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Oxidative coupling of methane over Li^+-added Y_2O_3 catalyst prepared from $Y(OH)_3$

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Abstract

Oxidative coupling of methane was carried out over various metal oxide catalysts (MgO, Y_2O_3, La_2O_3, Sm_2O_3 and Ho_2O_3) modified with Li^+ and the catalytic performance of the catalysts was examined. Li^+-added Y_2O_3 catalyst, which was prepared by impregnation of Y_2O_3 with an aqueous solution of Li_2CO_3, was the most effective for the formation of ethene and ethane among all the catalysts tested in this study. However, the Li^+-added Y_2O_3 catalyst was deactivated during the reaction at 1053 K, i.e., selectivities to ethene and ethane decreased and those to CO and CO_2 increased with time on stream. X-ray diffraction pattern and Raman spectrum of the Li^+-added Y_2O_3 catalyst showed that Li species was mainly localized on the surface of the catalyst and bulk structure of the catalyst did not change by the addition of Li^+. Therefore, this deactivation of the Li^+-added Y_2O_3 catalyst was caused by the elimination of Li species from the catalyst surface during the oxidation, due to the weak interaction between Li species and Y_2O_3. On the other hand, Li^+-added Y_2O_3 catalyst, which was prepared by impregnation of $Y(OH)_3$ with an aqueous solution of Li_2CO_3, showed almost the same initial catalytic performance as that of the catalyst prepared from Y_2O_3 and Li_2CO_3. The catalyst prepared from $Y(OH)_3$ was more stable during the reaction compared to that of Y_2O_3. The catalytic stability of the former results from a homogenous dispersion of Li species in the catalyst bulk. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Oxidative coupling of methane; Li^+-added Y_2O_3; $Y(OH)_3$; Deactivation of the catalyst

1. Introduction

Direct catalytic conversion of methane to ethene and ethane by oxidative coupling is considered to be a promising route for the production of useful chemicals from abundant natural gas. It is well known that basic metal oxides such as MgO, Sm_2O_3, La_2O_3, etc. are effective catalysts for the oxidative coupling of methane [1–3]. The modification of the basic metal oxides with alkali ions (such as Li^+ and Na^+) improves the catalytic performance of the metal oxides for the oxidative coupling of methane, i.e., the addition of alkali ions into the metal oxides brings about the suppression of total oxidation of methane and then the improvement of selectivities to ethane and ethene [4,5].

Recently, we have reported oxidative cracking of *n*-butane to ethene and propene over basic metal oxide catalysts (MgO, La_2O_3, Gd_2O_3, Sm_2O_3, Eu_2O_3 and CeO_2) [6]. Y_2O_3 was the most effective catalyst for the formation of ethene and propene from *n*-butane among all the catalysts examined. Further improvement in the catalytic performance of Y_2O_3, i.e., selectivities to ethene and propene, was achieved by addition of Li^+. We have expected that the Li^+-added Y_2O_3 catalyst was also effective for the oxidative coupling of methane.

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Although the Li^+-added metal oxide catalysts are often studied on the oxidative coupling of methane, the rapid deactivation of the catalysts is one of the problems to be solved [7]. Usually, the oxidative coupling of methane requires high temperatures (>1000 K). Therefore, the deactivation of the Li^+-added catalyst is believed to be caused by the loss of Li species from the catalyst.

In this work, the oxidative coupling of methane over the basic metal oxides modified by Li^+ and an improved preparation method of Li^+-added Y_2O_3 catalyst to depress the deactivation of the catalyst were studied.

2. Experimental

2.1. Catalysts

Li^+-added metal oxide catalysts were prepared by impregnating the oxides (MgO, Y_2O_3, La_2O_3, Sm_2O_3 and Ho_2O_3) with aqueous solutions of Li_2CO_3 at 353 K and drying up the impregnated samples at 373 K. The samples were calcined at 1073 K for 5 h in air.

