The oxidative dehydrogenation of ethane with CO_2 over Mo_2C/SiO_2 catalyst

F. Solymosi * and R. Németh

*Institute of Solid State and Radiochemistry of Attila József University and Reaction Kinetics Research Group of the Hungarian Academy of Sciences,** H-6701 Szeged, PO Box 168, Hungary*

Received 3 June 1999; accepted 2 September 1999

Mo_2C prepared on SiO_2 was found to be an effective catalyst for the dehydrogenation of ethane to produce ethylene in the presence of CO_2. The selectivity to ethylene at 850–923 K was 90–95% at an ethane conversion of 8–30%. With the increase of the temperature the dry reforming of ethane became also a significant process. It is assumed that the Mo oxycarbide formed in the reaction between CO_2 and Mo_2C plays an important role in the activation of ethane.

Keywords: oxidative dehydrogenation, ethane, Mo_2C/SiO_2 catalyst, carbon dioxide

1. Introduction

The oxidative dehydrogenation of ethane is an important catalytic process in the production of ethylene [1]. Using O_2, Li/MgO is probably the most effective catalyst [2,3]. A high yield of ethylene production was recently reported for a very rarely applied catalyst, Ho_2O_3, particularly when it was promoted by $BaBr_2$ [4]. By replacing O_2 with N_2O, higher selectivities were obtained on silica-supported MoO_3, molybdates and vanadates [5–12]. On these samples acetaldehyde was also produced, particularly when H_2O was added to the reacting gas mixture. In addition to O_2 and N_2O, CO_2 is also a suitable oxidant, but its use was hardly explored, yet [13–18]. Recently Liu et al. [15] developed a complex catalyst system, Na_2WO_4–Mn/SiO_2, for $C_2H_6 + CO_2$ reaction. They obtained that at 973–1123 K, C_2H_4 was produced with 90–97% selectivity at 18–69% conversion. Longya et al. [16] applied Cr–Mn–Ni and Cr–Mn–La oxide mixtures deposited onto silicate-2 zeolites. At 1073 K the conversion of ethane varied between 58 and 68% and the selectivity to ethylene between 80 and 86%. In the present paper we use Mo_2C/SiO_2 as a catalyst. Mo_2C on ZSM-5 and SiO_2 was found to be an effective catalyst in the aromatization of CH_4 [19–26] and ethane [27]. In the latter case, benzene was produced at 973 K with 31% selectivity at a conversion of 67%.

2. Experimental

Hexagonal Mo_2C was prepared by the method of Boudart et al. [28]. Following their suggestion, the sample was deactivated at 300 K with air or used *in situ* for catalytic studies. The BET surface area of this sample is 9.6 m^2/g. Supported Mo_2C catalyst was prepared by the carburation of calcined MoO_3/SiO_2 in the catalytic reactor, in a similar way as described above for the preparation of bulk Mo_2C. MoO_3/SiO_2 catalyst was prepared by impregnating silica (Cab-O-Sil, area: 200 m^2/g) with a basic solution of ammonium paramolybdate to yield a nominal 2 wt% of MoO_3. The suspension was dried at 373 K and calcined at 873 K for 5 h. The gases used were of commercial purity (Linde). The active sites of the Mo_2C on silica were determined by the adsorption of CO at 300 K. The value obtained is 77.0 μmol/g. Ar (99.996%) and CO_2 (9.999) were deoxygenated with an oxytrap. The other impurities were adsorbed by a 5A molecular sieve at the temperature of liquid nitrogen.

