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Oxidative Coupling of Methane over Lithium-Promoted Zinc Oxide Catalyst

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Alkali doped ZnO samples were examined as catalysts for the conversion of methane to ethylene and ethane. Among the catalysts tested, 12.5 mol% Li-promoted zinc oxide was the most active and selective for the formation of C_2-hydrocarbons. The highest yield of C_2-compounds was 24.8% and the fraction of ethylene in C_2-compounds was over 80%.

Since Keller and Bhasin 1) investigated the possibility of synthesizing ethylene and ethane by the oxidation of methane using an oxide catalyst, many researchers have paid great attention to the oxidative coupling of methane. Ito et al.2) recently reported that Li-promoted MgO is an effective catalyst for the reaction. Aika et al.3) found that Na-doped MgO is the most active catalyst in various metal-doped MgO. Otsuka et al.4,5) reported that rare-earth metal oxides, especially Li-doped Sm_2O_3, show high catalytic activity and selectivity for the formation of C_2-compounds in the oxidative coupling of methane. They 6) also studied the LiCl-added transition metal oxides and found that the oxides of Mn and Ni with LiCl produced ethylene with high selectivity and yield. These results indicate that alkali metal oxides promote the oxidative coupling of methane. In this communication, we report on the results of Li-promoted ZnO catalyst which show high catalytic activity and selectivity for the oxidative coupling of methane to ethylene and ethane.

The Li-promoted catalysts were prepared as follows: an ammonia solution was added to a zinc nitrate aqueous solution to precipitate zinc hydroxide which was filtered and thoroughly washed with water. The precipitate was then suspended in distilled water and a specified quantity of lithium carbonate was added to the suspension which was heated at 100 °C under vigorous stirring and was evaporated to dryness. The dried substance was calcined at 450 °C for 4h and then at 800 °C for 2 h. By this method, five catalysts with 3, 7, 12.5, 22 and 42 mol% Li in ZnO were prepared. We also prepared ZnO promoted with 12.5 mol% other alkalis in the same manner.

The catalytic experiments were carried out in a fixed bed reactor using 2 g of the catalyst 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. The total pressure of the mixed gas including CH_4 of 80 to 420 Torr (1 Torr = 133.32 Pa) and O_2 of 20 to 240 Torr was adjusted by He.

Figure 1 shows the results of ZnO added a different quantity of Li on the conversion of methane, selectivity of C_2-compounds including C_2H_4 and C_2H_6 and C_2-yield at 740 °C. The reaction was made under the partial pressure of 262 Torr of CH_4 and that of 124 Torr of O_2. The activity of unpromoted ZnO was not so high for the methane oxidation and the selectivity for C_2-compounds was rather low. Both activity and selectivity to the C_2-compounds were improved by adding Li to ZnO. The catalyst promoted with 12.5 mol % Li gave a maximum yield to the C_2-compounds and the selectivity as high as 20.9 % and 62.1 %, respectively. Both activity and selectivity did not change with the further addition of Li.

The results of the experiments, using the catalyst promoted with 12.5 mol% Li of the reaction temperatures between 600 to 800 °C are shown in Fig. 2. The formation of C_2-compounds starts at a temperature of 640 °C. The selectivity and C_2-yield increased up to the maximum as the reaction temperature is raised up to approximately 740 °C and decreased at higher temperatures.

