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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. 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 most recent Nobel Prize in chemistry for his work.

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

INTRODUCTION

In the preceding two reports in this series, we summarized the first results for the conversion of propane catalyzed by Fe- and Mn-promoted sulfated zirconia. In this report we add a number of additional results for this reaction.

Reactions of alkanes proceeding through carbocation intermediates in superacid solutions have been characterized extensively by Olah et al. [1-3], but the chemistry of hydrocarbon conversion in the presence of solid superacids is much less well developed. Some of the best opportunities for understanding of superacid-catalyzed alkane reactions are provided by small probe molecules, such as propane. Propane conversion catalyzed by conventional solid acids, such as zeolites, was investigated by Kitagawa et al. [4], who showed that about half the converted propane was transformed into C_4 and C_5 aliphatics in the presence of HZSM-5 in a flow reactor at 450°C. The selectivity for these higher aliphatics decreased with increasing temperature as more aromatics were formed. Kwak et al. [5] observed that methane and ethene were produced in equimolar amounts in the limit of zero conversion of propane in the presence of HZSM-5 at 530°C, consistent with cracking proceeding through a protonated propane intermediate. Most of these investigations were carried out at high temperatures so that cracking and aromatization were thermodynamically favored.

Low-temperature propane conversion has been catalyzed by solid superacids, including SbF_5 supported on SiO_2-Al_2O_3 [6] and sulfated zirconia incorporating Pt [7]. Hattori et al. [6] reported cracking of propane to give methane (the principal product) and ethane in a recirculation reactor at 20°C. Hino and Arata [7] observed the formation of methane, ethane, and butanes with traces of pentanes in a pulse reactor at 150°C.

We report the conversion of propane in the presence of iron- and manganese-promoted sulfated zirconia at temperatures $\leq$ 300°C. The promoted sulfated zirconia has been reported to be a catalyst for *n*-butane isomerization at room temperature; it has been suggested to be the strongest non-halide solid superacid [8]. The data presented here indicate that propane is converted in the presence of the promoted sulfated zirconia, but much more slowly than *n*-butane, and the product distributions are in agreement with Olah superacid chemistry.

EXPERIMENTAL

Rust-colored promoted sulfated zirconia containing 1 wt% Fe, 0.5 wt% Mn, and 1.8 wt% sulfur, was prepared from sulfated zirconium hydroxide (Magnesium Elektron, Inc.), as described elsewhere [9]. It was pretreated in N_2 (Liquid Carbonic, 99.997%) flowing at 30 mL(NTP)/min at 450°C for 1.5 h. Gas mixtures were fed to a once-through flow reactor containing the promoted sulfated zirconia powder. The feed stream contained propane, either 1 mol% (containing 0.002 mol% ethane, supplied by Liquid Carbonic) or 5 mol% (containing 0.01 mol% ethane and traces of butanes, supplied by Matheson), in N_2. The products were analyzed by on-line gas chromatography with a flame ionization detector; analysis for H_2 was not done. The equipment is described elsewhere [9]. The reaction conditions were as follows: temperature, 200, 250, or 300°C; pressure, 1 bar; mass of catalyst, 0.5-2.0 g; inverse space velocity, (1-6) x 10^6 (g of catalyst · s)/(mole of propane fed); propane partial pressure, 0.01, 0025, and 0.05 bar; and run length, 4 h to 16 days.

RESULTS

The normalized conversion of propane to each of the individual gas-phase products (containing *n* carbon atoms) was determined as follows: (*n* x number of moles of product)/(3 x number of moles of propane fed); overall propane conversion is defined as the sum of the individual conversions. Selectivity for formation of an individual product is defined as: (normalized conversion to gas-phase product)/(propane conversion to gas-phase products). Carbonaceous deposits formed on the surface of the promoted sulfated zirconia, but they were not accounted for in the calculations of conversion. These deposits formed on the surface of the material at all investigated temperatures, and the color changed from rust to gray or black.