Catalytic reaction was carried out at 1 atm of pressure in a fixed-bed, continuous-flow reactor consisting of a quartz tube connected to a capillary tube [23,27]. The flow rate was in most cases 12 ml/min. The carrier gas was Ar. The ethane content was 12.5%, which was kept constant in all experiments. Generally 0.5 g of loosely compressed catalyst sample was applied. Reaction products were analyzed gas chromatographically with a Hewlett–Packard 5890 gas chromatograph and a Porapak QS column using both the thermal conductivity and flame ionization detectors. The details of the experiments and the calculation of rates of product formation have been described in our previous papers [11,12]. The selectivity values of product formation represent the fraction of ethane that has been converted into specific products taking into account the number of carbon atoms in the molecules. Infrared spectra were recorded with a Biorad Fourier transform IR spectrometer (FTS 155). For IR measurements the MoO_3/SiO_2 sample was pressed into a 10 × 30 mm self-supporting disc, and the carburation of the disc was performed in the infrared cell.

* To whom correspondence should be addressed.
** This laboratory is a part of the Center for Catalysis, Surface and Material Science at the University of Szeged.

3. Results and discussion

First we tested the catalytic effect of pure Mo_2C. The ratio of the gas mixture, CO_2/C_2H_6, was 1.0. At 873 K we measured only a low conversion of 3–4% of ethane. Ethylene was produced with a selectivity of ~40%. Other products were CH_4, H_2, H_2O and CO. Similar measurements were performed on silica which exhibited even lower activity. The selectivity to ethylene was higher, 60–70% at a conversion of 3%. Deposition of Mo_2C on SiO_2 caused a dramatic change in the catalytic performance and produced an effective catalyst for the oxidative dehydrogenation of ethane.

Detailed measurements have been performed at 873 K, with the stoichiometric gas mixture, $CO_2/C_2H_6 = 1.0$. The main products were ethylene, methane, CO, H_2O and H_2. In a very low concentration, propane, pentane and benzene were also found. No acetaldehyde and formaldehyde, the products of selective oxidation of ethane, were identified. Apart from the initial very high value, the conversion of ethane was 15–16% and remained constant for the applied measuring time, 4 h. The rate of ethylene, CO and H_2 production slightly increased with time of stream while that of CH_4 decreased. Ethylene was formed with a high selectivity of 80–87%. Full mass balances (calculated on the basis of the hydrogen contents of the compounds) show a good agreement (with ±2%) with the theoretical value. The conversion of ethane, the rate of the formation of several products and the selectivity values are shown in figure 1. The turnover rate for ethylene formation at the steady state was 2.7×10^{-3} s^{-1}.

Note that MoO_3/SiO_2 exhibited very little catalytic activity for the $C_2H_6 + CO_2$ reaction at 873 K; the conversion remained below 3% and the selectivity to ethylene was only 25–28%. In contrast, Rh/SiO_2 was an active catalyst for this reaction, but instead of the oxidative dehydrogenation of C_2H_6, the production of CO and H_2 was the main route. In the empty reactor the conversion of ethane was less than 1%. In the presence of pure silica support it increased to about 2%.

Variation of the flow rate showed that the conversion of ethane decreased with the rise of space velocity, but the rate of H_2, CO and C_2H_4 formation increased. The selectivity to ethylene only slightly increased, maximum to 78–80%. The yield of ethylene exhibited only a little variation.

The effect of reaction temperature is displayed in figure 2. Products were detected even at 800 K, the conversion of ethane was 6.0%, which gradually increased to 60% at 960 K. The temperature rise was advantageous for the production of H_2 and CO, but it was far not so favorable for ethylene formation. The temperature rise only slightly increased the production of methane (figure 2). At the lowest temperature, the selectivity to ethylene exceeded 90%. At the highest temperature, 963 K, it decreased to 70%.

