Methane conversion to ethane in the presence of iron- and manganese-promoted sulfated zirconia

S. Rezgui, A. Liang, T.-K. Cheung and B.C. Gates

Department of Chemical Engineering and Materials Science, University of California, Davis, CA 95616, USA

Received 24 February 1998; accepted 29 April 1998

Sulfated zirconia promoted with 1.0 wt% Fe and 0.5 wt% Mn converts methane into ethane with traces of ethylene and acetylene. The initial reaction rate at 723 K and a methane partial pressure of 20 kPa was found to be about 10^{-9} mol(CH_4)(g s)$^{-1}$, and deactivation was rapid, with the reaction rate declining to half the maximum rate within an hour.

Keywords: methane, sulfated zirconia, promoted sulfated zirconia, ethane

1. Introduction

Sulfated zirconia and promoted sulfated zirconia are acidic and highly active catalysts for light alkane isomerization, potentially being of technological value for low-temperature isomerization of C_4–C_6 alkanes [1–3]. The available data are largely explained in the context of acid–base catalysis, but it is not resolved whether the catalysts incorporate some extremely strong acidic groups, that possibly initiate reactions by protonation of alkanes to form carbonium-ion-like transition states [4–6], or whether the catalysts incorporate only moderately strong acidic groups, catalyzing alkane conversions by protonation of alkenes formed by catalytic [7–9] or stoichiometric [10] dehydrogenation of the alkane. The catalysts are also active for conversion of propane and ethane, with the activity declining roughly an order of magnitude per carbon atom from butane to propane to ethane [3,5,11]. Our goal was to extend the investigation of these catalysts to conversion of the alkane expected to be the least reactive, methane.

2. Experimental

Sulfated zirconia (SZ) was prepared by drying sulfated zirconium hydroxide at 393 K for 24 h followed by impregnation with water by the incipient wetness method, drying at 393 K for 24 h, and calcination in static air at 923 K. Iron- and manganese-promoted sulfated zirconia (FMSZ) containing 1.0 wt% Fe, 0.5 wt% Mn, and 1.8 wt% S was prepared by drying sulfated zirconium hydroxide at 393 K for 24 h followed by impregnation with an aqueous solution of iron and manganese nitrates by the incipient wetness method, drying at 393 K for 24 h, and calcination in static air at 923 K.

Each catalyst was investigated for methane conversion in a once-through stainless-steel flow reactor. Gas-phase products were analyzed with an on-line gas chromatograph. Particles of SZ or FMSZ were placed in the flow reactor and treated in N_2 flowing at 0.5 ml(NTP) s^{-1} at 723 K for 1.5 h, and then flow of methane (containing <5 ppm ethane as the only impurity) was begun. Methane was converted under the following conditions: temperature 673–723 K, pressure 100 kPa, methane partial pressure 50–10 kPa, mass of SZ or FMSZ 1.0–2.0 g, total feed ($CH_4 + N_2$) flow rate 0.17–0.21 ml(NTP) s^{-1}.

3. Results

No methane conversion was observed in the presence of SZ, but with FMSZ in the reactor, methane was converted into ethane and traces of ethylene and acetylene. In the temperature range 623–723 K, conversions $<0.15\%$ were measured. The data obtained at 623 K (figure 1) indicate an increasing conversion followed by a decreasing conversion, consistent with the pattern observed with other light alkanes [4–6,11].

At 723 K and a space velocity of 9.3×10^{-7} mol(CH_4) (g s)$^{-1}$, the number of CH_4 molecules converted per sulfate group was about 0.8, when the experiment was stopped with reaction still occurring after 10 h of continuous operation in the flow reactor. If the number of sulfate groups may be taken as a rough upper-bound estimate of the number of catalytic sites in the promoted sulfated zirconia [5], the results suggest that the reaction at 773 was catalytic.

The rate of methane conversion at 723 K and 20 kPa CH_4 partial pressure is estimated to be 1.4×10^{-9} mol(CH_4) (g(catalyst) s)$^{-1}$ from the initial conversion determined by extrapolation from figure 1, assuming that the conversion was differential. This rate is more than an order of magnitude less than that of ethane conversion under similar conditions with the same catalyst [5,6].

