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Propane conversion in the presence of iron- and manganese-promoted sulfated zirconia: evidence of Olah carbocation chemistry

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Iron- and manganese-promoted sulfated zirconia was tested for conversion of propane at 1 bar, 200, 250, and 300°C, and propane partial pressures of 0.01, 0.025, and 0.05 bar. Propane was converted to pentanes, butanes, propene, ethane, ethene, and methane at 250°C, 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 s) and a propane partial pressure of 0.05 bar. Carbonaceous deposits formed rapidly. At 250°C, the number of propane molecules converted to gas-phase products was only about 1 per sulfate group after 16 days of operation in a continuous flow reactor. The observation of butanes and pentanes as products is consistent with Olah superacid solution 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 secondary reactions with propane to form higher-molecular-weight alkanes.

Keywords: propane; butane; zirconia; solid acid; sulfated zirconia; iron promoter; manganese promoter

1. Introduction

Reactions of alkanes proceeding through carbocation intermediates in superacid solutions have been characterized extensively by Olah et al. [1–3], but the chemistry of alkane conversion in the presence of very strong solid acids is much less well developed. Some of the best opportunities for understanding of acid-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 some of the converted propane was transformed into C_4 and C_5 aliphatics in the presence of HZSM-5 zeolite in a flow reactor at 450°C. The selectivity for these higher aliphatics decreased with increasing

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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 products were thermodynamically favored.

Reactions of propane also take place in the presence of strong solid acids at low temperatures. Hattori et al. [6] used SbF_5 supported on SiO_2–Al_2O_3, observing cracking of propane to give methane (the principal product) and ethane in a recirculation reactor at 20°C. Hino and Arata [7] used sulfated zirconia incorporating Pt, observing 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 $\leqslant 300°C$. The promoted sulfated zirconia has been reported [8] to be a catalyst for *n*-butane isomerization at temperatures as low as room temperature. It was suggested to be the strongest non-halide solid superacid [8], but there is debate about whether it is as strongly acidic as a superacid [9–11]. The data presented here indicate that propane in the presence of the promoted sulfated zirconia is converted, but much more slowly than *n*-butane, and the product distributions are consistent with Olah superacid solution chemistry.

2. 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 [12]. 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 an on-line gas chromatograph with a flame ionization detector, analysis for H_2 was not done. The equipment is described elsewhere [12]. The reaction conditions were as follows: temperature, 200, 250, or 300°C; pressure, 1 bar; mass of promoted sulfated zirconia, 0.5–2.0 g; inverse space velocity, $(1\text{–}6) \times 10^6$ (g s)/(mole of propane fed); propane partial pressure, 0.01, 0.025, or 0.05 bar; and run length, 4 h to 16 days.

3. Results

The normalized conversion of propane to each of the individual gas-phase products (containing *n* carbon atoms) was determined as follows: (*n* × number of moles of product)/(3 × number of moles of propane fed); propane conversion to gas-phase products is defined as the sum of the individual conversions. Selectivity to an individual product is defined as (normalized conversion to gas-phase product)/(propane conversion to gas-phase products). Carbonaceous deposits were observed on the surface of the promoted sulfated zirconia, but they were not accounted for in the calculations of conversion. These deposits formed under all reaction conditions on the surface of the material, and the color of the promoted sulfated zirconia 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 (fig. 1). At 250°C, the products included ethane, ethene, propene, and the products observed at 200°C. At 300°C, the products were the same as those observed at 250°C except for pentanes. The highest propane conversion observed (at 300°C) was 0.6%. A plot of propane conversion at 250°C at the end of the induction period as a function of inverse space velocity (fig. 2) is nearly linear, suggesting that the conversions were differential. Thus the slope of the line is taken as an approximation of the reaction rate, i.e., 3×10^{-10} mol/(g s). Rate data were reproducible within ±20%.

The change in product distribution with time on stream at 200°C and a propane partial pressure of 0.05 bar is shown in fig. 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%, whereas those at 300°C were only about 15%.

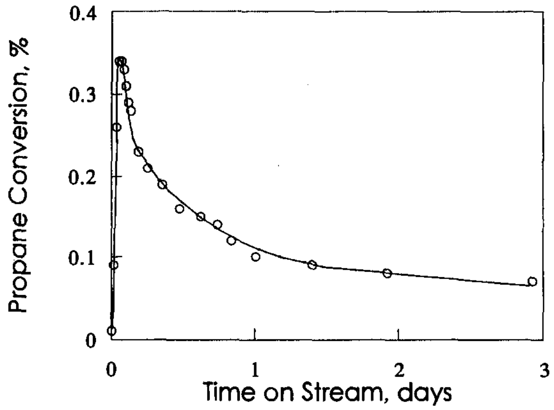

Fig. 1. Conversion of propane to gas-phase products at 200°C in the presence of iron- and manganese-promoted sulfated zirconia. Feed propane partial pressure = 0.05 bar; total feed flow rate = 10 ml(NTP)/min; mass of promoted sulfated zirconia = 2.0 g.

