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Superacid Catalysis of Light Hydrocarbon Conversion

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## SUMMARY

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. The propane conversion data reported here provide excellent insights into the chemistry of the catalytic conversions.

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  $\geq 400^\circ\text{C}$ . 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  $3.3 \times 10^{-8}$ ,  $0.3 \times 10^{-8}$ , and  $0.06 \times 10^{-8}$  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  $< 0^\circ\text{C}$ . 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  $>350^\circ C$  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  $450^\circ C$ ; the selectivity for 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  $530^\circ C$ , 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  $<200^\circ C$  (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  $150^\circ C$  (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  $200^\circ C$  (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. 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). USY zeolite (Si/Al atomic ratio 8.9) was supplied by W. R. Grace.

### *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<sub>2</sub> carrier gas. The 5 mol% propane stream was also diluted with N<sub>2</sub> 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) × 10<sup>6</sup> (g · s)/(mol of propane fed); propane partial pressure, 0.01, 0.025, or 0.05 atm; and

run length, 4 h to 16 days. Most experiments were done with an inverse space velocity of  $1 \times 10^6$  (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  $(n \times \text{number of moles of product}) / (3 \times \text{number of moles of propane fed})$ ; normalized selectivity for formation of an individual product is defined as  $(\text{normalized conversion to gas-phase product}) / (\text{propane conversion to gas-phase products})$ . 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  $>350^\circ\text{C}$  was  $>1$  after 8 h of operation in the flow reactor. However, to achieve one turnover per site at  $250^\circ\text{C}$ , the reaction experiment had to be continued for 16 days. The number of turnovers per site was about 0.1 at  $200^\circ\text{C}$  after 5 days of operation. The data taken at temperatures  $<350^\circ\text{C}$  therefore could represent noncatalytic reactions. In the temperature range of  $350\text{--}450^\circ\text{C}$ , 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  $\geq 200^{\circ}\text{C}$ . In contrast, the lowest temperature at which conversion was observed for USY zeolite was  $400^{\circ}\text{C}$ . The gas-phase products formed from propane in the presence of either promoted or unpromoted sulfated zirconia at  $200^{\circ}\text{C}$  were methane, butanes (the predominant product), and pentanes. The conversion of propane at  $200^{\circ}\text{C}$  increased with time on stream for the promoted sulfated zirconia, followed by a period of declining conversion (Fig. 1). 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. 1).

In the temperature range  $250\text{--}350^{\circ}\text{C}$ , ethane, ethylene, and propylene were observed as products in addition to those stated above. The propane conversion to gas-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  $>350^{\circ}\text{C}$ .

At  $450^{\circ}\text{C}$ , 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  $450^{\circ}\text{C}$  are shown in Tables 1, 2, and 3, respectively; data are presented for the unpromoted sulfated zirconia, the promoted sulfated zirconia, and USY zeolite. At 200 and at  $350^{\circ}\text{C}$ , the activity of the promoted sulfated zirconia was about twice that of the unpromoted sulfated zirconia, as measured by the conversions (Tables 1 and 2); 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  $450^{\circ}\text{C}$ , whereas more than half of the propane converted in the presence of USY zeolite gave propylene at  $450^{\circ}\text{C}$ .

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. 2. 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. 3. 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. 4 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 products observed 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 >0.3%.

#### *Formation of 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, 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  $1 \times 10^{-6}$  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, 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  $3.3 \times 10^{-8}$  mol/(s · g); that for the conversion catalyzed by sulfated zirconia under the same conditions was  $0.30 \times 10^{-8}$  mol/(s · g); and that for the conversion catalyzed by USY zeolite under the same conditions was  $0.06 \times 10^{-8}$  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. 5. The reaction order in propane and the rate constant for the total conversion were determined to be  $1.6 \pm 0.1$  and  $2.3 \times 10^{-7}$  mol/(s · g · atm<sup>1.6</sup>), respectively, at 250°C, and  $1.4 \pm 0.1$  and  $1.7 \times 10^{-6}$  mol/(s · g · atm<sup>1.4</sup>), respectively, at 350°C. At a propane partial pressure of 0.01 atm, the temperature dependence of the rate (Fig. 6) indicates an apparent activation energy of  $15 \pm 1$  kcal/mol.