$Y(OH)_3$ was prepared by using an aqueous solution of $Y(NO_3)_3$ and an ammonia solution. The precipitate was washed with water and dried at room temperature in air. The $Y(OH)_3$ was mixed thoroughly with an aqueous solution of Li_2CO_3 at 353 K. The Li^+-added sample was dried up at 373 K and calcined at 1073 K for 5 h in air. The catalyst thus prepared is denoted as $Y_2O_3(Li^+)$.

The catalyst was pressed into pellets and the pellets were crushed and sieved to 20/45 mesh size. The catalyst (0.2 g) packed in the reactor was heated to 1053 K in a flow of oxygen, prior to the reaction.

2.2. Reactions

The oxidation of methane was performed with a fixed-bed flow reactor made of an alumina tube (i.d. of 5.5 mm, length of 360 mm) at an atmospheric pressure. In order to minimize the contribution of the gas-phase chain reaction, quartz sands were filled in the space above and below the catalyst bed in the reactor. The temperature profile was measured by using a chromel–alumel thermocouple, which was placed in an axial thermowell and at a center of the catalyst bed. Methane and oxygen were fed with a helium carrier through the catalyst bed. The gas out of the catalyst bed was analyzed by gas chromatographs.

2.3. Characterization of catalysts

Raman spectra of the catalysts were measured at room temperature using a laser Raman spectrometer, JASCO NRS-2000 (Ar^+ 514.5 nm) [8]. The incident laser power at the sample was 10 mW. The spectra were recorded with a resolution of $4\,cm^{-1}$. X-ray diffraction (XRD) patterns of the catalysts were measured by a Rigaku RINT 2500 V diffractometer using Cu Kα radiation.

3. Results and discussion

3.1. Oxidative coupling of methane over Li^+-added metal oxide catalysts

Table 1 shows results on methane oxidation over various Li^+-added basic metal oxide catalysts. The amount of Li^+-added into metal oxides (MO_x) was adjusted to be $Li/M = 0.2$ in mole ratio. Over all the catalysts, ethane and ethene were produced mainly as partial oxidation products. Conversions of methane over Li^+-added Y_2O_3 and Li^+-added Ho_2O_3 were higher than those over other catalysts. However, for Li^+-added Ho_2O_3 catalyst, selectivities to ethene and ethane were lower and that to CO_2 was considerably high compared to those for other catalysts. On Li^+-added MgO, Li^+-added Sm_2O_3 and Li^+-added La_2O_3 catalysts, selectivities to ethene and ethane were considerably high, but the conversion of methane was low. The C_2 yields (ethene + ethane) at 1053 K over all the catalysts except for the Li^+-added Y_2O_3 catalyst were almost the same. On the other hand, the C_2 selectivities were kept relatively high over Li^+-added Y_2O_3 catalyst at high conversion of methane. Thus, the Li^+-added Y_2O_3 catalyst showed the highest yield of ethene and ethane. Thereafter, we focused on the catalytic performance of Li^+-added Y_2O_3 catalyst for the oxidative coupling of methane.

Table 1
Oxidative coupling of methane over Li^+-added metal oxide catalysts[a]

Catalyst	Reaction temperature (K)	Conversion of CH_4 (%)	Selectivity (%)				C_2 yield[b] (%)
			C_2H_4	C_2H_6	CO	CO_2	
Li^+–MgO	1023	8.8	20	42	4	33	5.5
	1053	25.1	28	24	7	41	13.0
Li^+–Y_2O_3	1023	29.1	27	27	2	44	15.7
	1053	39.9	27	19	2	52	18.4
Li^+–La_2O_3	1023	11.7	22	40	5	33	7.3
	1053	19.8	32	28	7	33	11.9
Li^+–Sm_2O_3	1023	14.6	21	36	5	38	8.3
	1053	22.3	28	29	6	37	12.7
Li^+–Ho_2O_3	1023	30.1	27	11	4	58	11.4
	1053	34.7	23	16	6	55	13.5

[a] $P(CH_4) = P(He) = 40.5$ kPa, $P(O_2) = 20.3$ kPa, flow rate = 50 ml min^{-1}, catalyst = 0.2 g. Li^+ was added to each metal oxide (MO_x) with mole ratio Li/M = 0.2.
[b] Yield of (ethane + ethene).