Taking into account the product ratios and distribution we can say that, in addition to the main process,

$$C_2H_6 + CO_2 \rightleftharpoons C_2H_4 + CO + H_2O$$

we can also count the dehydrogenation of ethane

$$C_2H_6 \rightleftharpoons C_2H_4 + H_2$$

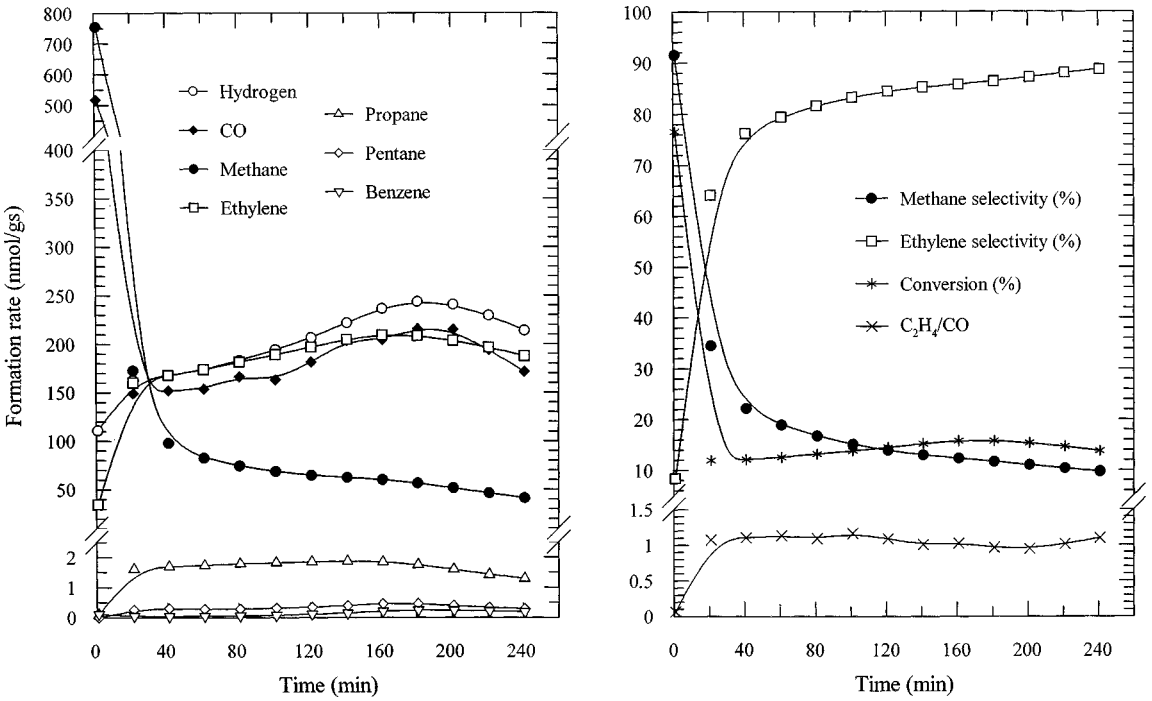

Figure 1. Conversion of ethane, the rate of formation of various products and the selectivity of ethylene production on Mo_2C/SiO_2 on time of stream at 873 K. C_2H_6/CO_2 ratio is 1 : 1.