## 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. 3), is consistent with a mechanism whereby propane is protonated by the catalyst to give penta-coordinated carbonium ions (presumably transition states) that collapse into methane and ethyl cations (or into H<sub>2</sub> 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<sub>2</sub> and propylene would be expected to form in equimolar amounts at the lowest conversions, but data for H<sub>2</sub> production are lacking).

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. 4), consistent with the distribution of cracking and dehydrogenation products formed from the carbonium ions, as illustrated in Fig. 7. In Fig. 7, 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 (reaction 2) leading to methane and ethyl cations, and one of them (reaction 3) leading to H<sub>2</sub> 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. 7 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 not possible 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 time on stream) and at particular conversions (although they represent reaction at different 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. 7. However, the molar ratio of methane to propylene was found to be about 2 for the promoted catalyst (Fig. 4) and 0.5 for the zeolite (Table 3); 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. 7) would be converted into paraffins only in secondary reactions. 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.,  $450^\circ\text{C}$  (1). Thus, the performance of the zirconia-supported catalysts at low temperatures (ca.  $200\text{--}300^\circ\text{C}$ ) is comparable to that of the zeolite HZSM-5 at high temperatures (ca.  $450^\circ\text{C}$ ). Consistent with this comparison, USY zeolite was found to have negligible activity for propane conversion at temperatures  $<400^\circ\text{C}$  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  $450^\circ\text{C}$ ; 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 4. 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  $450^\circ\text{C}$  are about the same. Propane is two orders of magnitude less reactive than these compounds at  $450^\circ\text{C}$ . 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 than *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 much 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 are greater for the more strongly acidic promoted sulfated zirconia than for the less strongly acidic zeolites. It has been postulated (25) 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.

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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Table 1. Comparison of activity<sup>a</sup> and selectivity for propane reaction<sup>b</sup> 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
<i>n</i> -butane	34.6	31.1
isopentane	6.6	10.7

<sup>a</sup>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.

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

Table 2. Comparison of initial<sup>a</sup> activity and selectivity for propane reaction<sup>b</sup> 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
<i>n</i> -butane	0.6	0.6

<sup>a</sup>The data were taken at 5 min on stream.

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



Table 3. Comparison of initial<sup>a</sup> activity and selectivity for propane reaction<sup>b</sup> 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

<sup>a</sup>The data were taken at 5 min on stream.

<sup>b</sup>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.

Table 4. Comparison of hydrocarbon reactivities in the presence of iron- and manganese-promoted sulfated zirconia and zeolites at 450°C.<sup>a</sup>

Reactant	Catalyst	P <sub>reactant</sub> , atm	Approximate observed rate <sup>b</sup> of reaction, mol/(s · g)	Reaction rate <sup>c</sup> normalized to reactant partial pressure 0.01 atm, mol/(s · g)
<i>n</i> -butane	promoted sulfated zirconia	0.0025	1 × 10 <sup>-7</sup>	4 × 10 <sup>-7</sup>
neopentane	promoted sulfated zirconia	0.005	5 × 10 <sup>-8</sup>	1 × 10 <sup>-7</sup>
propane	promoted sulfated zirconia	0.01	3 × 10 <sup>-8</sup>	3 × 10 <sup>-8</sup>
<i>n</i> -butane	HZSM-5 <sup>d</sup>	0.0025	1 × 10 <sup>-8</sup>	4 × 10 <sup>-8</sup>
neopentane	USY	0.005	6 × 10 <sup>-9</sup>	1 × 10 <sup>-8</sup>
propane	USY	0.01	6 × 10 <sup>-10</sup>	6 × 10 <sup>-10</sup>

<sup>a</sup>The data were taken at 5 min on stream.

<sup>b</sup>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.

<sup>c</sup>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.

<sup>d</sup>Values for *n*-butane conversion catalyzed by HZSM-5 were extrapolated from data of Krannila *et al.* (14).

## List of Figures

Figure 1. 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.

Figure 2. 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.

Figure 3. 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.

Figure 4. 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.

Figure 5. 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.

Figure 6. 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.

Figure 7. 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).