3.2. Oxidative coupling of methane over Li^+-added Y_2O_3 catalyst prepared from Y_2O_3

Fig. 1 shows experimental results obtained over Y_2O_3 catalysts modified by different amounts of Li^+. The reactions were carried out at 1053 K. Conversion of methane did not depend significantly on the amount of Li^+-added to Y_2O_3 in the range $0 \leq Li/Y \leq 0.4$, and at $Li/Y = 0.8$ the conversion decreased. On the other hand, product selectivities varied with the amount of Li^+. As increasing the amount of Li^+, the selectivity to C_2 compounds increased and those to CO and CO_2 decreased. The C_2 yield showed a maximum (20.0%) at $Li/Y = 0.4$. In the oxidative cracking of *n*-butane over the Li^+-added Y_2O_3 catalyst, selectivities to ethene and propene increased and those to CO and CO_2 decreased with rising the Li/Y ratios, although the conversion of *n*-butane did not depend on the Li/Y [6]. Thus, in the oxidative cracking of *n*-butane over the Li^+-added Y_2O_3 catalyst, the yields of ethene and propene resulted in the maximum at $Li/Y = 0.4$.

Fig. 2 shows changes in the conversion of methane, product selectivities, and C_2 yield with time on stream in the oxidative coupling of methane over the Li^+-added Y_2O_3 catalyst ($Li/Y = 0.4$) at 1053 K. Conversion of methane slightly and the C_2 yield gradually decreased with time on stream. It was reported that the deactivation of the Li^+-added MgO catalyst in the similar manner for the oxidative coupling of methane at higher temperatures than 973 K was attributed to the elimination of Li species from

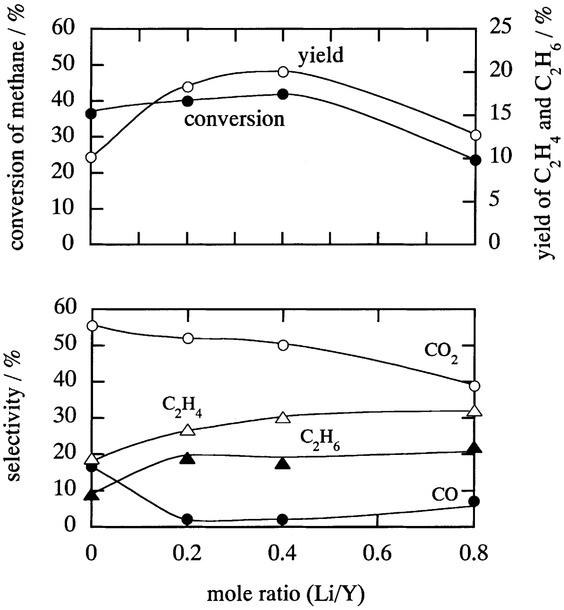

Fig. 1. Effect of the amount of Li^+ added on the oxidation of methane at 1053 K over the Li^+-added Y_2O_3 catalysts. Catalysts: 0.2 g; $P(CH_4) = P(He) = 40.5$ kPa; $P(O_2) = 20.3$ kPa; flow rate: 50 ml min^{-1}.