The gas-phase products formed from propane at 200°C were methane, butanes, and pentanes. The conversion to gas-phase products increased for the first hour on stream (the induction period), followed by a period of declining conversion (figure 1). At 250 and at 300°C, the products included ethane, ethene, propene, and the products observed at 200°C. The propane conversion at 300°C was at most 0.6%. A plot of propane conversion at 250°C at the end of the induction period as a function of inverse space velocity (figure 2) is nearly linear, suggesting that the conversion was differential. Thus the slope of the line is taken as an approximation of the reaction rate, i.e. 3×10^{-10} mol/(g of catalyst · s).

The change in product distribution with time on stream at 200°C is shown in figure 3. The initially formed gas-phase products were mostly methane and butanes. The selectivity to butanes initially increased with time on stream and then declined slowly as the selectivity to pentanes increased. Concomitantly, the selectivity to methane declined rapidly with time on stream. The selectivity to butanes was greatest at the lowest temperatures. After the induction period, typical selectivities to butanes at 200°C were about 85% and those at 300°C were about 15%.

The ratio of methane to ethene in the gas-phase products at 250°C is shown in figure 4. This ratio was approximately 1 as the conversion approached zero; however, it deviated significantly from unity when the conversion was higher than 0.09%.

The flow reactor experiment at 250°C was continued with a constant feed flow rate for 16 days. The conversion profile as a function of time on stream was similar to that observed at 200°C, and conversion was proceeding when the experiment was terminated. If we assume that the number of catalytic sites is the same as the number of sulfate groups, then these data demonstrate that the number of turnovers (propane molecules converted per catalytic site) was 1.0 ± 0.1 and that the reaction was catalytic. However, the number of turnovers per site estimated in this way from the data obtained at 200°C was only 0.12 ± 0.02 when the experiment was terminated after 5 days of operation.

DISCUSSION

Because the rates of reaction were so low, the data were sufficient to demonstrate catalysis only for propane conversion at 250°C after 16 days of operation. The data taken at 200°C may represent noncatalytic reactions. However, the estimate of the number of turnovers/site is regarded as conservative, because the number of sulfate groups is considered to be an upper limit of the number of active sites and the amount of propane converted into carbonaceous deposits is not included. Thus the data do not rule out the occurrence of catalysis at 200°C.

Olah et al. [3] investigated the conversion of alkanes, for example, propane in the temperature range of -78 to 150°C in the presence of excesses of liquid superacids in a Teflon-lined stainless steel bomb. The superacid was diluted with the weakly nucleophilic SO_2ClF. With propane, they observed protolysis of C–H and, predominantly, C–C bonds, leading to the formation of methane, ethane, H_2, and carbenium ions. Subsequent oligocondensation led to the formation of higher alkylcarbenium ions.

The products observed by Olah et al. [3] for propane conversion were also observed in the present work. The presumed analogy to Olah superacid chemistry implies that the solid superacid protonates propane to initiate its conversion. Thus the results are consistent with the earlier conclusion [8, 10] that the iron- and manganese-promoted sulfated zirconia is a superacid.

Furthermore, the ratio of methane to ethene, which approaches 1 in the limit of zero conversion at 250°C (figure 4), is consistent with protonation of propane as an initial reaction step to give carbonium ions (presumably transition states) that collapse into methane and ethyl cations (or into H_2 and *s*-propyl cations), so that the primary cracking products methane and ethene are formed in equimolar amounts. The lack of data for H_2 leaves open the question of the ratio of H_2 to propene, which would also be expected to approach 1 in the limit of zero conversion.

Cracking and dehydrogenation of alkanes via protonation has been demonstrated by Haag et al. [11, 12] catalyzed by zeolites at temperatures of 400-550°C. For example, they observed equimolar yields of ethane and ethene formed from *n*-butane in the limit of zero conversion [12]. The observation of a comparable cracking product distribution (with a much less reactive molecule) in our work at a temperature as low as 250°C is consistent with the suggestion that the promoted sulfated zirconia is a much stronger acid than the zeolites. However, its activity for neopentane cracking at 450°C appears to be only slightly greater than that of USY zeolite, which may be explained by an extremely rapid deactivation of the promoted sulfated zirconia at this temperature, possibly by the blockage of the superacid sites by stable surface species [13].