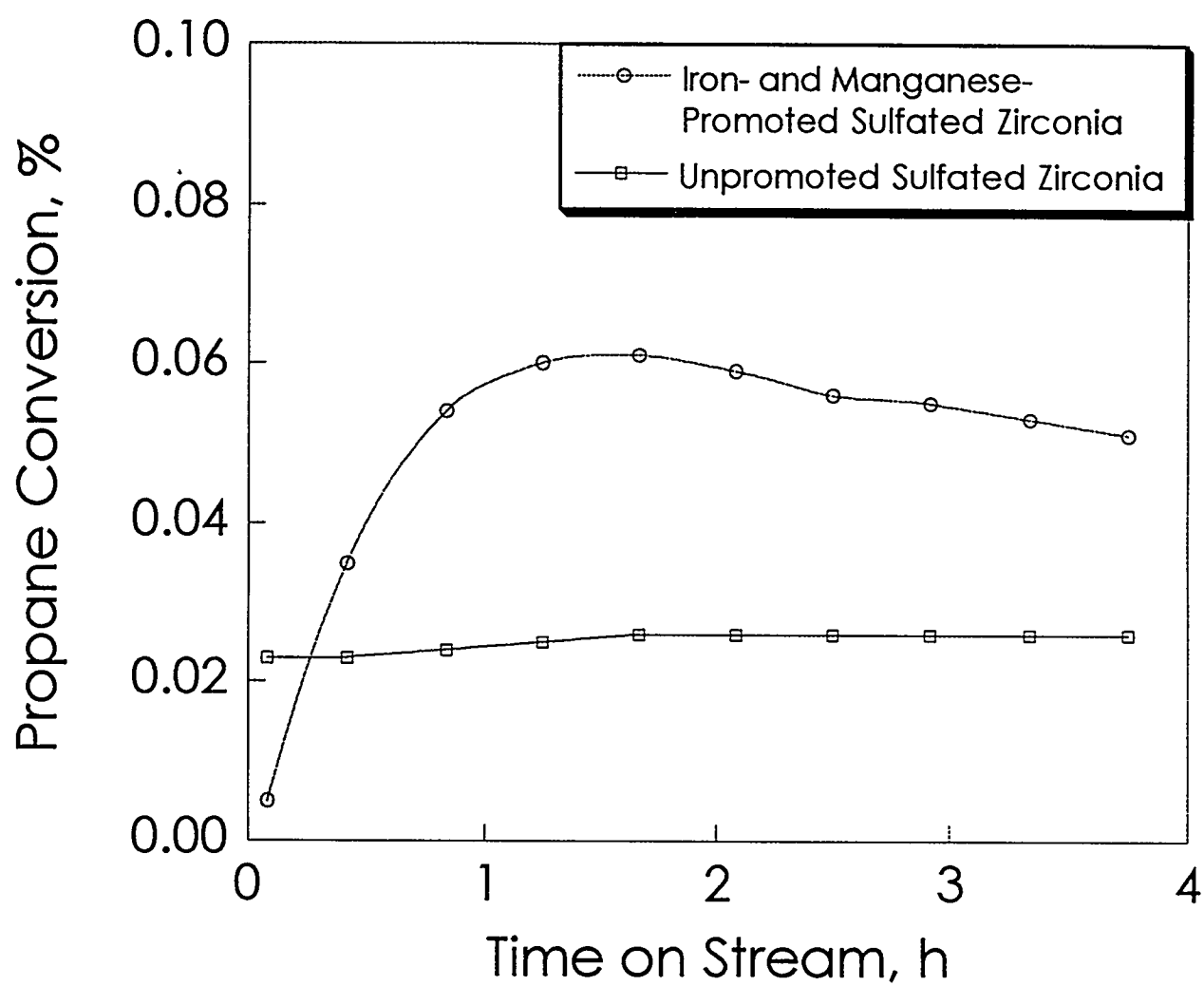
