Remarkable support effect of ZrO_2 upon the CO_2 reforming of CH_4 over supported molybdenum carbide catalysts

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In reforming of CH_4 with CO_2 over molybdenum carbide catalysts, the catalytic performance of unsupported hexagonal Mo_2C prepared by direct carburization of MoO_3 was considerably different from a similar composition, cubic MoC_{1-x} ($x \approx 0.5$), prepared through nitriding before carburization. The conversion levels over MoC_{1-x} were substantially higher than those over Mo_2C, although the turnover frequencies were lower. X-ray diffraction analysis indicated that Mo_2C deactivated by conversion to MoO_2 during the reaction, but the MoC_{1-x} was transformed to the hexagonal Mo_2C and remained stable. The activity of Mo_2C dispersed on various supports for the CH_4–CO_2 reaction was also investigated. The performance depended strongly on the property of supports, with the ZrO_2-supported Mo_2C catalyst exhibiting the highest activity and durability for this reaction. Moreover, deactivation of Mo_2C/ZrO_2 at ambient pressure was suppressed by decreasing the loading amount of Mo_2C.

Keywords: reforming of methane, carbon dioxide, molybdenum carbide, ZrO_2, Mo_2C loading

1. Introduction

Natural gas is an attractive energy resource as a substitute for petroleum due to its abundance and purities. In recent years many investigations about conversion of its main component, CH_4, to various chemicals have been carried out. Especially, reforming of CH_4 with CO_2 to synthesis gas has been paid great attention because its H_2/CO product ratio is nearer to unity than that from steam reforming of CH_4 or partial oxidation of CH_4.

It has been well known that supported group VIII precious metals like Pt [1–3], Rh [3–5], and Ru [6] exhibit high activities for reforming of CH_4 to synthesis gas, but because of their expense cheaper catalysts are desired. Since Levy and Boudart's pioneering work [7], considerable interest has been paid to the catalytic properties of metal carbides, particularly those of the group VI transition metals, in a variety of reactions. Because the starting materials for the preparation of these carbides are abundant and cheap, it has been suggested that they can replace the expensive noble metals in catalysis. Recently, Green et al. have demonstrated that carbides of molybdenum and tungsten are extremely active catalysts for the oxidation of CH_4 to synthesis gas with CO_2, O_2 or steam [8,9]. At ambient pressure the carbides deactivated, in all the processes, due to the oxidation of the catalysts to MoO_2, while operation at elevated pressure resulted in stabilization of the carbide and no catalysts deactivation.

In the present study we have investigated the dependence of the activity in the reforming of CH_4 with CO_2 upon the preparation methods of molybdenum carbide catalysts as well as the effects of dispersing them on various supports. We found that deactivation of carbides was perfectly suppressed even at ambient pressure by dispersing Mo_2C on ZrO_2 supports with less than 1 wt% loading level.

2. Experimental

The supported MoO_3 were prepared by impregnating a $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ precursor onto various supports (ZrO_2, SiO_2, Al_2O_3, CeO_2, TiO_2, and active carbon (AC)). The carbides were prepared by the following two methods [10,11]. The first one was direct carburization of molybdenum oxides in a 20% CH_4/H_2 mixture at 973 K for 3 h (heating rate of 1 K/min). And the second one was the nitridation of molybdenum oxides in NH_3 at 973 K for 3 h before carburization. Both preparation procedures were carried out in a flow type microreactor operated at atmospheric pressure. The former catalysts are designated as β-Mo_2C, while the latter are α-MoC_{1-x} in the literature but here will be denoted simply as Mo_2C and MoC_{1-x}.

