Novel Catalysts for Carbon Dioxide-induced Selective Conversion of Methane to C_2 Hydrocarbons

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(Received April 15, 2002; CL-020327)

The combination of Mn with $BaCO_3$ leads to active catalysts for carbon dioxide-induced selective conversion of methane to ethane and ethylene in the absence of oxygen.

The development of new routes for effective utilization of methane and carbon dioxide is of great interest in chemistry. In last two decades, a large amount of research papers have been published on the oxidative coupling of methane with O_2 to produce C_2 hydrocarbons (ethane and ethylene) and a number of catalysts have been found for this reaction.[1,2] The inevitable formation of CO_2, however, seems to be one of the most serious problems from a practical point of view.[3] A novel approach is to use CO_2 as an oxidant instead of O_2, CO will be the only by-product in this case. Moreover, unlike O_2, CO_2 will not induce gas-phase radical reactions, which result in the decrease in C_2 selectivity, it thus can be expected that the development of active catalyst achieves high selectivity to C_2 hydrocarbons.

Recently, some workers have attemped the CO_2-induced selective conversion of methane to C_2 hydrocarbon. The catalytic effectiveness of more than 30 metal oxides have been reported,[4,5] and a series of binary oxide catalysts have also been reported.[6–9] Unfortunately, there are very few reports on the Mn-containing catalysts, although Mn is one of the most extensively studied components in oxidative coupling of methane. Recently, methane conversion to C_2 hydrocarbons with CO_2 over unsupported MnO_2 catalyst was reported, but only 0.1–0.4% C_2 yield was obtained.[10] The present paper reports a novel effective Mn-containing catalyst, Mn–$BaCO_3$.

The catalysts with different Mn/Ba atomic ratios were prepared by simultaneously adding the solutions with appropriate concentration of $Mn(NO_3)_2$(A.R), $Ba(NO_3)_2$(A.R) to 1.1 times its stoichiometric requirement of a well stirred 0.5 M aqueous solution of K_2CO_3 maintained at 65 °C, the resulting slurry (pH of about 7.0) was filtered and washed several times with distilled water, the product was calcined at 900 °C after dried at 110 °C overnight, then the catalyst was crushed and sieved 20–40 mesh. The granular catalyst was first pretreated with air in a Y-type quartz reactor (I.D. 9.5 mm), followed by replacement with high pure N_2. Then, a mixture of CH_4 and CO_2 was introduced to the reactor. The standard reaction conditions were as follows: $t = 875$ °C, $P(CH_4) = 30.3$ kPa, $P(CO_2) = 70.7$ kPa, total flow rate $= 100\ cm^3 \cdot min^{-1}$, 3.0 g catalyst was used.

After removal of H_2O from the effluent, C_2H_6, C_2H_4, CO, and H_2 were analyzed with an on-line gas chromatograph. The following reactions were taken into account for data processing:

$$2CH_4 + CO_2 = C_2H_6 + CO + H_2O \quad (1)$$

$$2CH_4 + 2CO_2 = C_2H_4 + 2CO + 2H_2O \quad (2)$$

$$CH_4 + 3CO_2 = 4CO + 2H_2O \quad (3)$$

$$CH_4 + CO_2 = 2CO + 2H_2 \quad (4)$$

The data processing method has been described in reference 4.

The effect of Mn/Ba ratio on the catalytic performance of Mn–$BaCO_3$ is shown in Table 1. As may be seen, MnO_2 alone exhibited high CH_4 conversion of 9.8% with very low C_2 selectivity of 6.3%. It is very interesting that $BaCO_3$ alone showed no obvious catalytic effectiveness for the reaction. For the Mn-$BaCO_3$ catalysts, CH_4 conversion decreased to some extent compared with that of MnO_2, but C_2 selectivity and yield increased dramaticaly. The fact that not only C_2 selectivity but also C_2 yield for the Mn–Ba catalysts is higher than that for each component showed that obvious synergistic interaction in C_2 formation exists between MnO_2 and $BaCO_3$.

Table 1. Catalytic activity for the conversion of CH_4 by CO_2

Catalyst	CH_4 Conv./%	C_2H_4 Sel./%	C_2H_6 Sel./%	C_2 Yield/%
$BaCO_3$	0	—	—	—
Mn/Ba(0.2)	3.5	23.1	48.3	2.6
Mn/Ba(0.4)	5.5	28.4	45.2	4.0
Mn/Ba(0.6)	5.8	29.9	41.6	4.1
Mn/Ba(0.8)	6.2	24.7	35.4	3.7
Mn/Ba(1.0)	6.8	17.4	30.8	3.4
Mn/Ba(2.0)	8.1	15.0	23.2	3.0
MnO_2	9.8	1.1	5.2	0.6

All the data were obtained after 3 h reaction under the standard reaction conditions.

