Effect of Small Amounts of Ethane on the Selective Oxidation of Methane over Silicic Acid and Quartz Glass Surfaces

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In the reaction between methane and oxygen over silicic acid at 833—893 K the presence of ethane in the feed improved the selectivity for formaldehyde formation and decreased CO production, ethylene also being formed; in the reaction over quartz glass at 913 K the presence of ethane increased the extent of methane conversion, but high proportions (9%) of ethane increased the formation of CO and CO_2.

There has been much recent research on catalytic processes for the selective conversion of methane into intermediate oxidation products rather than the deep oxidation products CO and CO_2.[1] Studies have concentrated mainly on oxidative coupling leading to the formation of ethane and ethylene from methane[2—4] and production of oxygenates such as methanol and formaldehyde[5—8] and several promising catalytic systems have emerged although with low yields of desirable products. The ultimate goal is to obtain a high yield of useful higher hydrocarbons and/or oxygenates from natural gas, the main source of methane.

Besides methane, natural gas also contains higher hydrocarbons such as ethane or propane which are likely to improve the overall oxidation activity because of their relative ease of oxidation with respect to methane. Experimental evidence seems to verify this hypothesis. Gesser *et al.*[9] and Foster[10] report that whenever natural gas or mixtures of methane and ethane were used instead of pure methane, the oxidation reaction was triggered at lower temperatures. Ito *et al.*[2] found that an increase of the ethane concentration over a methane oxidative coupling catalyst (Li^+/MgO) improved the ethylene production. Westbrook and Pitz[11] reported that traces of ethane and propane shortened the ignition time of methane mixtures with air.

In recent work[12] we reported the formation of formaldehyde, ethylene, and ethane from methane with good selectivities over various silica surfaces including Vycor and quartz glass as well as various powdered silicas. A mixture of 10% of methane in argon was used with oxygen as oxidant. The methane to oxygen ratio varied from 2 to 0.1. A g.c. analysis of the methane feed stream, however, revealed an ethane impurity concentration of 0.14 mol% (based on methane in the feed). This prompted us to investigate more closely the effect of small amounts of ethane on the methane conversion and partial oxidation selectivity. We now report our results obtained by varying the amount of ethane in the feed over silicic acid in powder form and over quartz glass in the form of an empty U-tube.

First, we report the results obtained over silicic acid in the temperature range 833—893 K, in which range the reactor walls were inert. Figure 1 shows how the selectivity of the various products varied with increasing methane conversion

