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Oxidative Coupling of Methane over a Li_2O - BeO System Catalyst

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The lithium-added beryllium oxide was studied as a catalyst for the oxidative coupling of methane. For example, 3 mol% Li-added BeO catalyst gave 813 mmol h^{-1} g^{-1} of C_2- STY and 63% of selectivity under the reaction conditions of 760 °C, $P(CH_4)$ = 76.0 kPa, $P(CH_4)/P(O_2)$ = 3 and W/F = 0.0033 g h l^{-1}. The compound oxide $Li_2Be_2O_3$ was formed by Li_2O mixed with BeO at 700 °C. This compound oxide might be an active catalyst for the oxidative coupling of methane.

Since Ito et al.[1] reported that lithium-promoted magnesium oxide is an effective catalyst for the oxidative coupling of methane, Otsuka et al.[2] and Okazaki et al.[3] have published papers reporting that the addition of Li_2O to an active catalyst, Sm_2O_3 and BaO-CaO, respectively, enhances the activity and selectivity of this reaction. We reported that Li_2O-promoted ZnO catalyst also has a high activity and selectivity for the oxidative coupling of methane.[4]

In this communication, we report the results of oxidative coupling of methane over lithium-added beryllium oxide with a Wurzite structure similar to zinc oxide.

The Li-added BeO catalysts were prepared as follows; a specified quantity of lithium carbonate was added to a suspension of commercially available BeO in distilled water. This was heated to 100 °C with vigorous stirring and evaporated to dryness. The dried substance was calcinated at 800 °C for 4 h. By this method, six catalysts with 1, 3, 7, 12.5, 20, and 50 mol% Li in BeO were prepared. X-ray diffraction (XRD) results for Li-added BeO are shown in Fig.1. They indicate that the oxide is a mixture of BeO and the compound oxide $Li_2Be_2O_3$.[5]

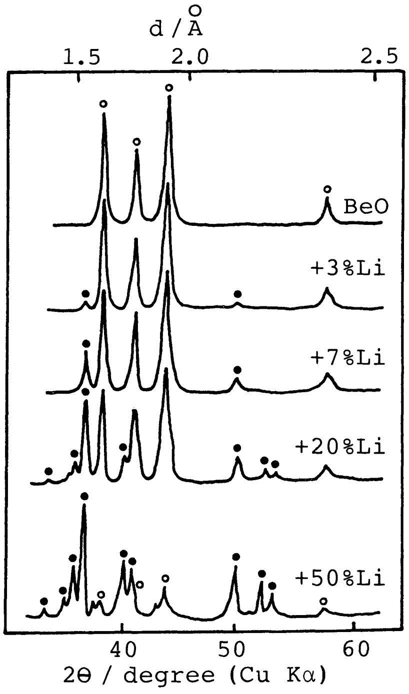

Fig. 1. XRD spectra of Li_2O-BeO system catalyst. ○, BeO; ●, $Li_2Be_2O_3$.

The catalytic experiments were carried out in a fixed bed reactor at a constant flow rate, 50 ml/min, of the mixed gas of CH_4, O_2, and He under the pressure of one atmosphere. Figures 2 - a, b, and c show the results obtained from the reaction performed in the temperature range of 600 to 800 °C using 0.1 g BeO, 3 mol% Li - BeO and 50 mol% Li - BeO ($Li_2Be_2O_3$), respectively. The reactions were carried out under the partial pressures of 35 kPa of CH_4 and 16.5 kPa of O_2. The activity of unpromoted BeO for the methane oxidation was not so high with the selectivity for C_2-compounds, including C_2H_4 and C_2H_6, being rather low. Using 3 mol% Li - BeO as the catalyst, some C_2-compounds were already produced at 600 °C with the reaction proceeding until the yield of C_2-compounds attained approximately 22%. The consumption of O_2 by this time was more than 95%. The selectivity of C_2-compounds increased as the temperature was raised. After the selectivity reached the maximum of 60% at 680 °C, it gradually dropped as the temperature was further increased. The catalytic activity of $Li_2Be_2O_3$ was not so high as that of 3 mol% Li - BeO but the selectivity for C_2-compounds reached the maximum of 65% at 740 °C.