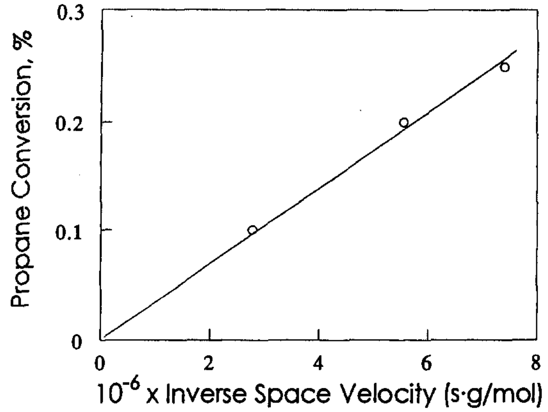

Fig. 2. Differential conversion of propane in the presence of iron- and manganese-promoted sulfated zirconia at 250°C in a flow reactor. Values correspond to the end of the induction period. Feed propane partial pressure = 0.01 bar.

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

Because the reaction rates were extremely low, some of the flow reactor experiments were continued for long times. At 250°C and a propane partial pressure of 0.05 bar, the reaction was carried out with a constant feed flow rate for 16 days, after which the reaction was still proceeding. The number of propane molecules converted to gas-phase products per sulfate group after this time was only 1.0 ± 0.1. Similarly, the number of propane molecules converted to gas-phase products per sulfate group at 200°C and a propane partial pressure of 0.05 bar after

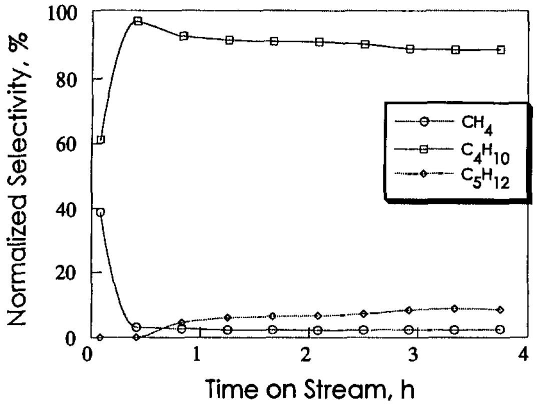

Fig. 3. Normalized selectivity for propane conversion in the presence of iron- and manganese-promoted sulfated zirconia at 200°C. Feed propane partial pressure = 0.05 bar, total feed flow rate = 10 ml(NTP)/min; mass of promoted sulfated zirconia = 2.0 g.

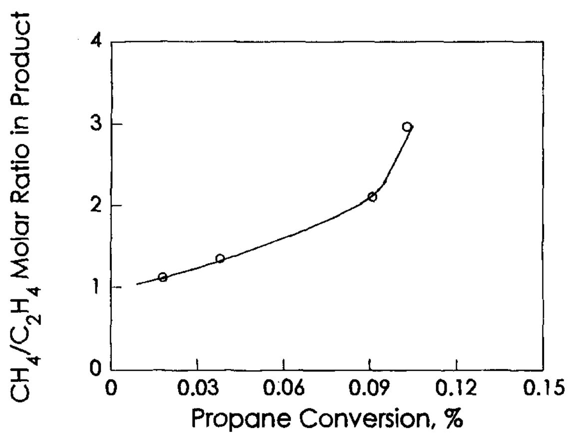

Fig. 4. Methane to ethene molar ratio in the product of propane conversion in the presence of iron- and manganese-promoted sulfated zirconia at 250°C. Feed partial pressure = 0.01 bar; total feed flow rate = 40 ml(NTP)/min; mass of promoted sulfated zirconia = 2.0 g.

5 days of operation was only 0.12 ± 0.02; and at 300°C and a propane partial pressure of 0.01 bar after 5 h of operation the value was only 0.03 ± 0.005. Because the sites of reaction on the surface of the solid are unidentified, these data leave open the question of whether the propane reaction was catalytic.