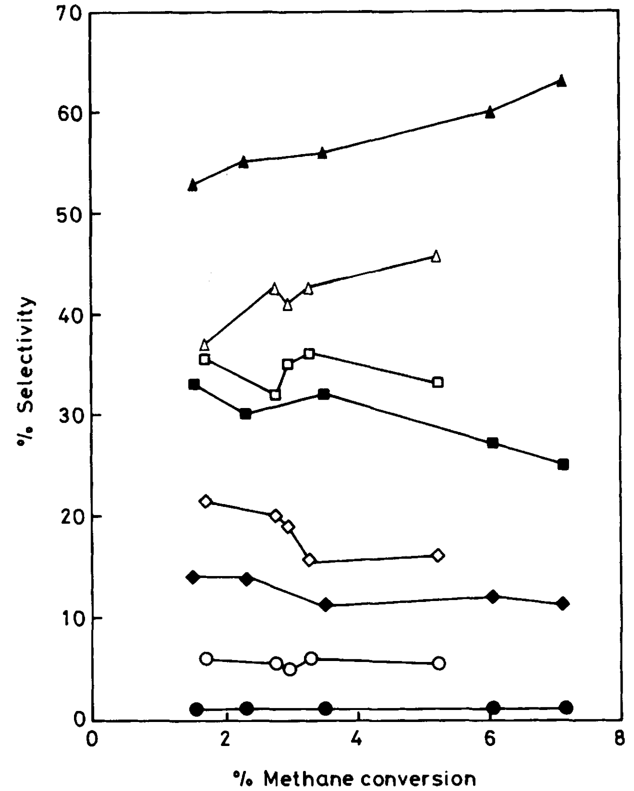

Figure 1. Selectivity (%) for formation of various products *vs.* CH_4 conversion (%) over silicic acid at 833—893 K for two different concentrations of ethane in the methane feed stream: (1) (filled symbols): 10% CH_4 in Ar with 0.14 mol% of ethane (based on CH_4) at a flow rate of 31 cm^3 s.t.p./min, O_2 flow rate = 3 cm^3 s.t.p./min, total pressure = 380 kPa, catalyst weight = 535 mg. (2) (open symbols): 10% CH_4 in Ar with 1.25 mol% of ethane (based on methane) at a flow rate of 50 cm^3 s.t.p./min, O_2 flow rate = 5 cm^3 s.t.p./min, total pressure = 360 kPa, catalyst weight = 504 mg; ●, ○, $C_2{}^=$; ■, □, HCHO; ▲, △, CO; ◆, ◇, CO_2.

when the ethane concentration in the methane feed was changed from 0.14 mol% to 1.25 mol%. Increasing the ethane concentration in the feed enhanced the yield of ethylene, formaldehyde, and CO_2 and suppressed CO production. The most dramatic relative increase occurred in the ethylene selectivity which was 5% in the 1.25 mol% ethane run *vs.* only 1% in the 0.14 mol% ethane run. In the case of 0.14 mol% of ethane in the feed, the contribution of ethane to the formation of the products was less than 1%. In the case of the 1.25 mol% of ethane, however, the contribution was as much as 7%. As a consequence, a portion of the products must have originated from the ethane. In view of the dramatic increase of the ethylene selectivity with increasing ethane concentration it would be reasonable to attribute the ethylene formation mainly to the conversion of the ethane trace in the feed.

The fact that ethane and/or ethylene are oxidized more easily than methane could explain the higher CO_2 production in the case of 1.25 mol% of ethane in the feed. The higher formaldehyde and lower CO selectivities can be explained if we take into account that CO originates mainly from the destruction of formaldehyde. It appears that the ethane and/or ethylene interactions with the surface inhibit the destruction of formaldehyde. At a conversion level of 5% the increase of the ethane percentage in the feed from 0.14 to 1.25% improves the selectivity of useful products (ethylene and formaldehyde) from 30 to 38%.

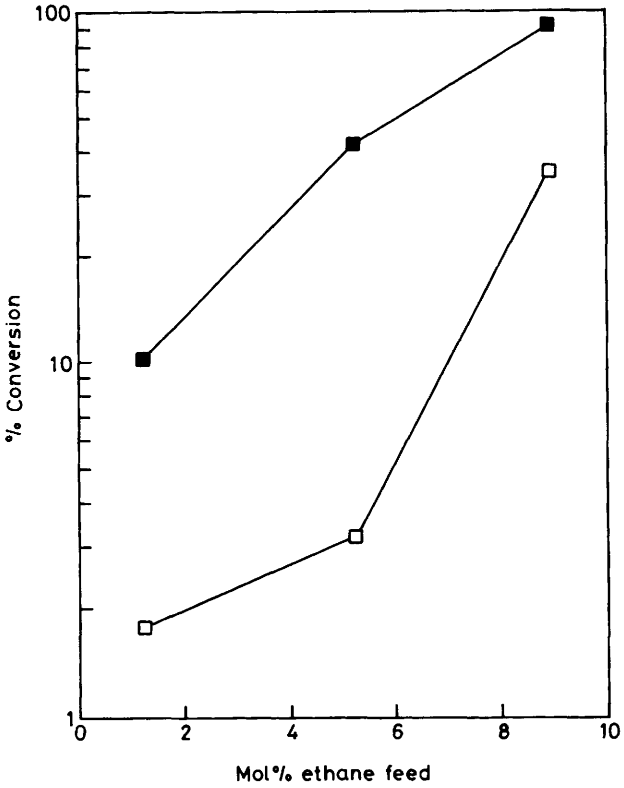

Figure 2. □ Methane and ■ ethane conversions over quartz glass at 913 K and 445 kPa as a function of mol% ethane (based on sum of methane and ethane). The molar ratio of C to O_2 ranged from 0.988 to 1.043.

