Effective Catalysts for Conversion of Methane to Ethane and Ethylene Using Carbon Dioxide

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The combination of CaO with Cr_2O_3 leads to active catalysts for selective conversion of methane to ethane and ethylene by carbon dioxide in the absence of oxygen.

A large variety of catalysts have been reported for the oxidative coupling of CH_4 by O_2 to produce C_2 hydrocarbons (C_2H_6 and C_2H_4). The inevitable formation of CO_2, however, seems to be one of the most important issues from a practical point of view.[1] Use of CO_2 as an oxidant instead of O_2 can remove such side reactions, and thus the increase in C_2 selectivity would be expectable. Only a few attempts on this topic have been made,[2,3] and the results observed indicate that an active catalyst with high selectivity and long life should be developed. For this purpose, recently, our research group has systematically investigated the catalytic activity of more than 30 metal oxides for the conversion of CH_4 by CO_2 and has shown that, among these oxides, Pr and Tb oxides, which possess both redox ability and basicity, give the highest C_2 yield of 1.5% at CH_4 conversion of 3.5% at 850 °C.[4] The observations also suggest that redox property may activate CO_2 for the conversion of CH_4 and that basicity may control C_2 selectivity. It can thus be expected that a combination of two metal oxides with different functions, high redox potential and strong basicity, may provide an active catalyst for C_2 formation. The present paper reports a novel binary catalyst, CaO-Cr_2O_3.

The catalysts with different atomic ratios of Ca/Cr were prepared by impregnating powdery Cr_2O_3 with $Ca(NO_3)_2$ aqueous solution. The resultant was calcined at 850 °C in an air flow after water was evaporated at 90 °C. The granular catalyst was first pretreated with air in a cylindrical quartz reactor, followed by replacement with pure He. Then, a mixture of CH_4 and CO_2 was introduced to the reactor. The standard reaction conditions were as follows: T= 850 °C, $P(CH_4)$= 30.3 kPa, $P(CO_2)$= 70.7 kPa, total flow rate= 100 cm^3 min^{-1}, catalyst weight= 2 g.

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

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

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

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

$$CH_4 + CO = 2CO + 2H_2 \qquad (4)$$

Since CO arises from both CH_4 and CO_2, the CO from CH_4 is first calculated by the stoichiometry of the above four equations, as reported previously.[4] Then, CH_4 conversion and C_2 selectivity are evaluated on the basis of the amounts of CH_4, C_2H_6, C_2H_4, and CO in the effluent.

The effect of Ca/Cr ratio on the catalytic performance of CaO-Cr_2O_3 is shown in Table 1. As observed earlier,[4] Cr_2O_3 alone exhibited high CH_4 conversion of 18% without C_2 formation, whereas CaO alone provided very low conversion. Compared with Cr_2O_3 alone, for the binary oxides, CH_4 conversion decreased to some extent, but C_2 selectivity and yield increased drastically. The yield at Ca/Cr of 0.5 was about 3 times that observed for the best single catalysts such as Pr and Tb oxide. It should be noted that not only C_2 selectivity but also C_2 yield for the Ca-Cr oxides is higher than that for each component. It is therefore evident that synergy effect in C_2 formation exists between CaO and Cr_2O_3.

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

Catalysts	CH_4 conv./%	C_2 select./%	C_2 yield/%
Cr_2O_3	18	0	0
Ca/Cr (0.5)	6.6	61	4.0
Ca/Cr (1.0)	6.3	64	4.0
Ca/Cr (2.0)	5.1	71	3.7
CaO	0.13	50	0.06

All the data were obtained after 2 h reaction under standard reaction conditions.

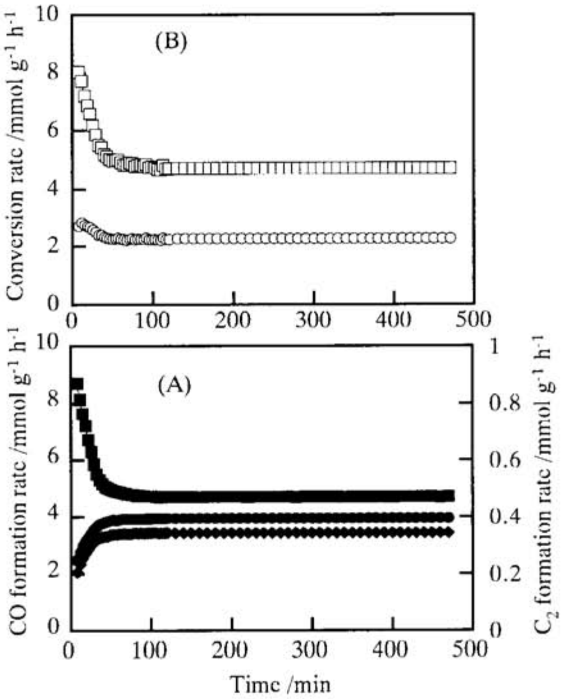

Figure 1. Reaction profiles over the binary catalyst with Ca/Cr ratio of 0.5.
(○). CH_4; (□). CO_2; (●). C_2H_6; (◆). C_2H_4; (■). CO.
Standard reaction conditions.