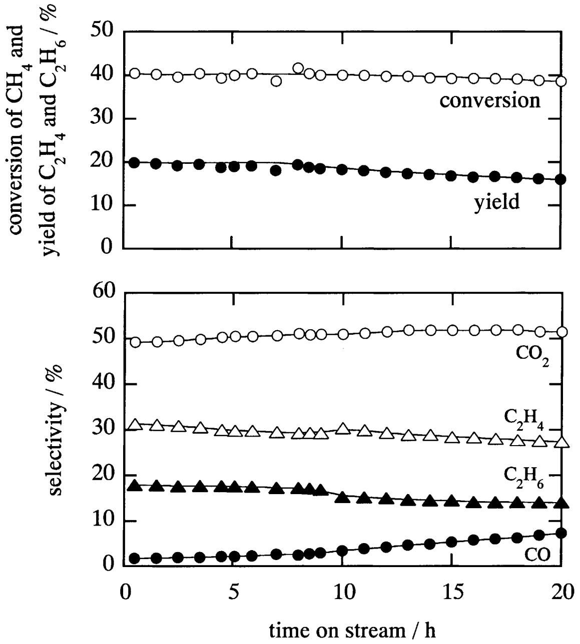

Fig. 2. Changes in methane conversion, selectivity to each product, and C_2 yield with time on stream. The methane oxidation was carried out at 1053 K over the Li^+-added Y_2O_3 catalyst (Li/Y = 0.4). Catalyst: 0.2 g; $P(CH_4) = P(He) = 40.5$ kPa; $P(O_2) = 20.3$ kPa; flow rate: 50 ml min^{-1}.

the catalyst surface during the oxidation [7]. Also for the Li^+-added Y_2O_3 catalyst shown in Fig. 2, the decrease in the C_2 yield seems likely to result from the elimination of Li species from the catalyst.

3.3. Characterization of Li^+-added Y_2O_3 catalyst

In order to clarify the reason for the deactivation of the Li^+-added Y_2O_3 catalyst, characterization of the catalysts was carried out. Fig. 3 shows XRD patterns of Li^+-added Y_2O_3 catalysts, Y_2O_3, and Li_2CO_3. The XRD pattern of Li^+-added Y_2O_3 with Li/Y = 0.2 was compatible with that of Y_2O_3. In the XRD patterns of Li^+-added Y_2O_3 with Li/Y $\geq$ 0.4, the diffraction lines due to Li_2CO_3 were found in addition to those for Y_2O_3. The position of diffraction lines due to Y_2O_3 did not change by the addition of Li^+. These results indicate that the Li^+-added Y_2O_3 consists of Li_2CO_3 and Y_2O_3 phases.

Fig. 4 shows Raman spectra of the Li^+-added Y_2O_3 catalysts, Y_2O_3, and Li_2CO_3. By the addition of Li^+ to Y_2O_3, a peak due to Li_2CO_3 appeared at 1080 cm^{-1}. As the amount of Li^+ added increased, the peak intensity due to Li_2CO_3 increased and those due to Y_2O_3 decreased. However, neither new Raman bands nor shift of the Raman bands due to Y_2O_3 were observed, confirming that the Li^+-added Y_2O_3 consists mainly of Li_2CO_3 and Y_2O_3 phases. These results were consistent with those in the XRD patterns. Raman spectra generally give the information about the surface structure of the catalysts, and XRD patterns give rather the information about the bulk structure. The intense band due to Li_2CO_3 was found in the Raman spectra of the Li^+-added Y_2O_3 with Li/Y $\geq$ 0.4, while the intensity of diffraction lines due to Li_2CO_3 was very weak in the XRD patterns of the catalysts. These observations suggest that the surface of Li^+-added Y_2O_3 catalyst is covered with a thin layer of Li_2CO_3. Since most of Li species was present on the surface of the Li^+-added Y_2O_3 catalyst and the interaction between Li species and Y_2O_3 was weak, it was clear that the catalyst deactivation due to the elimination of Li species occurred