The observed formation of butanes and pentanes from propane at the lower reaction temperatures is consistent with oligocondensation chemistry proceeding via carbocation intermediates. Olah et al. [3] pointed out that almost all low-molecular-weight alkanes are converted with increasing temperature into stable carbocations, e.g. *t*-butyl cations, in the presence of a superacid. Our observation of butanes as products is consistent with the formation of *t*-butyl cations and hydride abstraction to form isobutane; isomerization would give *n*-butane. At longer times on stream, pentanes were observed, and these can also be accounted for by oligocondensation reactions. The data are explained by the reaction network of figure 5, which is based on Olah chemistry.

The similarities in the product distributions observed in this work and in the work of Olah et al. [3] with reactions in superacid solutions lead to the postulate that the chemistry on the surface was analogous to that in superacid solutions. But the differences in the experimental conditions were significant, leaving the fundamental issues distinguishing solution and solid superacid chemistry and catalysis largely unresolved.

CONCLUSION

Propane is converted into butanes and pentanes in the presence of iron- and manganese-promoted sulfated zirconia at temperatures of 200-300°C. The observation of these products accompanied by methane suggests that the reactions are initiated by protonation of propane to form a carbonium ion which collapses into methane and ethyl cation, followed by oligocondensation of the ethyl cation with propane. The product distribution is consistent with Olah superacid chemistry; the chemistry has been demonstrated to be catalytic at 250°C, but it may not be catalytic at lower temperature.