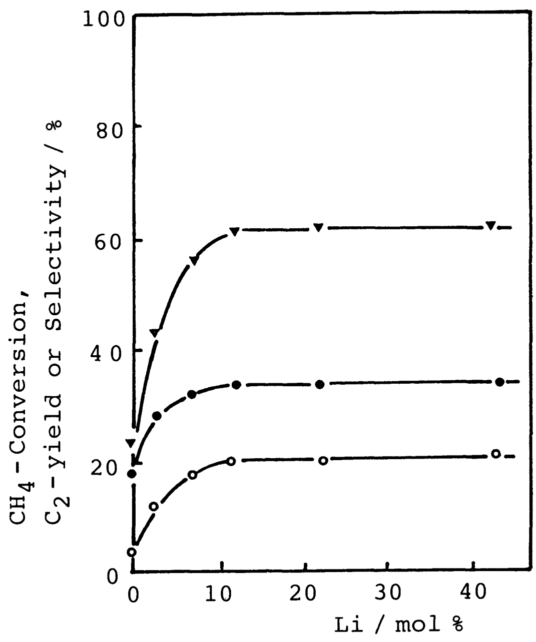

Fig. 1. Amount of CH_4 converted with Li in ZnO. CH_4 = 262 Torr, O_2 = 124 Torr. ●, total; ○, $C_2H_4+C_2H_6$; ▼, C_2-selectivity.

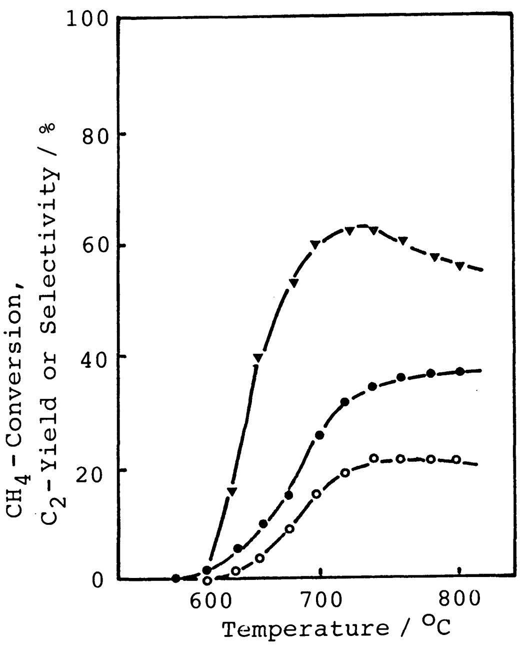

Fig. 2. Amount of CH_4 converted with reaction temperature over 12.5 mol % Li-promoted ZnO. CH_4= 262 Torr, O_2 = 124 Torr. ●, total; ○, $C_2H_4+C_2H_6$; ▼, C_2-selectivity.

Figure 3 shows the conversion of CH_4 at 740 °C as a function of the pressure of each reactant gas. The amount of CH_4 converted increased smoothly with the increase in O_2 pressure below 100 Torr, but above this pressure, the increase was much faster because the oxidation was accelerated. The selectivity to