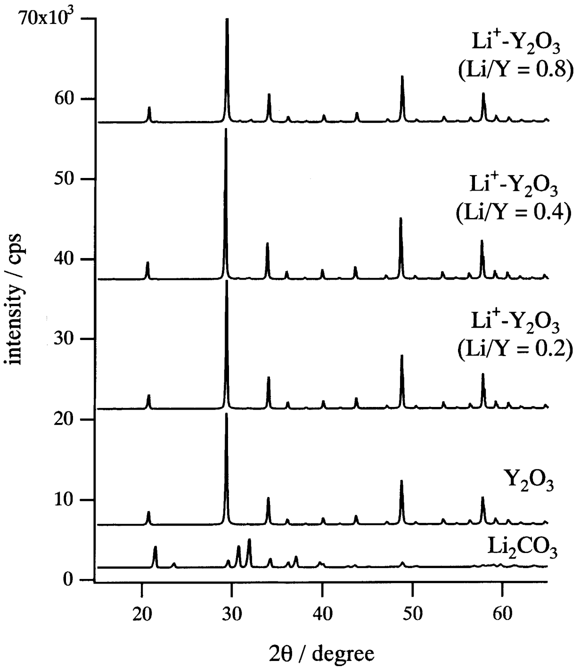

Fig. 3. XRD patterns of the Li^+-added Y_2O_3 catalysts, Y_2O_3, and Li_2CO_3.

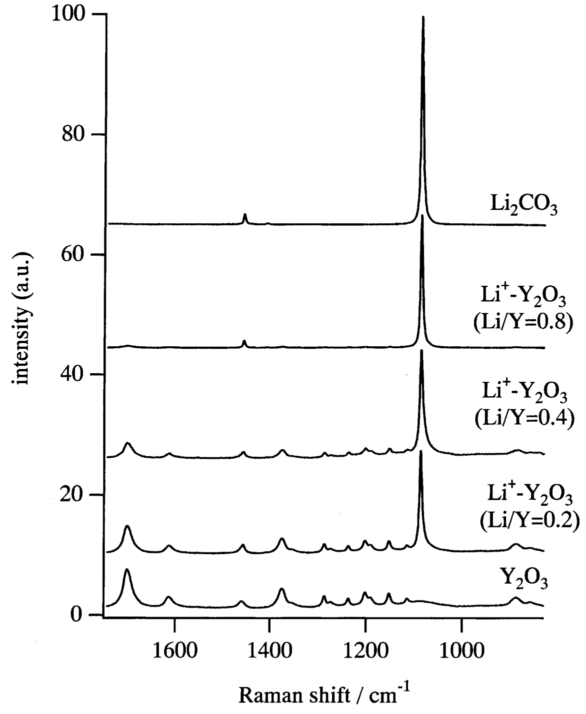

Fig. 4. Raman spectra of the Li$^+$-added Y$_2$O$_3$ catalysts, Y$_2$O$_3$, and Li$_2$CO$_3$.

easily during the oxidative coupling of methane at 1053 K.

3.4. Oxidative coupling of methane over Li$^+$-added Y$_2$O$_3$ catalyst prepared from Y(OH)$_3$

The Li$^+$-added Y$_2$O$_3$ catalyst described above was prepared by the impregnation of Y$_2$O$_3$ with an aqueous solution of Li$_2$CO$_3$. This preparation method inevitably causes the deposition of Li$_2$CO$_3$ on the surface of the catalyst. In general, a metal hydroxide has a larger surface area than the corresponding metal oxide. Thus, we expected that Li species could be dispersed into the catalyst bulk, when the Li$^+$-added Y$_2$O$_3$ catalyst is prepared by impregnating Y(OH)$_3$ with an aqueous solution of Li$_2$CO$_3$ (denoted as Y$_2$O$_3$(Li$^+$)). Fig. 5 shows the results for the oxidation of methane over the Y$_2$O$_3$(Li$^+$) catalysts. Conversion of methane unchanged approximately in the range $0 \leq$ Li/Y ≤ 0.8, while the conversion decreased on the catalyst with Li/Y = 1.0. The C$_2$ selectivity