Changes in conversion of reactants and formation of products are shown in Figure 1, where the catalyst with Ca/Cr of 0.5 is used. Although not shown in the figure, a large amount of H_2O was formed for the initial 5 min, and the concentration of CO_2 in the effluent was also increased. These were due to the reduction of the catalyst with CH_4. After 5 min, CO_2 was consumed, and CO, C_2H_6 and C_2H_4 were detected. CH_4 and CO_2 conversion and formation of these products reached a steady state after ca. 1 h and did not change even after 8 h.

Such the stable performance of the binary catalyst after 1 h strongly suggests that C_2 formation at the steady state proceeds through the reaction of CH_4 with CO_2, not with lattice oxygen atoms. To verify this point, the catalyst before reaction (i.e., after pretreatment at 850 °C) and after 1 or 8 h reaction was quenched to room temperature and immediately subjected to X-ray diffraction measurements. Although the Cr in the catalyst was reduced from 6+ to 3+ for the initial 1 h, as shown in Table 2, the crystalline phase at 1 h did not change during further reaction. It is thus reasonable to conclude that the lattice oxygen of the binary catalyst does not take part in C_2 formation after 1 h. In fact, no significant amounts of C_2 hydrocarbons were observed when CH_4 alone was passed over the catalyst, though CO was mainly formed for ca. 1 h.

Table 2. XRD results of $CaO-Cr_2O_3$ catalyst with Ca/Cr ratio of 0.5

Time /h	Crystalline phase
0	$CaCrO_4$, Cr_2O_3
1	$Ca(CrO_2)_2$
8	$Ca(CrO_2)_2$

Figure 2 shows the change of catalytic results with partial pressure of CO_2, $P(CO_2)$. All the data in this figure were obtained at a steady state (after 3 h reaction). C_2 selectivity increased remarkably with increasing $P(CO_2)$, but CH_4 conversion leveled off at high $P(CO_2)$. It should be noted that CO_2 plays a key role in achieving high C_2 selectivity and that product selectivity in partial oxidation reactions increases with partial pressure of an oxidant.

The mechanism of C_2 formation over the binary catalyst of Ca and Cr is proposed as follows; CO_2 may first be chemisorbed on Ca sites with strong basicity. This would be supported by higher C_2 selectivity at high $P(CO_2)$ (Figure 2) and by the absence of crystalline $CaCO_3$ after reaction (Table 2). The CO_2 chemisorbed may then be activated on reduced Cr sites by accepting electrons to produce simultaneously CO and active oxygen species (e.g. adsorbed O^-), which subsequently reacts with CH_4 to form C_2 hydrocarbons. It is likely that high $P(CO_2)$ increases the amount of the CO_2 chemisorbed, consequently suppresses undesirable site reactions of CH_4 and lattice oxygen atoms to yield CO, and finally leads to high C_2 selectivity with keeping CH_4 conversion almost constant (Figure 2).

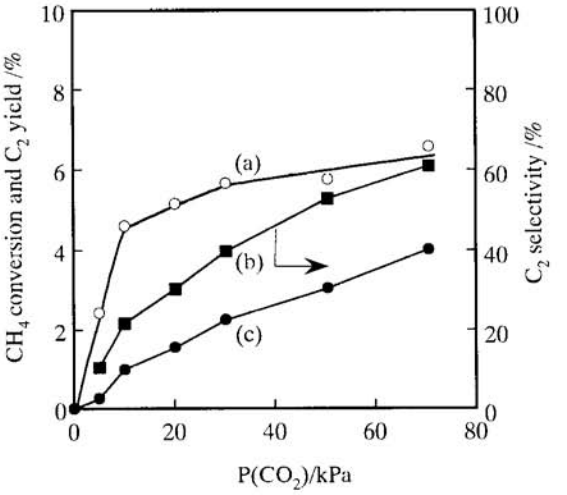

Figure 2. Catalytic activity as a function of partial pressure of CO_2 over the catalyst with Ca/Cr ratio of 0.5. (a) CH_4 conversion, (b) C_2 selectivity, (c) C_2 yield.

References and Notes

1 J. H. Lunsford, *Angew. Chem., Int. Ed. Engl.*, **34**, 970 (1995).

2 K. Aika and T. Nishiyama, *J. Chem. Soc., Chem. Commun.*, **1988**, 70; T. Nishiyama and K. Aika, *J. Catal.*, **122**, 346 (1990).

3 K. Asami, T. Shikada, and K. Fujimoto, *Bull. Chem. Soc. Jpn.*, **64**, 266 (1991).

4 K. Asami, K. Kusakabe, N. Ashi, and Y. Ohtsuka, *Appl. Catal. A: General*, **126**, 245 (1995); K. Asami, K. Kusakabe, N. Ashi, and Y. Ohtsuka, *Appl. Catal. A: General*, **156**, 43 (1997).