To examine the effects of the $Li_2Be_2O_3$, catalytic runs were performed at 740 °C using various amounts of catalyst composed of differing proportion of Li, until about 80% of the oxygen had been consumed. The results are shown in Table 1. When the amount of Li exceeded more than 3 mol% in the catalyst, the catalytic activity decreased as the surface area of the catalyst was reduced. However, the selectivity for C_2-compounds increased with increasing Li concentration in the catalyst until the maximum value of 65% was attained on $Li_2Be_2O_3$. Thus, the compound oxide $Li_2Be_2O_3$ may be an active component of the Li_2O - BeO system catalyst for the oxidative coupling of methane.

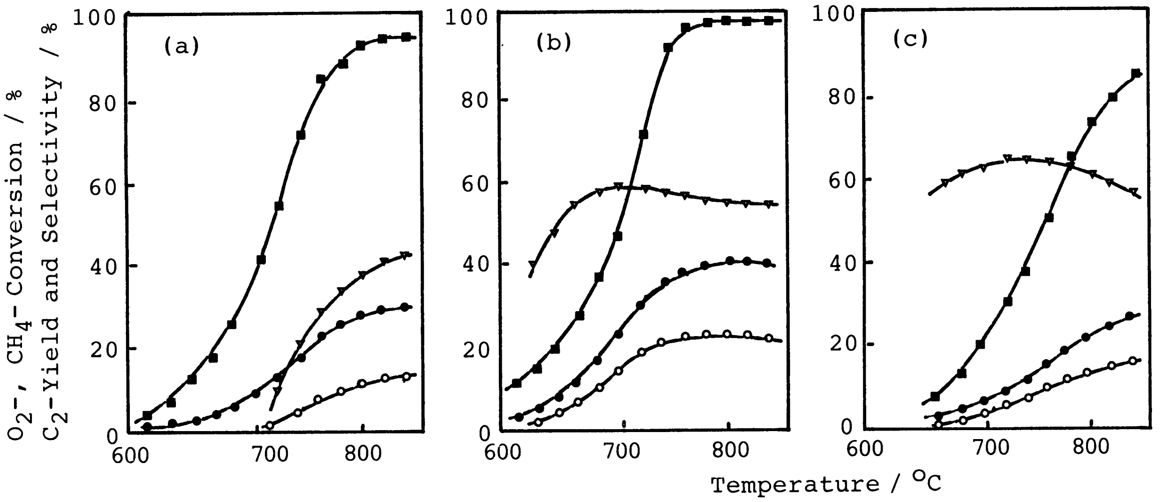

Fig. 2. Amount of CH_4 converted with reaction temperature over Li_2O - BeO system catalyst. (a) BeO, (b) 3 mol% Li-BeO, (c) 50 mol% Li-BeO ($Li_2Be_2O_3$). ■, O_2-conversion; ●, CH_4-conversion; o, C_2-yield; ▼, C_2-selectivity.

Figure 3 shows the results obtained from the reaction carried out under the pressure of one atmosphere. The partial pressure of CH_4 and O_2 were varied using 0.5 g at 680 °C and 0.05 g at 760 °C. The figure reveals that the selectivity of

Table 1. Catalytic Activity for Oxidative Coupling of Methane at 760 °C[a)]

Catalyst	BeO	+ Li / mol%					
		1	3	7	12.5	20	50[b)]
Surface area / $m^2\ g^{-1}$	14.1	7.0	1.1	0.4	0.2	0.1	0.1
Amounts of catalyst / g	0.2	0.1	0.05	0.2	0.3	0.5	0.5
O_2- Conversion / %	81.2	87.4	91.3	83.5	81.4	81.0	80.1
CH_4- Conversion / %	26.0	35.9	39.9	36.6	35.6	37.4	37.7
C_2- Yield / %	8.1	18.4	22.6	20.8	21.5	22.8	24.5
C_2- Selectivity / %	31.2	51.6	56.6	56.9	58.8	61.0	65.0
$C_2^= / (C_2^= + C_2) \times 100$ / %[c)]	57.9	62.1	65.1	64.4	66.2	70.6	68.0

a) $P(CH_4)$ = 35.0 kPa, $P(O_2)$ = 16.5 kPa. b) $Li_2Be_2O_3$.
c) $C_2^= = C_2H_4$, $C_2 = C_2H_6$.