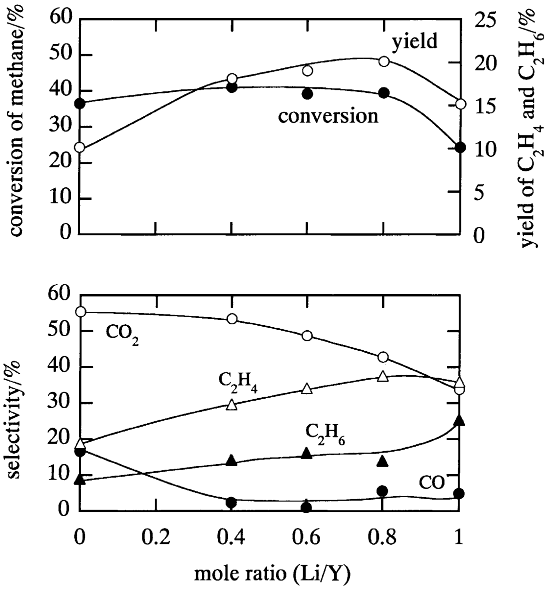

Fig. 5. Effect of the amount of Li$^+$ added on the oxidation of methane at 1053 K over the Y$_2$O$_3$(Li$^+$) catalysts. Catalysts: 0.2 g; P(CH$_4$) = P(He) = 40.5 kPa; P(O$_2$) = 20.3 kPa; flow rate: 50 ml min^{-1}.

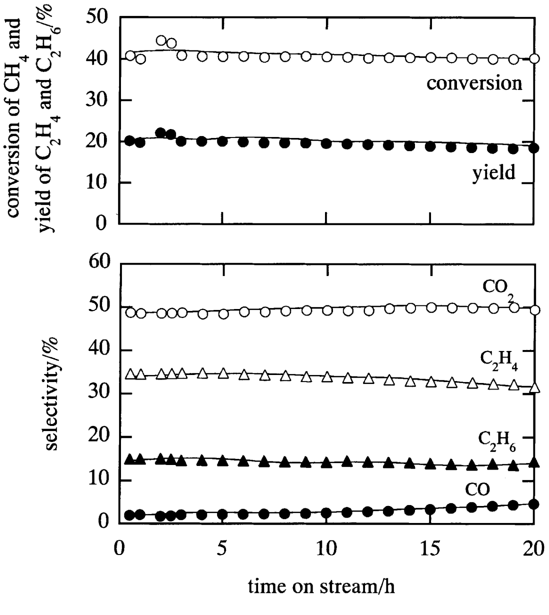

Fig. 6. Changes in methane conversion, selectivity to each product and C$_2$ yield with time on stream. The methane oxidation was carried out at 1053 K over the Y$_2$O$_3$(Li$^+$) catalyst (Li/Y = 0.8). Catalyst: 0.2 g; P(CH$_4$) = P(He) = 40.5 kPa; P(O$_2$) = 20.3 kPa; flow rate: 50 ml min^{-1}.

increased with increasing the Li/Y mole ratio. The changes in the methane conversion and the C_2 selectivity with the Li/Y mole ratio were very similar to those for the Li^+-added Y_2O_3 catalysts (Fig. 1). Therefore, it would be natural to consider that the catalytic active site which activates methane and/or oxygen is the same on the two kinds of catalysts. However, the highest C_2 yield was observed at different Li/Y ratios, i.e., for the $Y_2O_3(Li^+)$ the highest yield (20.0%) appeared at the mole ratio $Li/Y = 0.8$, whereas the highest yield (20.0%) for Li^+-added Y_2O_3 catalysts at $Li/Y = 0.4$. These results might indicate that the surface concentration of Li species on the $Y_2O_3(Li^+)$ catalyst with $Li/Y = 0.8$ agreed with that on the Li^+-added Y_2O_3 catalyst with $Li/Y = 0.4$.

Fig. 6 shows the catalytic stabilities of $Y_2O_3(Li^+)$ with $Li/Y = 0.8$ in terms of the methane conversion, C_2 yield, and selectivities. The methane conversion as well as C_2 selectivity were almost constant for 20 h. Thus, the yield of $(C_2H_4 + C_2H_6)$ maintained a 20% level over 20 h. The catalytic stability of $Y_2O_3(Li^+)$ was obviously improved, compared to that of the Li^+-added Y_2O_3 catalyst. Although Li species on the $Y_2O_3(Li^+)$ catalysts would be lost from the surface during the reaction, in this case the amount of Li species lost can be compensated from the catalyst bulk. This compensation effect seems likely to be one of the reasons that the $Y_2O_3(Li^+)$ catalyst maintains its catalytic activity for a long time.

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