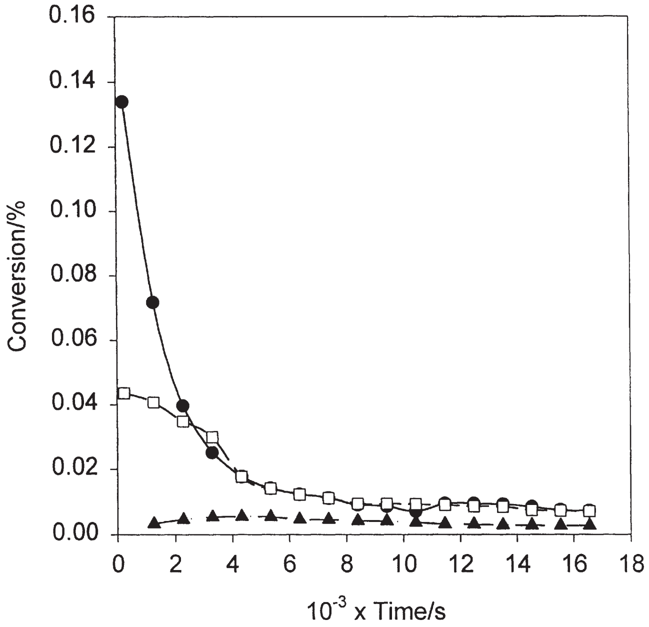

Figure 1. Conversion of methane to ethane catalyzed by iron- and manganese-promoted sulfated zirconia. Feed methane partial pressure 20 kPa, total feed flow rate 0.21 ml(NTP) s^{-1}. (●) 773 K, (□) 673 K, (▲) 623 K.

H_2 was not demonstrated to be a product, and it is considered likely that hydrogen was incorporated in carbonaceous deposits on the surface [12,13].

4. Discussion

The data are not sufficient to determine the nature of the surface reaction. One possibility, suggested by the results characterizing the reactions of the higher-molecular-weight alkanes, is that the methane conversion was catalyzed by acidic groups in the catalyst. An essential question is then how the reaction is initiated [14]; one plausible suggestion is that, consistent with Olah superacid solution chemistry [15–17], methane is protonated by a minority of extremely strongly acidic sites on the catalyst and undergoes oligocondensation reactions to give the observed products. Simple dehydrogenation to give an alkene is not an appropriate suggestion, in contrast to the situation for the higher alkanes. It is also possible that redox chemistry occurs to initiate carbocation reactions [18]. Alternatively, the reactions might somehow be analogous to the methane coupling that is known to take place in the presence of metal oxides at much higher temperatures; this possibility would suggest the involvement of the iron oxide species identified on the surface of the catalyst [19].

Acknowledgement

The work was supported by the University of California Energy Institute.

References

[1] M. Hino and K. Arata, J. Chem. Soc. Chem. Commun. (1980) 851.
[2] X. Song and K. Arata, Catal. Rev. Sci. Eng. 38 (1996) 329.
[3] C.-Y. Hsu, C.R. Heimbuch, C.T. Armes and B.C. Gates, J. Chem. Soc. Chem. Commun. (1992) 1645.
[4] T.-K. Cheung and B.C. Gates, Chem. Commun. (1996) 1937.
[5] T.-K. Cheung and B.C. Gates, J. Catal. 168 (1997) 522.
[6] T.-K. Cheung and B.C. Gates, Topics Catal. 6 (1998) 41.
[7] V. Adeeva, G.D. Lei and W.M.H. Sachtler, Appl. Catal. 118 (1994) L11.
[8] K.T. Wan, C.B. Khouw and M.E. Davis, J. Catal. 158 (1996) 311.
[9] J.E. Tabora and R.J. Davis, J. Am. Chem. Soc. 118 (1996) 12240.
[10] F.C. Lange, T.-K. Cheung and B.C. Gates, Catal. Lett. 41 (1996) 95.
[11] T.-K. Cheung, F.C. Lange and B.C. Gates, J. Catal. 159 (1996) 99.
[12] T.-K. Cheung and B.C. Gates, J. Chem. Soc. Chem. Commun. (1996) 1937.
[13] D. Spielbauer, G.A.H. Mekhemer, E. Bosch and H. Knözinger, Catal. Lett. 36 (1996) 59.
[14] C.J.A. Mota, J. Sommer, M. Hachoumy and R. Jost, J. Catal. 172 (1997) 194.
[15] T.-K. Cheung and B.C. Gates, Chemtech 27 (1997) 28.
[16] G.A. Olah, Y. Halpern, J. Shen and Y.K. Mo, J. Am. Chem. Soc. 95 (1973) 4960.
[17] G.A. Olah, Angew. Chem. 34 (1995) 1393.
[18] A. Ghenciu and D. Fărcaşiu, Chem. Commun. (1996) 169.
[19] M. Scheithauer, E. Bosch, U.A. Schubert, H. Knözinger, T.-K. Cheung, F.C. Jentoft, B.C. Gates and B. Tesche, J. Catal., in press.