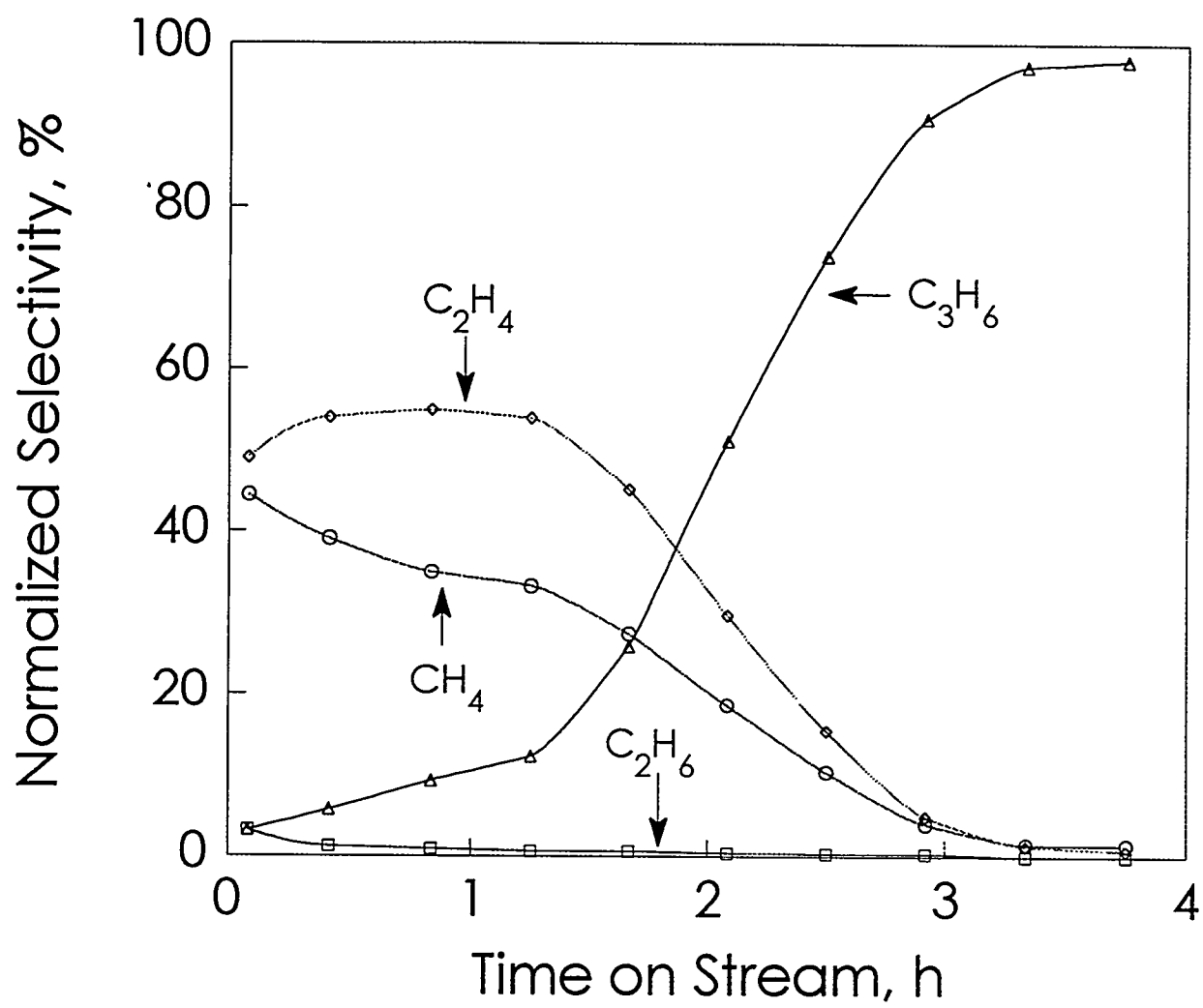