Ethylene is considered as a primary product of the ethane combustion formed *via* the oxidative dehydrogenation of the $C_2H_5{}^{\bullet}$ radicals, just as formaldehyde is a primary product of the methane combustion formed from the oxidation of $CH_3{}^{\bullet}$ radicals.[13] The $CH_3{}^{\bullet}$ as well as the $C_2H_5{}^{\bullet}$ radicals are generated by hydrogen abstraction which may be induced by interaction of methane or ethane with the silica surface.[12] Therefore, the same silica surfaces that produce formaldehyde from methane can lead to the formation of ethylene from ethane. The conversion of ethane was always 3—5 times higher than the conversion of methane and this is in qualitative agreement with the experimental values of Bohme and Fehsenfeld,[14] who reported that the probability for the first hydrogen abstraction increases with the size of the hydrocarbon chain.

We next summarize the results of the methane oxidation experiments over quartz glass surfaces in the form of empty U-tubes.[12] A 10% methane in Ar mixture, containing 1.25 mol% of ethane (based on methane) was fed at a flow rate of 50 cm^3 STP/min. The ethane concentration was increased further to 5.2 mol% and 8.9 mol%, respectively (based on the sum of methane and ethane) by adding appropriate flowing mixtures of ethane and oxygen. The oxygen flow rate was adjusted for a total carbon to O_2 ratio of *ca.* 1 : 1. The runs were carried out at 913 K and 445 kPa pressure. The results obtained are shown in Figure 2. The presence of ethane in the feed had a dramatic effect on the conversion of methane. By increasing the ethane concentration to 5.2 mol%, the conversion of methane nearly doubled from 1.8 to 3.2%. The ethane conversion also increased from 10 to 40% and always remained higher than the methane conversion. At the highest ethane concentration of 8.9 mol%, almost complete conversion of ethane (90%) and 34.4% conversion of methane occurred. High conversions favoured the CO and CO_2 formation, at the expense of formaldehyde and ethylene.

Ethane, apart from forming $C_2H_5^{\bullet}$ radicals by hydrogen abstraction, is also likely to act as a source of $CH_3^{\bullet}$ radicals formed *via* C–C bond breakage. Experimental data show that the rate of formation of $CH_3^{\bullet}$ radicals from ethane in this way is two orders of magnitude higher than the rate of formation of these radicals from methane.[15] Therefore, the $C_2H_5^{\bullet}$, $CH_3^{\bullet}$ and $H^{\bullet}$ radicals, which are generated more readily from ethane than from methane, could activate methane molecules and/or even interfere in the propagation of the chain reaction steps contributing to methane oxidation or combustion. This could explain the increase in methane conversion as a result of the presence of ethane in the feed stream. Further work on the effect of ethane on the selective oxidation of methane is in progress.

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References

1 R. Pitchai and K. Klier, *Catal. Rev., Sci. Eng.*, 1986, **28**, 13.
2 T. Ito, J.-X. Wang, C.-H. Lin, and J. H. Lunsford, *J. Am. Chem. Soc.*, 1985, **107**, 5062.
3 K. Otsuka, K. Jinno, and A. Morikawa, *J. Catal.*, 1986, **100**, 353.
4 J. A. Sofranko, J. J. Leonard, and C. A. Jones, *J. Catal.*, 1987, **103**, 302.
5 H.-F. Liu, R.-S. Liu, K. Y. Liew, R. E. Johnson, and J. H. Lunsford, *J. Am. Chem. Soc.*, 1984, **106**, 4117.
6 M. M. Khan and G. A. Somorjai, *J. Catal.*, 1985, **91**, 263.
7 K. Otsuka and M. Hatano, *J. Catal.*, 1987, **108**, 252.
8 N. D. Spencer, *J. Catal.*, 1988, **109**, 187.
9 H. D. Gesser, N. R. Hunter and C. B. Prakash, *Chem. Rev.*, 1985, **85**, 235.
10 N. R. Foster, *Appl. Catal.*, 1985, **19**, 1.
11 C. K. Westbrook and W. I. Pitz, *Combustion Science and Technology*, 1983, **33**, 315.
12 G. N. Kastanas, G. A. Tsigdinos and J. Schwank, *Appl. Catal.*, in the press.
13 D. J. Hucknall, 'Chemistry of Hydrocarbon Combustion,' Chapman and Hall, New York, 1985.
14 D. K. Bohme and F. C. Fehsenfeld, *Can. J. Chem.*, 1969, **47**, 2717.
15 W. C. Gardiner, 'Combustion Chemistry,' Springer-Verlag, Heidelberg, 1984.