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LIST OF FIGURES

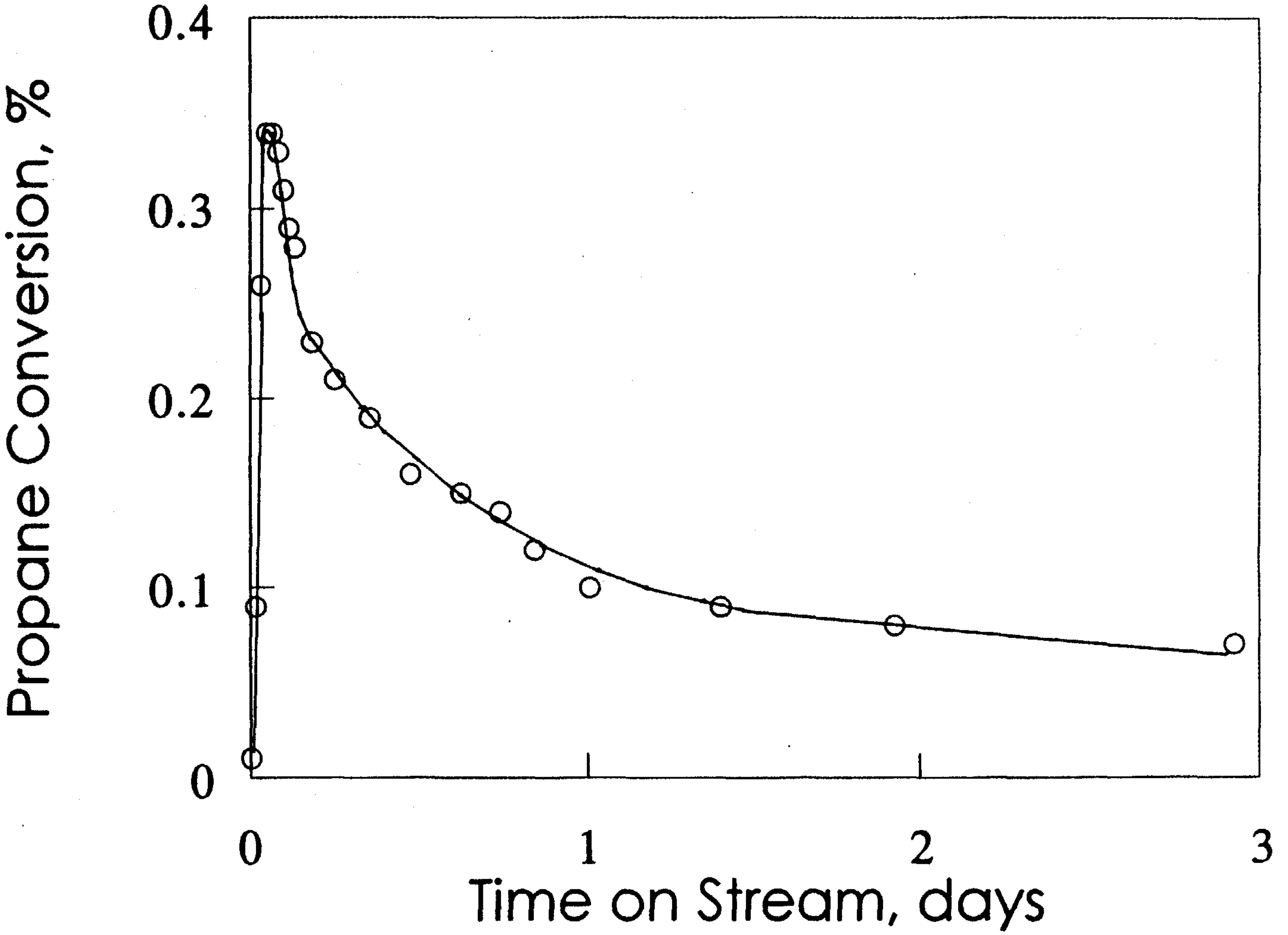


Fig 1