To investigate the effects of supports on activity, only the Mo_2C type preparation method was employed. The reaction was carried out in the same flow reactor as mentioned above, using 0.3 g of catalyst pretreated in hydrogen at 773 K for 3 h. The composition of the feed gases was $CH_4/CO_2 = 1:1$ and the flow rate was 27 μmol/s (40 cm^3/min). The composition of the gas phase during the reaction was analyzed by FID and TCD (both Porapak Q columns) gas chromatography. The catalysts were characterized by various techniques such as X-ray powder diffraction (XRD), BET surface area measurement and CO chemisorption. Catalysts were passivated in flowing

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3% O_2/He for 12 h at room temperature before removal from the reactor for XRD and BET surface area measurements. XRD was carried out using a RAD-γA spectrometer (Rigaku) with Cu K_α radiation to determine the bulk structure of unsupported Mo_2C. CO chemisorption was performed at room temperature over freshly reduced catalysts to calculate the dispersion of Mo_2C assuming a stoichiometry of one CO per exposed Mo atom.

3. Results and discussion

Figure 1 shows the changes in conversions of CH_4 and CO_2 with time on stream over the unsupported Mo_2C and MoC_{1-x} catalysts. The characteristic feature of the reaction was that the conversion of CO_2 was 1.3 (MoC_{1-x}) or 2.7 (Mo_2C) times larger than that of CH_4, and at the same time the rate of CO formation was considerably larger than that of H_2 formation. The mass balance analysis suggested the occurrence of the reverse water–gas shift reaction ($CO_2 + H_2 \rightarrow CO + H_2O$) during CH_4 reforming with CO_2.

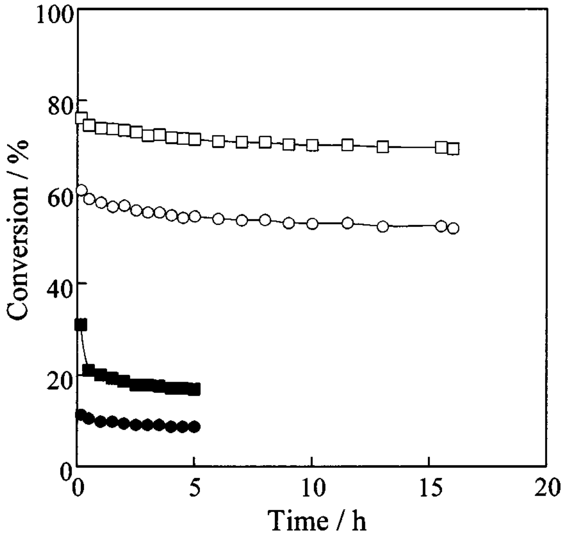

Figure 1. Conversions of CH_4 and CO_2 at 1123 K over unsupported Mo_2C prepared by different methods: (●) CH_4 and (■) CO_2 (Mo_2C); (○) CH_4 and (□) CO_2 (MoC_{1-x}).

The overall activity of MoC_{1-x} was more than three times higher than that of Mo_2C. In addition, its high activity was maintained for a moderate reaction period, and the conversions of CH_4 and CO_2 after 16 h on stream were about 90% of the initial conversions. In contrast, the activity of the Mo_2C catalyst was decreased abruptly to two thirds of its initial conversion (figure 1).

Table 1 summarizes the results of the characterization of these two kinds of carbide catalysts prepared by different methods, as well as their turnover frequencies (TOF) for H_2 and CO formation and their ratios in the CH_4–CO_2 reaction at 1123 K. TOF was estimated from the initial formation rate of H_2 and CO divided by the dispersion, assuming that the catalytic active sites are the exposed Mo atoms measured by CO chemisorption. It is worth noticing that the dispersion of MoC_{1-x} was much larger than that of Mo_2C. It has been well recognized that carbides of fcc structure formed through nitridation possess higher surface areas than those with hcp structure made through direct carburization from the oxides [11,12]. This is also the case in our study, as seen from the results of BET measurements, suggesting the formation of smaller particle size crystallites in the MoC_{1-x} catalyst. Eventually, the TOF of MoC_{1-x} was estimated to be ten to twenty times lower than that of Mo_2C, although its overall conversion was much higher than that of Mo_2C, as shown in figure 1.