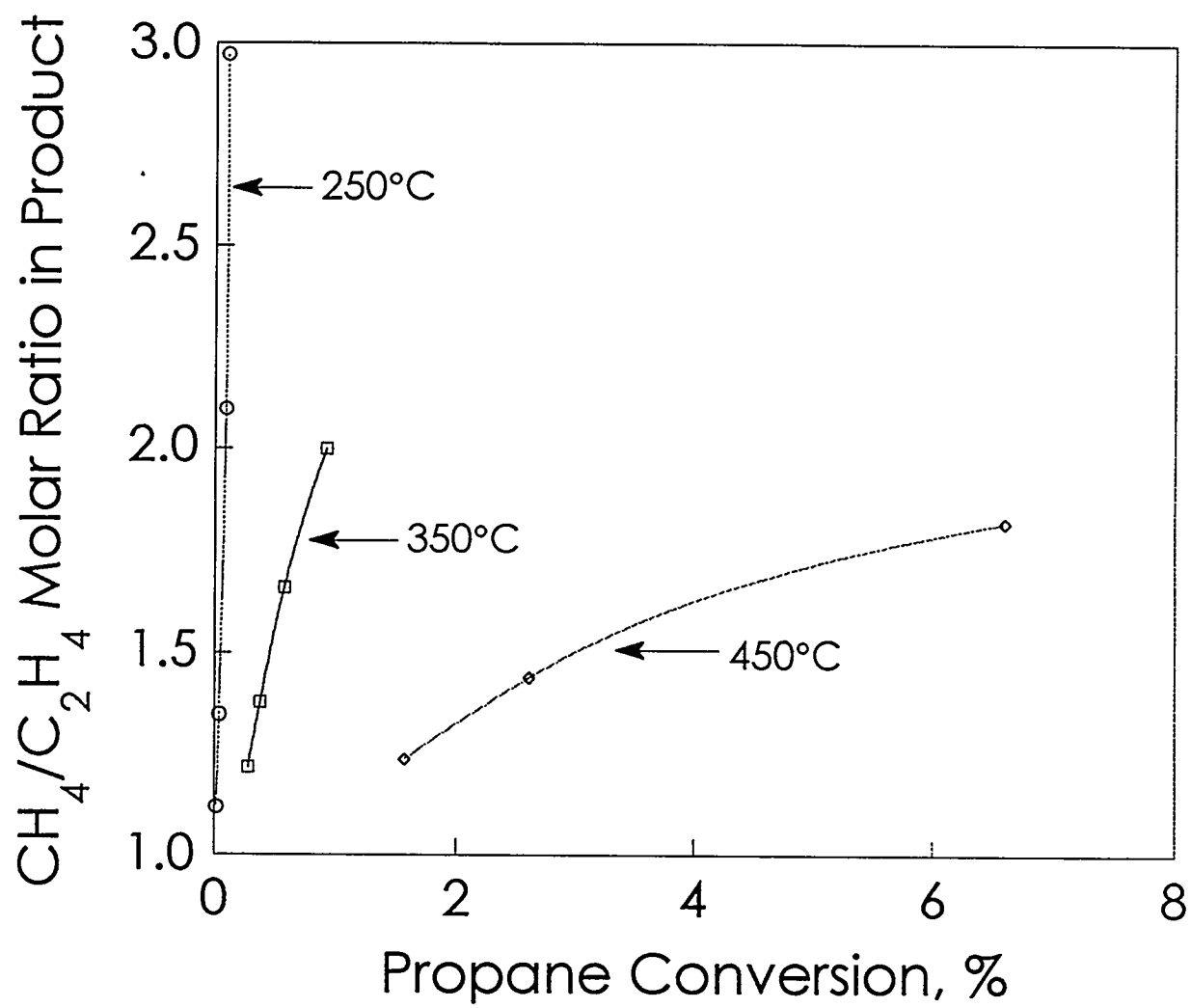