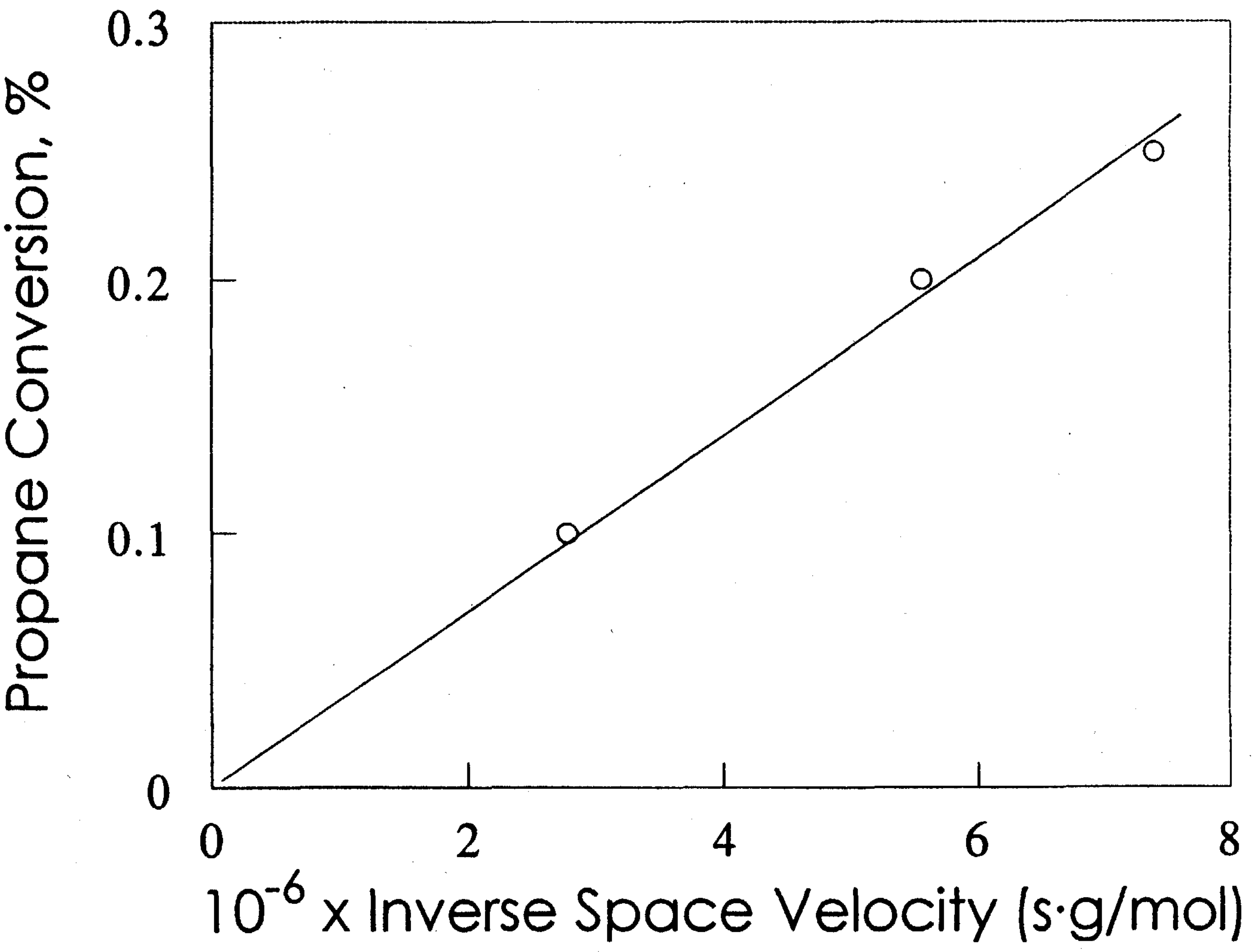

0.3
0.2
0.1
0
Propane Conversion, %
0
2
4
6
8
10^-6 x Inverse Space Velocity (s·g/mol)

Fig 2.