Figure 2 shows XRD patterns of these catalysts before and after the reaction. Crystal structures of Mo_2C and MoC_{1-x} as prepared were different from each other, the former being hcp and the latter fcc, as mentioned already. In the case of Mo_2C, several new peaks assignable to MoO_2 emerged after the reaction. This was not observed in the case of MoC_{1-x}, which remained stable. These results suggest that the oxidation of Mo_2C to MoO_2 at the initial stage of the reaction might cause the abrupt deactivation shown in figure 1. The H_2/CO product ratio over MoC_{1-x} was higher than that over Mo_2C, which suggests the suppression of the reverse water–gas shift reaction over MoC_{1-x} in comparison with Mo_2C. The XRD pattern of MoC_{1-x} after the reaction indicated that the crystal structure was transformed from fcc to hcp during the reaction, accom-

Table 1
Characterization and TOF (1123 K) of various molybdenum carbide catalysts.

Catalyst	BET surface area[a] (m^2/g)	CO capacity (μmol/g)	Dispersion ($\times 10^{-2}$)	TOF[b] ($\times 10^{-2}$ s^{-1}) H_2	CO	H_2/CO
Unsupported Mo_2C I	15.4 (0.6)	14.4	0.1	10.6	74.3	0.1
Unsupported Mo_2C II	121.1 (21.3)[c]	823.8	8.4	1.4	3.3	0.4
5 wt% Mo_2C I/ZrO_2	– (18.9)	6.2	1.3	65.0	311.3	0.2
5 wt% Mo_2C II/ZrO_2	– (20.0)	13.6	2.8	30.1	151.5	0.2
8.1 wt% Mo_2C I/SiO_2	– (278.6)	33.9	4.3	3.5	22.5	0.2
5 wt% Mo_2C I/Al_2O_3	– (94.6)	75.1	15.3	6.3	23.6	0.3
5 wt% Mo_2C I/CeO_2	– (6.1)	24.1	4.9	3.1	37.4	0.1
5 wt% Mo_2C I/TiO_2	– (10.8)	11.7	2.4	33.3	161.5	0.2
5 wt% Mo_2C I/AC	493.9 (49.9)	16.4	3.3	38.7	97.0	0.4

[a] After 5 h on stream in parentheses.
[b] After 0.17 h on stream.
[c] After 16 h on stream in parentheses.

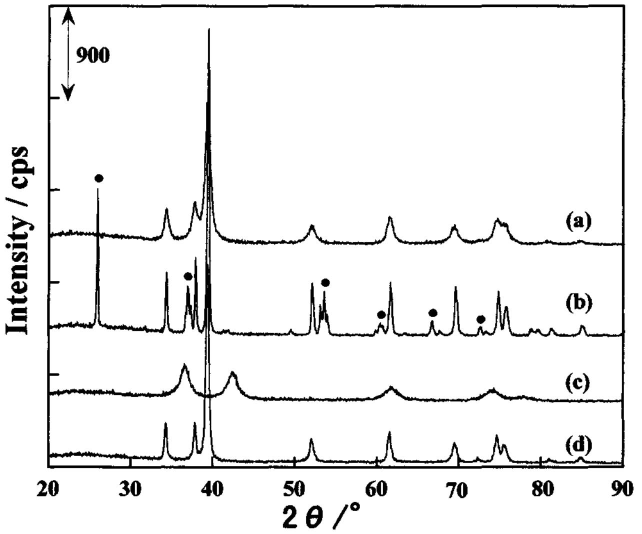

Figure 2. XRD patterns of unsupported Mo_2C: (a) and (b) Mo_2C, (c) and (d) MoC_{1-x}; (a) and (c) before the reaction, (b) and (d) after the reaction; (●) MoO_2.

panied by an increase in crystallite size. Green et al. also reported a similar deactivation process of β-Mo_2C catalysts and their transformation into MoO_2 [8].