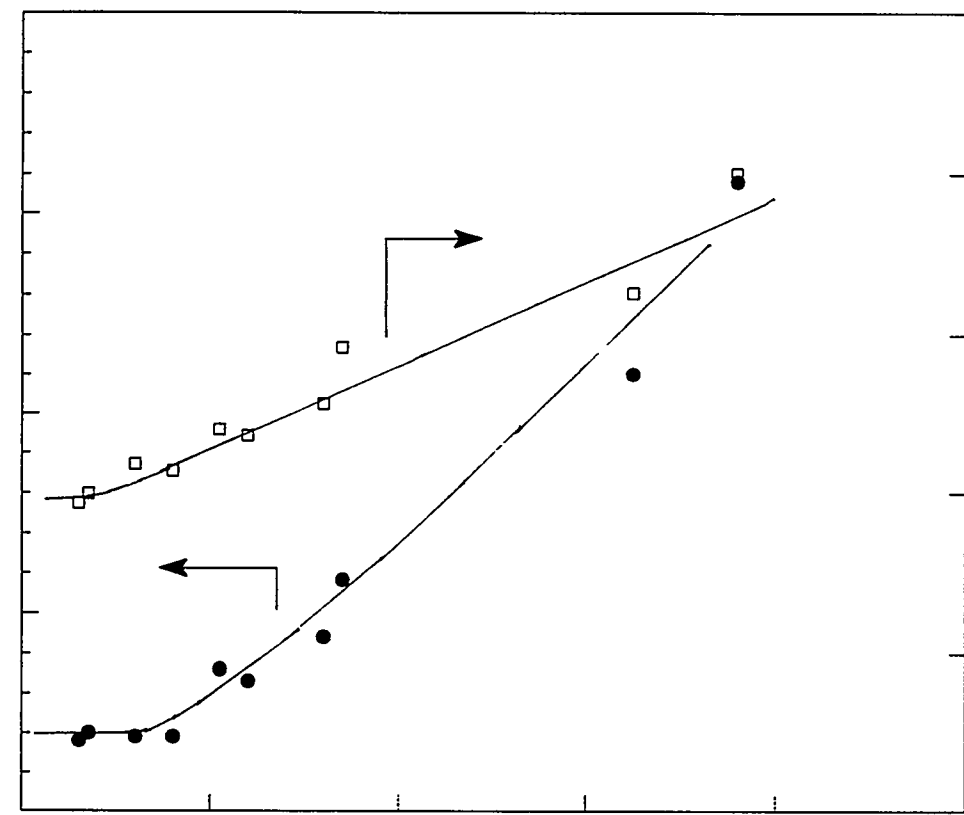
Fig 2





$\text{CH}_4/\text{C}_3\text{H}_6$  Molar Ratio in Product

20  
15  
10  
5  
0

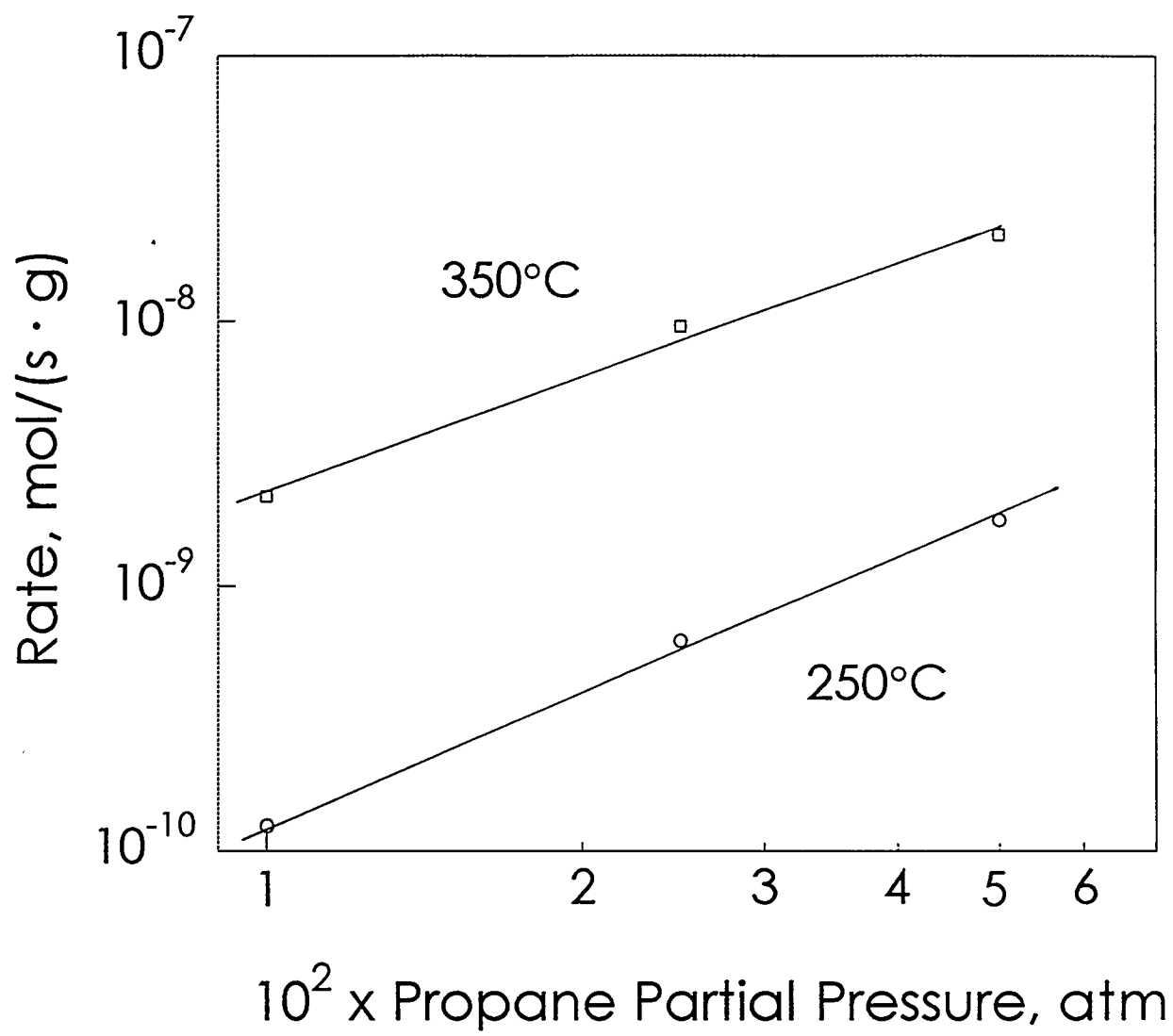