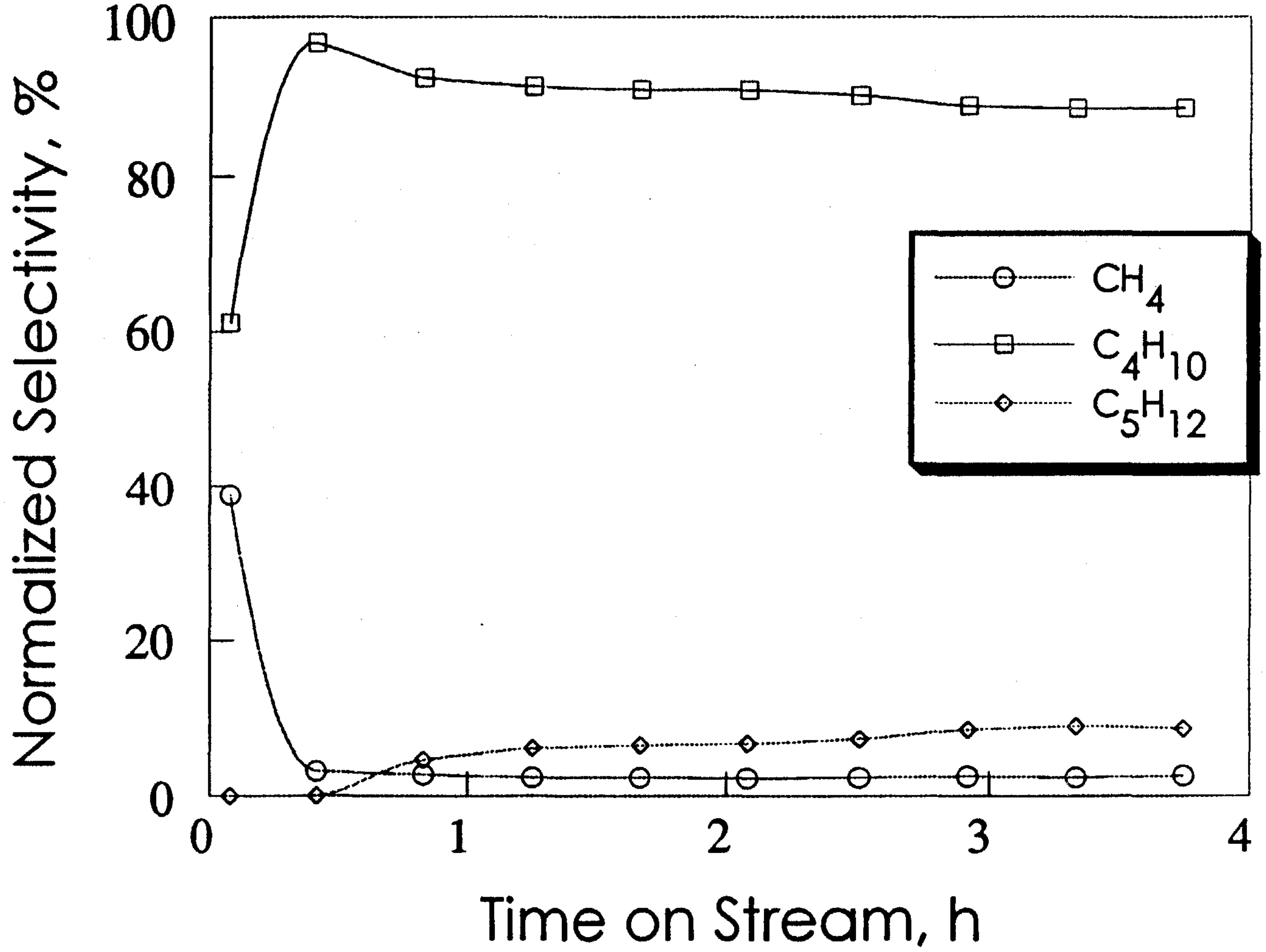
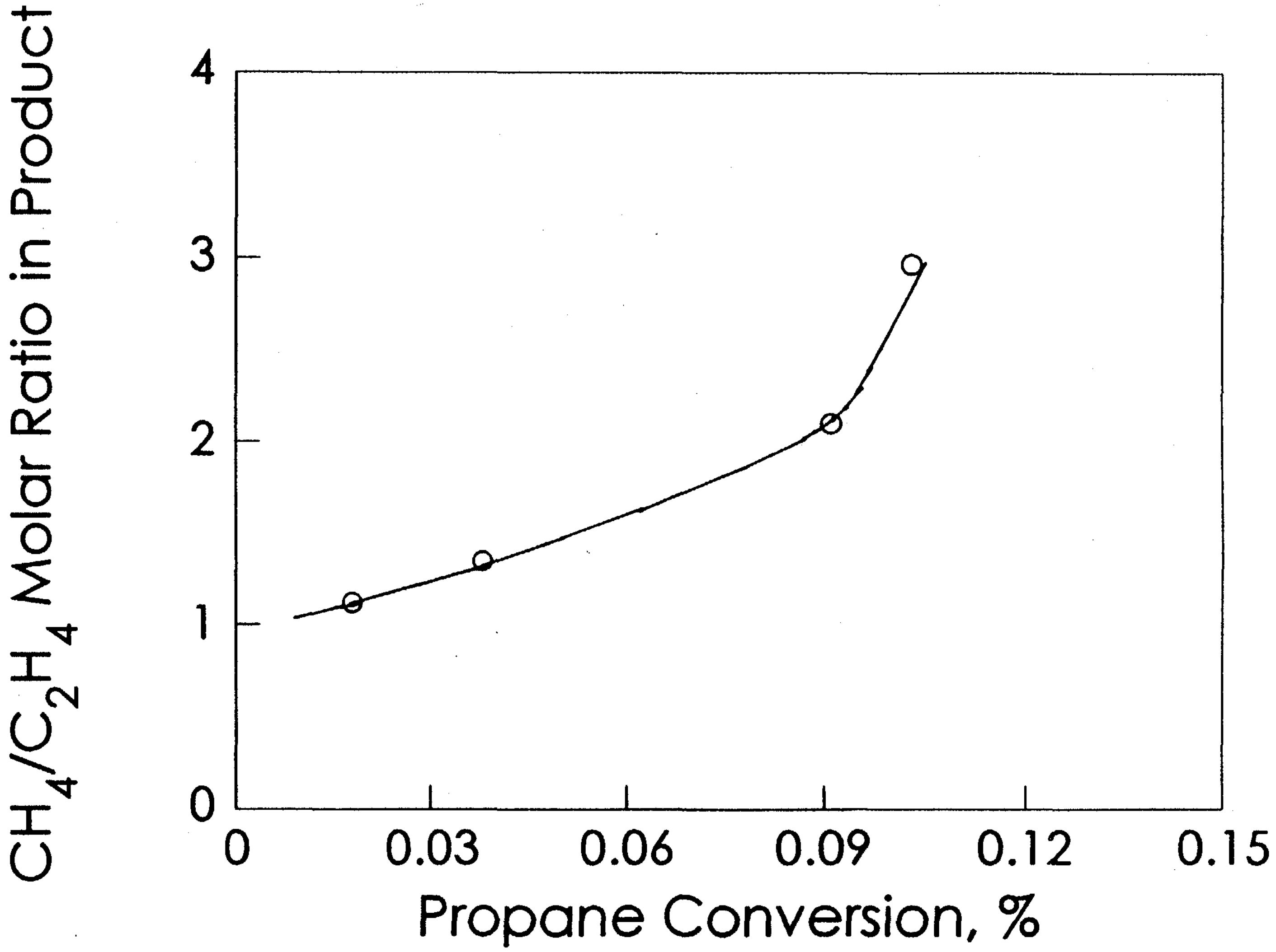