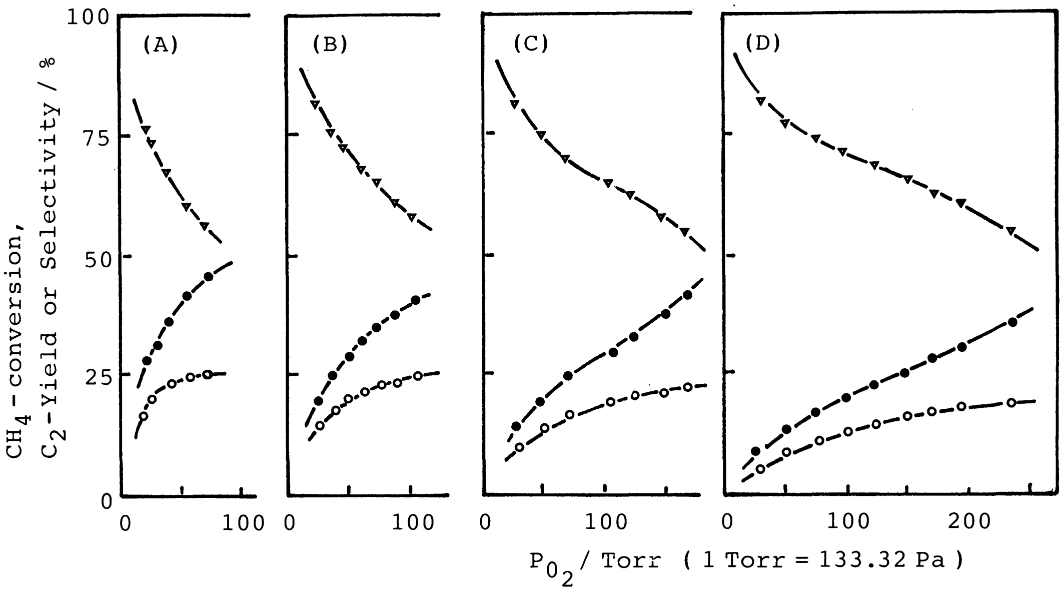

Fig. 3. Amount of CH_4 converted with respect to an increase in O_2 pressure over 12.5 mol% Li-promoted ZnO at 740 °C. (A) CH_4=82 Torr, (B) CH_4=166 Torr, (C) CH_4=262 Torr, (D) CH_4=415 Torr. ●, total; ○, $C_2H_4 + C_2H_6$; ▼, C_2-selectivity.

Table 1. Effect of Catalyst and CH_4 to O_2 Ratio of Oxidative Coupling of CH_4[a)]

Catalyst[b)]		Li				Na	K	Rb	Cs
Reactant / Torr[c)]	He	637	516	374	147	374	372	374	376
	CH_4	82	166	262	415	262	262	262	262
	O_2	43	78	124	198	124	126	122	119
Product / Torr	CO_2	10.0	21.1	36.7	59.2	61.0	64.7	60.5	57.0
	C_2H_4	8.3	15.7	25.8	39.1	15.1	7.9	7.0	5.4
	C_2H_6	1.7	3.6	4.9	6.1	6.5	7.1	6.0	6.0
	CH_4	53.6	114.7	191.4	348.1	189.3	196.2	201.2	208.9
	O_2	13.3	20.0	31.2	73.6	0.0	0.0	0.0	0.0
Conversion / %		35.8	34.2	33.6	30.0	35.5	33.5	30.0	26.2
C_2-Yield / %		23.9	22.1	20.9	18.2	14.1	9.9	9.0	4.0
C_2-Selectivity / %		66.8	64.6	62.1	60.5	41.5	29.6	30.0	27.0
$C_2^= / C_2^= + C_2$ x 100 / %[d)]		82.6	81.3	83.8	86.2	70.0	52.6	53.5	44.1

a) Reaction temperature = 740 °C. b) 12.5 mol% alkali-promoted ZnO.
c) 1 Torr = 133.32 Pa. d) $C_2^= = C_2H_4$ and $C_2 = C_2H_6$.

C_2-compounds increased with a lowering of the partial pressure of O_2. On the other hand, the selectivity to C_2-compounds becomes higher with an increase in the CH_4 pressure. Under the reaction conditions of the partial pressure of CH_4 of 82 Torr, the yield of the C_2-compounds reached 24.8 % and the fraction of ethylene in the C_2-compounds was over 80 %. Table 1 summarizes the results obtained for a reactant gas mixture of $CH_4/O_2 = 2$.

The deactivation of the catalyst with reaction time was examined for the catalyst promoted with 12.5 mol % Li . The catalytic activity and product distribution did not change even after a reaction of 50 h.

We also extended this work to other alkali-promoted ZnO in order to compare them with Li-promoted ZnO as catalysts for the oxidative coupling of methane. The results of the conversion of methane at 740 °C using catalysts promoted with 12.5 mol % of alkali metals are shown in Table 1. The oxygen conversion was 100 % over all the catalysts with the exception of the Li-promoted one. The amount of CH_4 converted and the selectivity to the C_2-compounds decreased in the following order of alkali metals added, Li > Na > K > Rb > Cs. This order is the sams as that reported by Otsuka et al.[5] on the effect of addition of alkali metals to Sm_2O_3 catalyst.

In conclusion, ZnO promoted with Li was found to have the high activity and selectivity for the oxidative coupling of methane. The 12.5 mol % Li-promoted ZnO catalyst showed the highest C_2-yield with 24.8 % and the fraction of ethylene in C_2-compounds was over 80 % .

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