Propane Conversion, %

2.5  
2.0  
1.5  
1.0  
0.5  
0

$\text{CH}_4/\text{C}_2\text{H}_4$  Molar Ratio in Product





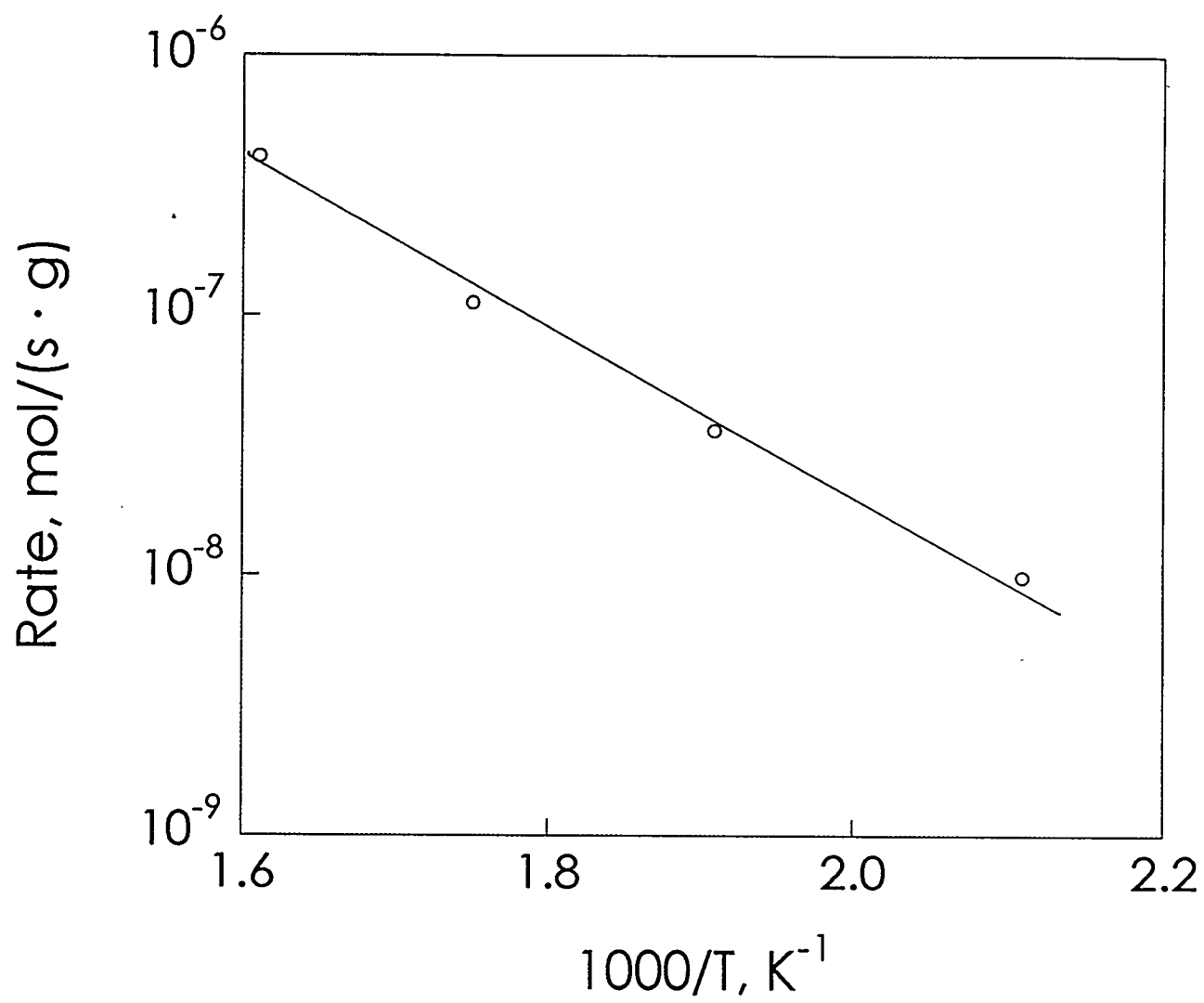


Fig. 2

