing N₂ [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. Reactions were carried out in a once-through plug-flow reactor at atmospheric pressure and temperatures in the range of 40–450°C. Some experiments were also conducted to characterize the reactivities of propane and of ethane in the presence of HZSM-5 and USY zeolite.

RESULTS

Conversion of n-Butane. In the presence of FMSZ, *n*-butane was converted catalytically into *i*-butane, propane, *i*-pentane, and *n*-pentane at temperatures <200°C. The selectivity for *i*-butane formation was >95% for *n*-butane conversions <10%. The

overall *n*-butane conversion and the conversions of *n*-butane into products as a function of time on stream in the temperature range of 40-100°C are characterized by a break-in period followed by a period of rapid deactivation. The molar ratio of propane to pentanes approached a value of about 1 at 40°C, after about 25 h on stream. The initial (5 min time on stream) rate of *n*-butane conversion at 75°C and 0.0025 atm *n*-butane partial pressure was 4×10^{-8} mol/(s · g).

Conversion of Propane. The gas-phase products formed from propane in the temperature range of 200-300°C with FMSZ were methane, butanes, and pentanes. The conversion of propane was characterized by an initial break-in period followed by a declining period. The initially formed products were mostly methane and butanes. The selectivity to butanes increased with time on stream initially and then declined slowly, with the selectivity to pentanes increasing. The selectivity to methane simply declined with time on stream. At 250°C, the number of turnovers per sulfate group was greater than 1 after 16 days of operation. At temperatures >300°C, the only gas-phase products observed were methane, ethane, ethene, and propene. The rates of formation of methane and ethene were approximately the same at low conversions. The initial (5 min time on stream) rate of propane conversion with FMSZ at 250°C and 0.01 atm propane partial pressure was 3×10^{-10} mol/(s · g).

USY zeolite was active in converting propane into propene, methane, and ethene only at temperatures >400°C. At a propane conversion of 0.1%, the products observed were methane, ethene, and propene. Because the experiments were not run long enough, the number of turnovers (per Al site) was less than 1.

Conversion of Ethane. In the presence of FMSZ, the products observed for ethane conversion were H₂, methane, ethene, and butanes; at 200°C the products were predominantly butane and ethene. Selectivity to butanes decreased from 30% (at 0.01% conversion) at 200°C to 10% (at 0.1% conversion) at 400°C. In the temperature range of 200-350°C, the conversion to butane, ethene, and methane decreased with time on stream. At temperatures >350°C, the conversion to butanes decreased with increasing time on stream, but the conversion to ethene and to methane decreased and then increased with time on stream, followed by another declining period (Fig. 1). H₂ was observed only at temperatures >400°C; its rate of formation was characterized by an initial increase, followed by a slow decline with time on stream. Because experiments were run for only a few hours, the number of turnovers (per sulfate group) was less than 1. The initial (5 min time on stream) rate of ethane conversion in the presence of FMSZ at 450°C and 0.2 atm ethane partial pressure was 4×10^{-8} mol/(s · g).

With HZSM-5, ethane was converted into ethene in the temperature range of 300-450°C; butane and methane were also formed, but only at temperatures >400°C. In contrast, ethene and H₂ (at nearly the same rates) were formed from ethane in the presence of USY zeolite at temperatures >300°C, and traces of butane were sometimes observed at 450°C. Conversion of ethane with either of the zeolites decreased with time on stream.

The initial (5 min on stream) selectivities observed for FMSZ, HZSM-5, and USY zeolite at low ethane conversions, 450°C, and 0.2 atm ethane partial pressure are summarized in Table 1. At about 0.1% conversion, FMSZ is characterized by the lowest ethene selectivity (94%), whereas USY zeolite is characterized by the highest (99%). Butane formed with a selectivity of 4.1% with FMSZ and 1.8% with HZSM-5; it was not observed for USY zeolite, except for a trace at 0.3% conversion. At 400°C and an ethane conversion of 0.1%, the selectivity to butane with FMSZ was 10%, whereas the selectivity to butane with HZSM-5 was negligible.

DISCUSSION

Alkane Reaction Data. The data allow a rough comparison of reaction rates and product distributions for conversions of relatively unreactive alkanes in the presence of several strong solid acid catalysts, namely, FMSZ, HZSM-5, and USY zeolite. The product distributions obtained at low conversions provide some insight into the reaction mechanisms and how the reactions were initiated.

Because the rates of *n*-butane conversion with FMSZ were high, the butane conversion data demonstrate catalytic reactions. However, the rates of propane and of ethane conversion with FMSZ and with the zeolites were much lower than that of butane conversion, and catalysis was not demonstrated for these reactions.