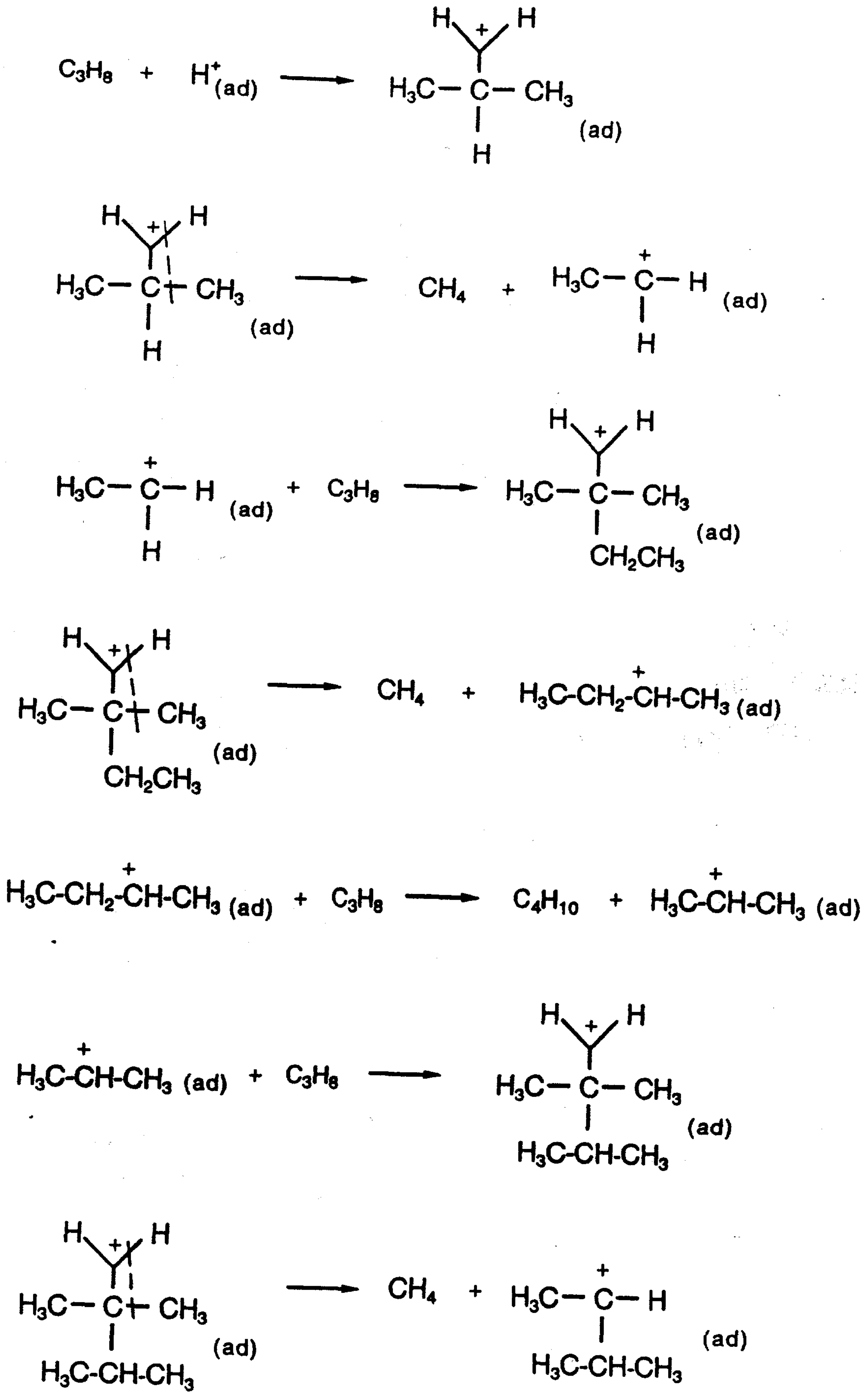