We prepared Mo_2C/ZrO_2 and MoC_{1-x}/ZrO_2 (5 wt% Mo_2C) by the same method as unsupported Mo_2C and MoC_{1-x}, respectively, and compared their activities for the CH_4–CO_2 reaction. As shown in figure 3, the conversions of CH_4 and CO_2 over Mo_2C/ZrO_2 were similar to those over MoC_{1-x}/ZrO_2 from the beginning of the reaction to 5 h on stream. The characterization as well as TOF of both catalysts are also summarized in table 1. The dispersion of MoC_{1-x}/ZrO_2 was twice as large as that of Mo_2C/ZrO_2, and consequently, its TOF was estimated to be half. This tendency of the activity order was the same as in the case of unsupported catalysts already mentioned, although the difference was not so large (only a factor of two). On the other hand, the H_2/CO ratio on both supported catalysts was the same, though different from the case of unsupported catalysts. Since we could not observe any XRD peaks for both catalysts besides those assignable to ZrO_2, it was not clear whether there is any structural difference between these two catalysts or not.

To investigate the support effect, we employed only the direct carburization method for the preparation of supported Mo_2C catalysts dispersed on various supports. Table 1 summarizes the characterization and the TOFs of molybdenum carbide catalysts supported on silica, alumina, ceria, titania, and active carbon. The TOF of Mo_2C/ZrO_2 was the highest of all the catalysts employed in the present study. It was also five to six times more active than the unsupported Mo_2C catalyst. On the other hand, Mo_2C/CeO_2 exhibited excellent activity for the formation of CO, therefore the H_2/CO product ratio of Mo_2C/CeO_2 was small compared with those of the other molybdenum carbide catalysts. The deactivation of Mo_2C/ZrO_2 was small and the conversions of CH_4 and CO_2 after 5 h on stream were about 80% of the initial values, whereas the activities of Mo_2C/SiO_2 and Mo_2C/AC suddenly decreased to less than half after 0.5 h on stream. Over the SiO_2 support, surface hydroxide, produced by the reverse water–gas shift reaction, may promote the oxidation of the carbides. The marked decrease in the surface area might cause the deactivation in Mo_2C/AC. Over Mo_2C/AC the conversions of CH_4 and CO_2 after 2 h on stream were the same (5%) and the H_2/CO product ratio was nearly 1, which suggests that the active carbon is effective to suppress the reverse water–gas shift reaction. The activity of Mo_2C/AC for methane coupling was high, especially the amount of ethylene over Mo_2C/AC was ten times as much as that of unsupported Mo_2C.

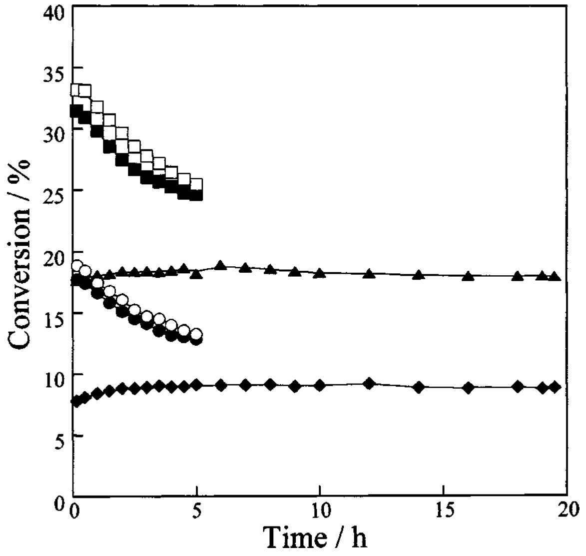

Figure 3. Conversions of CH_4 and CO_2 at 1123 K over various Mo_2C/ZrO_2: (●) CH_4 and (■) CO_2 (5 wt% Mo_2C/ZrO_2); (○) CH_4 and (□) CO_2 (5 wt% MoC_{1-x}/ZrO_2); (◆) CH_4 and (▲) CO_2 (1 wt% Mo_2C/ZrO_2).