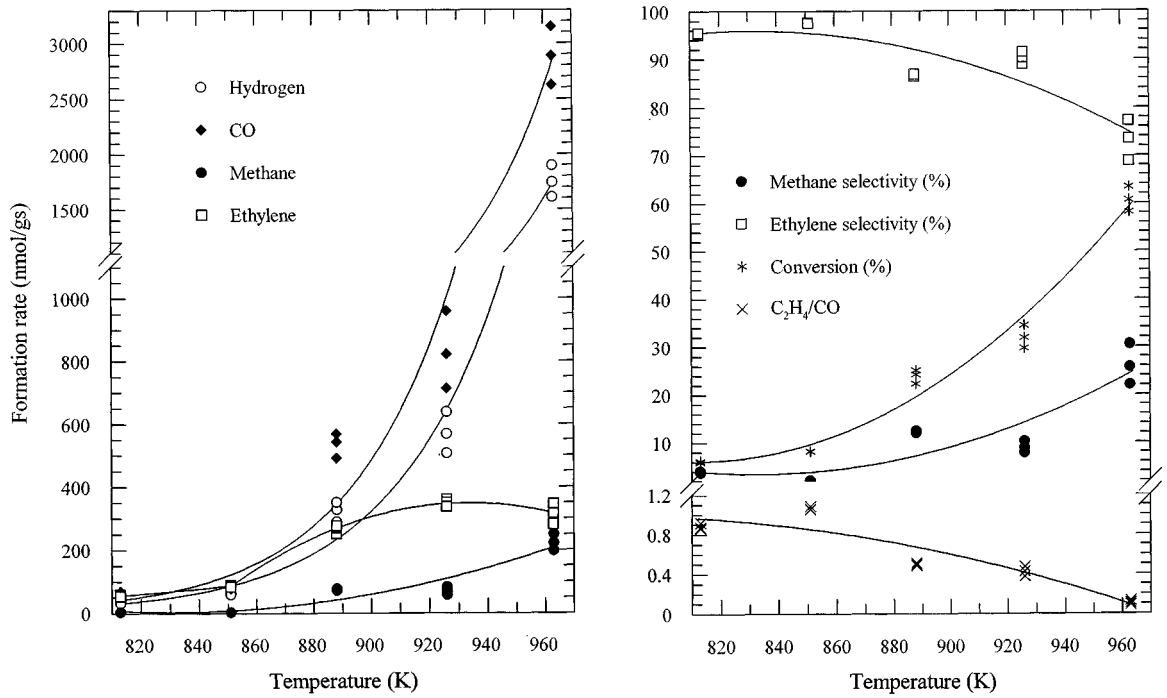

Figure 2. Effects of temperature on the conversion of ethane, rate of formation of various products and selectivity of product formation on Mo_2C/SiO_2. C_2H_6/CO_2 ratio is 1 : 2.7.

and the dry reforming of ethane

$$C_2H_6 + 2CO_2 \rightleftharpoons 4CO + 3H_2$$

producing synthesis gas. This latter process comes into prominence at high temperature as indicated by the significant decrease in the C_2H_4/CO ratio from 0.9 measured at 800 K, to 0.3–0.2 determined at 963 K. The cracking of ethane into other hydrocarbons,

$$C_2H_6 + H_2 \rightleftharpoons 2CH_4$$

also proceeds, which is not very much influenced by CO_2.

In order to understand the surface process occurring during the reaction, we performed FTIR spectroscopic measurements on the interaction of C_2H_6 with the catalyst. The following approach was used: 10 Torr of ethane was contacted with the catalyst for 10 min at 300 K, then the cell was degassed and spectra were registered as a function of temperature. We found a weak absorption band at 1342 cm^{-1}, and extremely weak ones at 2800 and 2878 cm^{-1}. The intensities of these bands decreased with the rise of the temperature, and disappeared completely above 473 K. Taking into account the results of previous IR spectroscopic studies on the adsorption of ethane and ethylene [29,30], we attribute these bands to the vibrations of ethylidyne. This adsorbed species is very likely produced through the dehydrogenation of ethane, and then ethylene transitorily formed. Note that the ethylidene was also detected in the interaction of ethane with Pt/SiO_2 [29,30] and Rh/ZSM-5 [31] catalysts.

The interaction of CO_2 with the Mo_2C/SiO_2 catalyst was also investigated. We could not detect any absorption bands due to the adsorbed CO_2 at 300–500 K after degassing the sample. A partial oxidation of Mo_2C with CO_2 was observed at 773 K, the extent of which increased with the temperature. Note that the Mo oxycarbide and oxides can be converted with ethane readily to Mo_2C above 773 K [27].

Taking into account these results, we assume that the first step in the oxidative dehydrogenation process is the partial oxidation of Mo_2C with CO_2 and the formation of Mo oxycarbide. Ethane will react with this activated oxygen attached to Mo to produce ethylene and water. We cannot exclude the other route, the activation of ethane molecule on Mo_2C and the stepwise dehydrogenation of C_2H_6 to C_2H_4. CO_2 then reacts with H_2 to produce CO and water. The side reaction (hydrogenolysis of ethane) may also occur, but the reaction of H_2 with CO_2 reduces its extent. Further investigations are needed to elaborate the exact mechanism of the reaction.