Carbenium Ion Reactions. Classical acid catalysis of alkane conversion involves reactions of carbenium ions, $C_nH_{2n+1}^+$, which can be formed by protonation of alkenes or hydride abstraction from alkanes. In the presence of FMSZ, the low-temperature (40-100°C) *n*-butane conversion data are consistent with such chemistry, whereby $C_4H_9^+$ reacts with butene (formed by dehydrogenation of butane) to give $C_8H_{17}^+$, which rearranges and undergoes β -scission to give isobutylene, which then undergoes protonation and hydride transfer to yield *i*-butane (4-7). The observation of a nearly 1 to 1 molar ratio of propane and pentanes suggests the occurrence of stoichiometric disproportionation, involving the $C_8H_{17}^+$ intermediate. A question still remains about how the carbenium ion and the butene may be formed at low temperatures with FMSZ.

With FMSZ, the data for propane conversion in the temperature range of 200-300°C are also consistent with classical carbenium ion reactions. Propene formed by dehydrogenation of propane can react with the secondary carbenium ion $C_3H_7^+$ to form $C_6H_{13}^+$, which reacts with propene to form $C_9H_{19}^+$, which then rearranges and undergoes β -scission to give butene and $C_5H_{11}^+$. Butene would undergo protonation and then hydrogen transfer to form butane.

At temperatures >300°C, the observed formation of butane from ethane in the presence of FMSZ, HZSM-5, or USY zeolite could also be explained by carbenium ion chemistry, with butane being formed by reaction of $C_2H_5^+$ and ethene. However, the chemistry now involves a highly unstable primary carbenium ion, and one would expect the reaction to form butane from ethane to be more than the observed two or three orders of magnitude slower than that of propane.

Thus, the results raise the question of whether there is more to the chemistry than carbenium ion reactions. The suggestion of very strong acidity raises the possibility of the involvement of carbonium ions.

Carbonium Ion Reactions. The reactions involving the formation of penta-coordinated carbonium ions, $C_nH_{2n+3}^+$, which can be formed by protonation of alkanes, occur in superacidic solutions (1). This non-classical chemistry has been invoked to explain zeolite-catalyzed cracking of alkanes at low conversions (8). According to a simplified picture of the chemistry, a zeolite catalyst at a temperature of approximately 500°C protonates alkanes to give carbonium ions, which collapse to give alkanes + carbenium ions or H_2 + carbenium ions. Thus, the observations of H_2 in this work suggests the occurrence of such chemistry.

In the temperature range of 40-100°C, the *n*-butane data observed with FMSZ are consistent with carbonium ion and oligocondensation chemistry, whereby *n*-butane is protonated to form $C_4H_{11}^+$, which collapses to give H_2 and $C_4H_9^+$, which reacts (undergoes oligocondensation) with *n*-butane to form $C_8H_{19}^+$; $C_8H_{19}^+$ then rearranges and collapses to yield *i*-butane and $C_4H_9^+$.

At temperatures <300°C, the propane and ethane conversion data observed with FMSZ are also consistent with the hypothesis that oligocondensation occurs. $C_2H_5^+$, formed from protonation of propane, followed by cleavage to give methane, could react with propane to form $C_3H_{13}^+$, which would collapse to give methane and $C_4H_9^+$, which would abstract a hydride to form butane. Similarly, ethane could be protonated to form $C_2H_7^+$, which would decompose to give H_2 and $C_2H_5^+$ or methane and CH_3^+ ; $C_2H_5^+$ would then combine with ethane to form $C_4H_{11}^+$, which would be deprotonated to give butane.

Thus, the results mentioned in the preceding two paragraphs are consistent with both carbenium ion and carbonium ion chemistry. However, the occurrence of simple stoichiometric dehydrogenation of ethane observed with USY zeolite at low conversions is explained only by a carbonium ion mechanism. Ethane is presumably protonated to form $C_2H_7^+$, which decomposes into H_2 and $C_2H_5^+$, which is deprotonated to form ethene, giving a 1 to 1 molar ratio of H_2 to ethene.

Similarly, propane is protonated to form $C_3H_9^+$, which decomposes into H_2 and $C_3H_7^+$ or methane and $C_2H_5^+$. Propene and ethene are formed after deprotonation of $C_3H_7^+$ and $C_2H_5^+$, respectively. The nearly equal rates of formation of methane and ethene from propane in the presence of FMSZ suggest the occurrence of carbonium ion reactions rather than carbenium ion reactions at low conversions.