Figure 1 shows the temperature dependence of the catalytic performance of Mn–$BaCO_3$ catalyst with Mn/Ba ratio of 0.6. As shown in Figure 1, CH_4 conversion and C_2 yield increased with the increase of reaction temperature, C_2 selectivity increased with the reaction temperature at $\leqslant$825 °C, the increase in reaction temperature decreased C_2 selectivity when the temperature exceeded 825 °C. CH_4 conversion of 5.8% and 8.0% was attained at 875 °C and 900 °C respectively, while C_2 selectivity was 71.5% and 58.8%. The C_2H_4/C_2H_6 ratio in C_2 hydrocarbons was not shown in Figure 1, but the selectivity of C_2H_4 and C_2H_6 was shown respectively, the results show that the C_2H_4/C_2H_6 ratio increased with the increase of reaction temperature.

The change in reaction performance with time on stream is shown in Figure 2, where the catalyst with Mn/Ba ratio of 0.6 is used. As may be seen, conversion of CH_4 and CO_2 and selectivity of C_2 reached a steady state after reaction of ca. 1.5 h and not change even after 20 h. Such the stable performance of the Mn–$BaCO_3$ catalyst after 1.5 h suggests that the C_2 hydrocarbons are from the reaction of CH_4 with CO_2, not with lattice oxygen atom. To verify this point, the fresh catalyst and the catalyst after reaction of 2 h, 10 h, 20 h was subjected to XRD measurement. As shown in Table 2, the crystalline phase of the fresh catalyst was

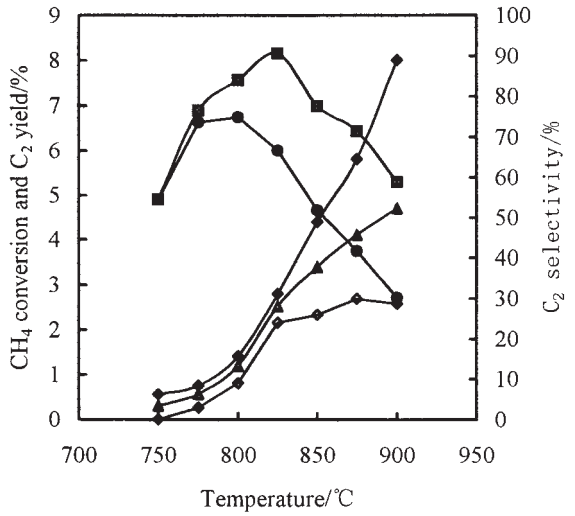

Figure 1. Dependence of cayalytic peformance on reaction temperture. Symbols: (◆)CH_4 conversion; (▲)C_2 yield; (■)C_2 selectivity; (●)C_2H_6 selectivity; (◇)C_2H_4 selectivity.

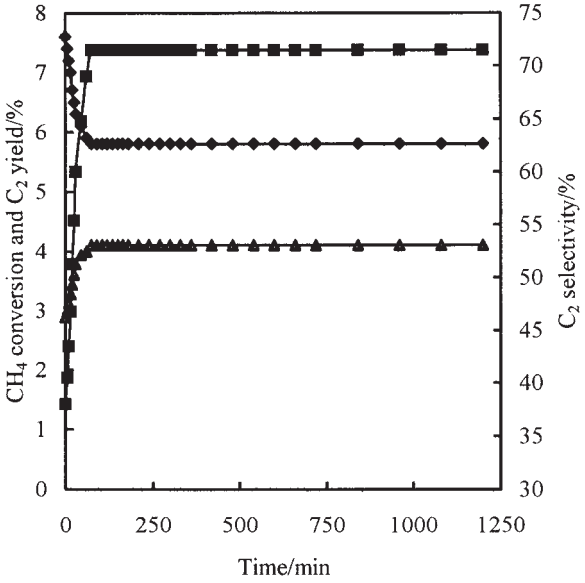

Figure 2. Change in catalytic performance of MnO_2–$BaCO_3$ with time on stream. Symbols: the same as Figure 1. Standard reaction conditions.