Acknowledgement

This work was supported by the Hungarian Academy of Sciences and by OTKA 022869.

References

[1] H.H. Kung, in: *Transition Metal Oxides: Surface Chemistry and Catalysis*, Studies in Surface Science Catalysis, Vol. 45, eds. B. Delmon and J.T. Yates (Elsevier, Amsterdam, 1989).
[2] D. Wang, M.P. Rosynek and J.H. Lunsford, J. Catal. 151 (1995) 155.
[3] S.J. Conway and J.H. Lunsford, J. Catal. 131 (1991) 513.
[4] C.T. Au, K.D. Chen, H.X. Dai, Y.W. Liu, J.Z. Luo and C.F. Ng, J. Catal. 179 (1998) 300.
[5] E.M. Thorsteinson, T.P. Wilson, F.G. Young and P.H. Kasai, J. Catal. 52 (1978) 116.

[6] M. Iwamoto, T. Taga and S. Kagawa, Chem. Lett. (1982) 1496.
[7] L. Mendelovici and J.H. Lunsford, J. Catal. 94 (1985) 37.
[8] E. Iwamatsu, K. Aika and T. Onishi, Bull. Chem. Soc. Jpn. 59 (1986) 1665.
[9] A. Erdőhelyi and F. Solymosi, Appl. Catal. 39 (1988) L11.
[10] A. Erdőhelyi and F. Solymosi, J. Catal. 123 (1990) 31.
[11] A. Erdőhelyi and F. Solymosi, J. Catal. 129 (1991) 497.
[12] A. Erdőhelyi and F. Solymosi, J. Catal. 135 (1992) 563.
[13] K.H. Steinberg, U. Mroczek and F. Roessner, Appl. Catal. 66 (1990) 37.
[14] F. Roessner, O. Klepel and A. Hagen, Stud. Surf. Sci. Catal. 107 (1997) 517.
[15] Y. Liu, J. Xue, X. Liu, R. Hou and S. Li, Stud. Surf. Sci. Catal. 119 (1998) 593.
[16] X. Longya, L. Liwu, W. Qingxia, Y. Li, W. Debao and L. Weichen, Stud. Surf. Sci. Catal. 119 (1998) 605.
[17] F. Solymosi, A. Szőke and L. Egri, Topics Catal. 8 (1999) 249.
[18] N. Minura and M. Sito, Catal. Lett. 58 (1999) 59.
[19] L. Wang, L. Tao, M. Xie, G. Xu, J. Huang and Y. Xu, Catal. Lett. 21 (1993) 35.
[20] Y. Xu, L. Wang, M. Xie and X. Gou, Catal. Lett. 30 (1995) 135.
[21] F. Solymosi, A. Erdőhelyi and A. Szöke, Catal. Lett. 32 (1995) 43.
[22] F. Solymosi and A. Szöke, Catal. Lett. 39 (1996) 157.
[23] F. Solymosi, J. Cserényi, A. Szöke, T. Bánsági and A. Oszkó, J. Catal. 165 (1997) 150.
[24] J.H. Lunsford, M.P. Rosynek and D.W. Wang, Stud. Surf. Sci. Catal. 107 (1997) 257.
[25] D. Wang, J.H. Lunsford and M.P. Rosynek, Topics Catal. 3 (1996) 299.
[26] D. Wang, J.H. Lunsford and M.P. Rosynek, J. Catal. 169 (1997) 347.
[27] F. Solymosi and A. Szöke, Appl. Catal. A 166 (1998) 225.
[28] J.S. Lee, S.T. Oyama and M. Bondart, J. Catal. 106 (1987) 125.
[29] C. De La Cruz and N. Sheppard, J. Catal. 127 (1991) 445.
[30] N. Sheppard, Ann. Rev. Phys. Chem. 39 (1988) 589, and references therein.
[31] F. Solymosi, A. Szöke and L. Óvári, J. Catal., in press.