Similarly, with HZSM-5 (9), the *n*-butane data at about 500°C are consistent with the hypothesis that $C_4H_{11}^+$ is formed by protonation of *n*-butane. At low *n*-butane conversions, the observation of nearly equal rates of formation of H_2 and of butenes; of methane and of propene; and of ethane and of ethene with HZSM-5 provides further evidence of the occurrence of the carbonium ion mechanism.

However, we emphasize that once alkenes are formed, carbenium ion chemistry takes over because alkenes are readily protonated, and the classical carbenium ion reactions are much faster than those involving protonation of alkanes.

Chemistry of Alkane Conversions. Thus, in summary, the data for light alkane reactions in the presence of solid acids are consistent with chemistry analogous to that occurring in superacidic solutions, provided that conversions are low. As conversions increase, alkenes are increasingly formed via carbonium ion reactions, and classical carbenium ion reactions dominate. The implication is that carbonium ion chemistry appears to play a role in initiation of light alkane conversions with strong solid acids. The lower the temperature at which an alkane is to be activated, the stronger is the acid required; thus, the data suggest that FMSZ may be much more strongly acidic than the zeolites.

However, the chemistry involving FMSZ and alkane conversions is still not fully elucidated, in part because the roles of Fe and Mn are not well understood; the reactions of light alkanes at low temperatures may not be entirely acid-catalyzed. Although there is no evidence in the high-temperature product distribution data of any enhancement in dehydrogenation activity of sulfated zirconia resulting from addition of iron and manganese to sulfated zirconia, these promoters may act as catalysts (10) or redox initiators (11) to produce alkenes, which would then be protonated to form carbenium ions and kick off the conventional catalytic cycles. Alternatively, the promoters may be catalytically involved in alkane conversions as they may somehow increase the acidity of the sulfated zirconia, so that it is capable in protonating alkanes at low temperatures.

CONCLUSIONS

In the presence of FMSZ at 40°C, *n*-butane was catalytically isomerized into *i*-butane and disproportionated into propane and pentanes. Propane and ethane reacted to give butane with FMSZ at 200°C; however, the rate of ethane conversion was about 2 to 3 orders of magnitude less than that of propane conversion, which is 3 to 4 orders of magnitude less than that of *n*-butane conversion. At temperatures >300°C and in the presence of FMSZ, HZSM-5, or USY zeolite, these alkanes are inferred to be protonated to form carbonium ions, which then collapse to give smaller alkanes or H₂ and (after deprotonation) alkenes. The comparison of the product distributions for ethane and for propane conversion suggests that there is no evidence of enhancement in dehydrogenation activity of sulfated zirconia resulting from incorporating Fe and Mn. The chemistry by which these alkanes are converted in the presence of FMSZ is complicated; both classical carbenium ion and non-classical carbonium ion mechanisms seem to contribute to the products observed, and the roles of Fe and Mn promoters are not yet resolved.

ACKNOWLEDGMENTS

We thank Magnesium Elektron, Inc., for providing the sulfated zirconium hydroxide. The research was supported in part by the U.S. Department of Energy, Pittsburgh Energy Technology Center.

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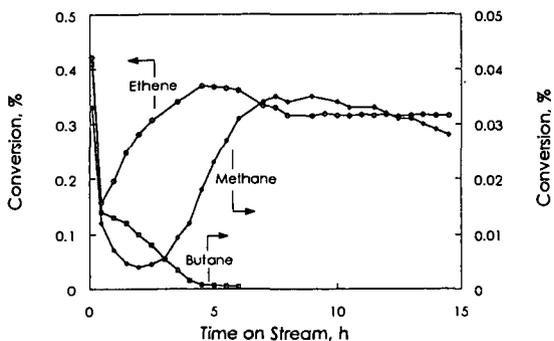


Figure 1. Conversion of ethane into ethene, butane, and methane with FMSZ at 450°C. Feed ethane partial pressure = 0.2 atm, inverse space velocity = 3.7×10^5 ($s \cdot g$)/mol.

Table 1. Comparison of initial selectivity^a for ethane conversion in the presence of FMSZ, HZSM-5, and USY zeolite at 0.2 atm ethane partial pressure and 450°C.

Solid acid	$10^{-5} \times$ Inverse space velocity, ($s \cdot g$)/mol	Ethane Conversion, %	Normalized Selectivity, %		
			Methane	Ethene	Butane
FMSZ	1.83	0.38	3.4	89.7	6.9
FMSZ	1.14	0.29	2.6	91.1	6.3
FMSZ	0.46	0.13	1.7	94.2	4.1
HZSM-5	0.28	0.11	0.9	97.3	1.8
USY zeolite	7.32	0.30	1.7	96.8	1.5
USY zeolite	1.83	0.08	0.7	99.3	0

^aData taken at 5 min on stream.