4. Discussion

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, Olah et al. observed protolysis of C–H and, predominantly, C–C bonds, leading to the formation of methane, ethane, H_2, and carbenium ions. Subsequent reactions of the carbenium ions and propane led to the formation of higher alkylcarbenium ions.

Consistent with the products observed by Olah et al. [3], alkanes and secondary products of (higher) alkylcarbenium ions were observed for propane conversion in the present work. The presumed analogy to Olah superacid chemistry is consistent with the postulate that the solid acid protonates propane to initiate its conversion. Furthermore, the ratio of methane to ethene, which approaches 1 in the limit of zero conversion at 250°C (fig. 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.

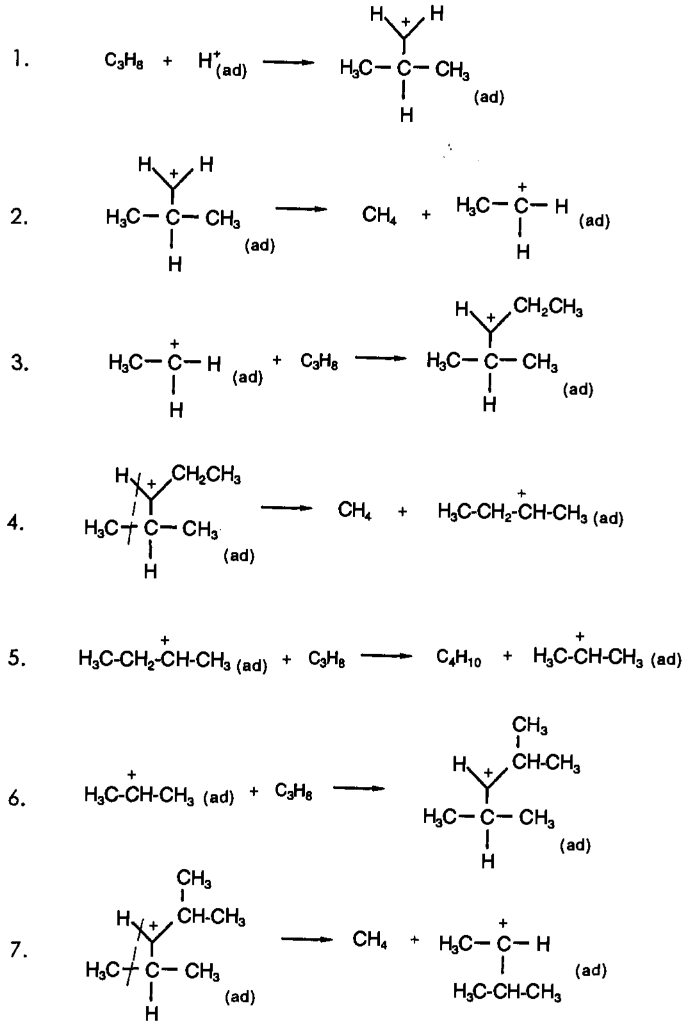

Fig. 5. Reaction network postulated for propane conversion in the presence of iron- and manganese-promoted sulfated zirconia.

Cracking and dehydrogenation of alkanes via protonation, catalyzed by zeolites at temperatures of 400–550°C, has been demonstrated by Haag et al. [13,14]. For example, they observed equimolar yields of ethane and ethene, methane and propene, and H_2 and butenes formed from *n*-butane in the limit of zero conversion [14]. The observation of a comparable cracking product distribution (with a much less reactive alkane) 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, the catalytic activity of the promoted sulfated zirconia for neopentane cracking after 5 min on stream at 450°C is only slightly greater than that of USY zeolite [9], which could be explained by an extremely rapid deactivation of the promoted sulfated zirconia at this temperature, possibly by the blockage of the strongly acidic sites by stable surface species. The issues of acid strength and catalytic activity of these materials for alkane conversion remain to be resolved.

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, with increasing temperature, almost all low-molecular-weight alkanes tend to be converted 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 their combination with a hydride 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 or by disproportionation of butane. The data are explained by the reaction network of fig. 5, which is based on Olah carbocation 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 the chemistry of alkane conversion in the presence of superacid solutions and solid acids largely unresolved.

5. Conclusions

Propane is converted into butanes and pentanes in the presence of iron- and manganese-promoted sulfated zirconia at temperatures as low as 200°C. The observation of these products accompanied by methane suggests that the reactions are initiated by protonation of propane to form carbonium ions, which collapse into methane and ethyl cations, followed by reaction of the ethyl cations with propane. The product distribution is consistent with Olah superacid solution chemistry.

Acknowledgement

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