Table 2. XRD results of MnO_2–$BaCO_3$ catalyst with Mn/Ba ratio of 0.6

Time/h	Crystalline phase
0	$BaCO_3$ $BaMnO_3$
2	$BaCO_3$ MnO
10	$BaCO_3$ MnO
20	$BaCO_3$ MnO

$BaCO_3$ and $BaMnO_3$. $BaCO_3$ and MnO were detected after 2 h reaction but $BaMnO_3$ was no longer detected. It is obvious that under the reaction conditions, $BaMnO_3$ changed into $BaCO_3$ and MnO. The XRD peaks of MnO are very small, this may attribute to the high dispersion of Mn component. Although the Mn in the catalyst is reduced from Mn^{4+} to Mn^{2+} at the intial 2 h, the crystalline phase at 2 h didn't change during further reaction, so it is reasonable to deduce that no lattice oxygen of the catalyst takes part in C_2 formation.

Figure 3 shows dependence of the peformance of Mn–$BaCO_3$ catalyst on $P(CO_2)$. All the data in Figure 3 were obtained after 3 h reaction. The considerable increase in C_2 selectivity with increasing $P(CO_2)$ was observed. The observations pointed out that CO_2 plays a crucial role in the selective formation of C_2 hydrocarbons over Mn–$BaCO_3$ catalyst.

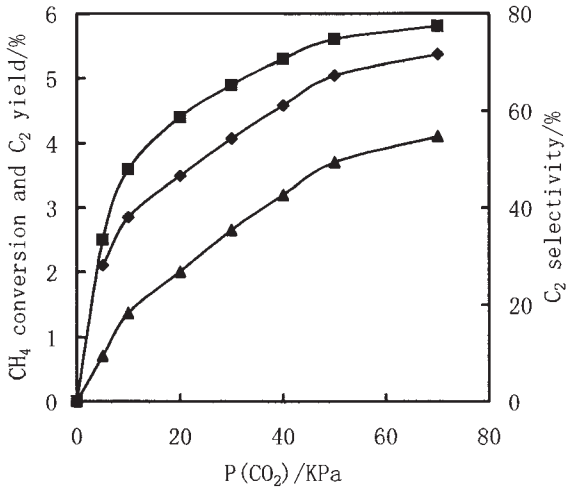

Figure 3. Dependence of catalytic activity on partial pressure CO_2 over the catalyst with Mn/Ba ratio of 0.6. Symbols: the same as Figure 1.

The mechanism of C_2 formation over the Mn–$BaCO_3$ catalyst is proposed as follows: CO_2 may first be chemisorbed on the sites with strong basicity, this may be the Ba sites, the fact that C_2 selectivity increased with $P(CO_2)$ may partly verify this point. The CO_2 chemisorbed may then be activated on reduced Mn sites by accepting electrons to produce CO and active oxygen species O^-, then the active oxygen species reacts with CH_4 to form C_2 hydrocarbons. The C_2 selectivity increase with $P(CO_2)$ may suggest that high $P(CO_2)$ increases the amount of the CO_2 chemisorbed, consequently inhibit the reaction via the redox mechanism involving the lattice oxygen and thus leads to high C_2 selectivity, keeping CH_4 conversion almost constant.

References

1 J. H. Lunsford, *Angew. Chem., Int. Ed. Engl.*, **34**, 970 (1995).
2 S. B. Li, *Chin. J. Chem.*, **19**, 16 (2001).
3 J. H. Lunsford, *Stud. Surf. Sci. Catal.*, **81**, 1 (1994).
4 K. Asami, T. Fujita, K. Kusakabe, Y. Nishiyama, and Y. Otsuka, *Appl. Catal., A*, **126**, 245 (1995).
5 K. Asami, T. Fujita, N. Ashi, and Y. Otsuka, *Stud. Surf. Sci. Catal.*, **107**, 279 (1997).
6 C. L. Chen, Y. D. Xu, G. J. Lin, and X. X. Guo, *Catal. Lett.*, **42**, 149 (1996).
7 Y. Wang, Y. Takahashi, and Y. Ohtsuka, *Chem. Lett.*, **1998**, 1209.
8 Y. Wang, Y. Takahashi, and Y. Ohtsuka, *J. Catal.*, **186**, 160 (1999).
9 Y. Wang and Y. Ohtsuka, *J. Catal.*, **192**, 252 (2000).
10 K. Asami, T. Fujita, K. Kusakabe, Y. Nishiyama, and Y. Otsuka, *J. Jpn. Petrol. Inst.*, **39(2)**, 137 (1996).