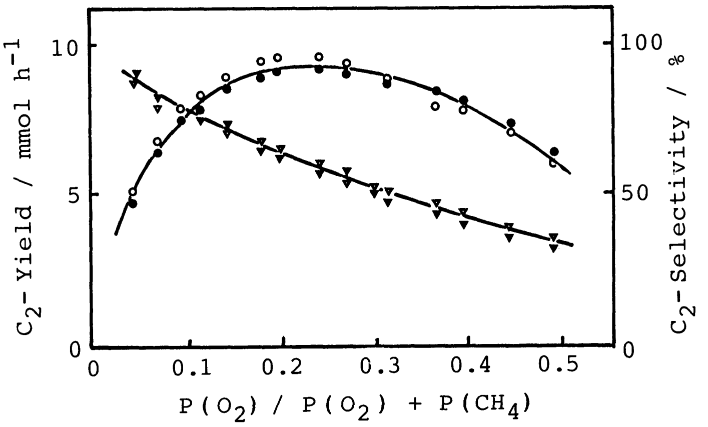

Fig. 3. Dependence on partial pressures of reaction gases for C_2-yield on 3 mol% Li-BeO. ○ and ▽, C_2-yield and selectivity using 0.5 g at 680 °C. ● and ▼, C_2-yield and selectivity using 0.05 g at 760 °C.

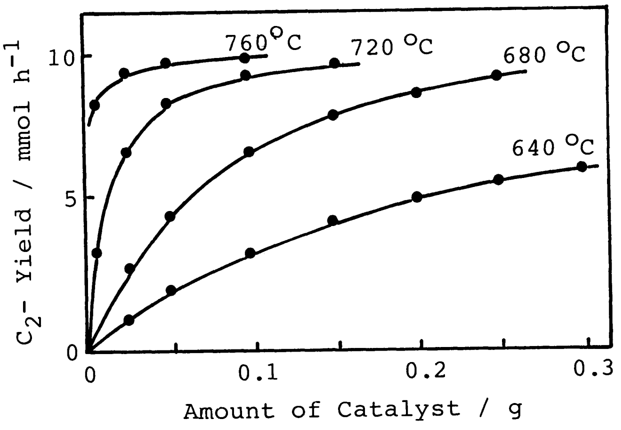

Fig.4. Effect of amount of catalyst for C_2-yield. Catalyst: 3 mol% Li-BeO; $P(CH_4)$ = 76.0 kPa, $P(O_2)$ = 25.0 kPa.

C_2-compounds was as high as 84% under the low partial pressure of O_2 with the value dropping with increases in the oxygen pressure. In both of the experiment, the optimum yield of C_2-compounds was obtained with the ratio of $P(O_2) / P(O_2) + P(CH_4)$ being between 0.2 and 0.3.

Table 2. C_2-STY to Oxidative Coupling of Methane on 3 mol% Li-BeO Catalyst[a)]

React. temp	C_2-STY	O_2-Conv.	CH_4-Conv.	C_2-Yield	C_2-Select.	W / F
°C	mmol g^{-1} h^{-1}	%	%	%	%	g h l^{-1}
640	11	69.6	19.8	10.1	51.0	0.1666
680	17	96.6	27.5	14.3	52.0	0.1666
	43	40.5	13.5	8.1	60.0	0.0333
720	61	81.6	25.5	14.9	58.4	0.0333
	128	54.8	18.7	12.0	64.2	0.0166
760	178	93.3	28.4	16.6	58.5	0.0166
	813	72.5	24.2	15.2	63.1	0.0033

a) $P(CH_4)$ = 76.0 kPa, $P(O_2)$ = 25.0 kPa.

In Fig.4, the methane oxidation is represented, performed under the partial pressure conditions of 76.0 kPa of CH_4 and 25.0 kPa of O_2 with different weights of catalyst at various reaction temperatures. On the basis of these results we calculated C_2-STY (Space Time Yield of C_2-compounds) for W / F at various temperatures and listed the values in Table 2. Otsuka and Komatsu[6)] recently reported that Sm_2O_3 is the most effective catalyst for the reaction. As described in their report, the C_2-STY for the catalyst of Sm_2O_3 is 527 mmol g^{-1} h^{-1} at 0.0033 g h l^{-1} of W / F at 750 °C. Table 2 reveals that the C_2-STY of the catalyst 3 mol% Li - BeO is the same that of the above Sm_2O_3 catalyst.

In conclusion, BeO promoted with Li was found to have the high activity and selectivity for the oxidative coupling of methane. The Li_2O reacts with BeO to form the compound oxide $Li_2Be_2O_3$ at 700 °C easily. This compound oxide could be an active catalyst for the oxidative coupling of methane.

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