Normalized Selectivity, %
100
80
60
40
20
0
0
1
2
3
4
Time on Stream, h
CH_4
C_4H_{10}
C_5H_{12}

Fig3



CH_4/C_2H_4 Molar Ratio in Product
4
3
2
1
0
0
0.03
0.06
0.09
0.12
0.15
Propane Conversion, %

Fig 4.



1. $C_3H_8 + H^+_{(ad)} \longrightarrow H_3C-\underset{H}{\overset{H\overset{+}{\vee}H}{C}}-CH_3\ _{(ad)}$

2. $H_3C-\underset{H}{\overset{H\overset{+}{\vee}H}{C}}\mathbin{+}CH_3\ _{(ad)} \longrightarrow CH_4 + H_3C-\underset{H}{\overset{+}{C}}-H\ _{(ad)}$

3. $H_3C-\underset{H}{\overset{+}{C}}-H\ _{(ad)} + C_3H_8 \longrightarrow H_3C-\underset{CH_2CH_3}{\overset{H\overset{+}{\vee}H}{C}}-CH_3\ _{(ad)}$

4. $H_3C-\underset{CH_2CH_3}{\overset{H\overset{+}{\vee}H}{C}}\mathbin{+}CH_3\ _{(ad)} \longrightarrow CH_4 + H_3C\text{-}CH_2\text{-}\overset{+}{C}H\text{-}CH_3\ _{(ad)}$

5. $H_3C\text{-}CH_2\text{-}\overset{+}{C}H\text{-}CH_3\ _{(ad)} + C_3H_8 \longrightarrow C_4H_{10} + H_3C\text{-}\overset{+}{C}H\text{-}CH_3\ _{(ad)}$

6. $H_3C\text{-}\overset{+}{C}H\text{-}CH_3\ _{(ad)} + C_3H_8 \longrightarrow H_3C-\underset{H_3C\text{-}CH\text{-}CH_3}{\overset{H\overset{+}{\vee}H}{C}}-CH_3\ _{(ad)}$

7. $H_3C-\underset{H_3C\text{-}CH\text{-}CH_3}{\overset{H\overset{+}{\vee}H}{C}}\mathbin{+}CH_3\ _{(ad)} \longrightarrow CH_4 + H_3C-\underset{H_3C\text{-}CH\text{-}CH_3}{\overset{+}{C}}-H\ _{(ad)}$

Fig 5