It has been well recognized that methane dry reforming over supported group VIII metal catalysts is very sensitive to the particle sizes of the metal as well as the property of the support employed. In Pt/ZrO_2 catalysts for methane reforming to syngas, not all accessible Pt contributed equally to the activity, but the catalytic activity was determined by the accessibility of Pt on the Pt–ZrO_2 perimeter. Lercher et al. explained these phenomena in terms of the CO_2 activation via carbonate species on the support which must be in the proximity of the Pt particles to react with the methane activated on the metal [1,3]. Zhang et al. also reported that the specific activity and the rate of deactivation of Rh catalysts for dry reforming of methane were strongly dependent on the supports employed, decreasing in the order yttria-stabilized zirconia (YSZ) $>$ Al_2O_3 $>$ TiO_2 $>$ SiO_2 $>$ La_2O_3 $>$ MgO [5]. They concluded that at least three kinds of factors contribute to catalyst activities and deactivation, namely, carbon deposition, metal sintering and poisoning of surface Rh sites by species originating from the supports.

Figure 3 also shows the changes of conversions of CH_4 and CO_2 with time on stream over 1 and 5 wt%

Mo_2C/ZrO_2. The activity of 1 wt% Mo_2C/ZrO_2 was quite stable for 20 h, while that of 5 wt% Mo_2C/ZrO_2 decreased slightly in 5 h. The 0.2 wt% Mo_2C/ZrO_2 catalysts also gave similar results to the 1 wt% Mo_2C/ZrO_2. According to Green's experiments, elevated pressures were needed to maintain a constant high activity for 72 h, while their activity dropped abruptly after 7 h in the reaction at ambient pressure [8]. They proposed two possible competing mechanisms for the formation of synthesis gas. The first is the cycling or redox mechanism and the second is a noble metal type mechanism. In the redox type route, after the dissociation of CO_2 the formed O(a) reacts with carbon in the carbide surface to leave vacancies. These are then filled with either carbon from methane, reforming the carbide, or oxygen to form MoO_2. For the former step to maintain predominant, the elevated pressure is required. On the other hand, in the noble metal type mechanism, dissociation of methane to carbon and H_2 as well as dissociation of CO_2 to oxygen and CO are believed to proceed over the metal carbide surface, from which another CO is formed. Because no deactivation is observed over 1 and 0.2 wt% Mo_2C/ZrO_2 catalysts, the latter noble metal type mechanism may be predominant on these catalysts. It is also worth noticing that Fujimoto et al. reported an effectiveness of smaller Ni particles in high resistance to carbon deposition over Ni/MgO catalysts [13]. Accordingly, the ZrO_2 support may play an important role in the stabilization of CO_2 and smaller particles of Mo_2C may enhance the activation of CO_2 as well as the dissociation of methane.

4. Conclusion

We have investigated the dependence of the activity in reforming CH_4 with CO_2 upon the preparation methods of molybdenum carbides. The catalytic performance of unsupported Mo_2C prepared through nitriding of the oxide before carburization was considerably different from that prepared by direct carburization of the oxide. The deactivation was significantly suppressed in the former catalyst, although its TOF for syngas formation was smaller than the latter. By dispersing on ZrO_2 this different catalytic behavior disappeared and both catalysts exhibited much higher activity than unsupported carbides. Moreover, by lowering the loading amount of Mo_2C over ZrO_2, deactivation was perfectly suppressed and excellent activity was maintained for more than 20 h even at ambient pressure. The ZrO_2 support may play an important role in the creation of smaller crystallites of Mo_2C which would enhance the dissociation of methane, and at the same time to activate CO_2 at the vicinity of the carbide and the support.

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