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Mechanistic difference of the CO_2 reforming of CH_4 over unsupported and zirconia supported molybdenum carbide catalysts

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Abstract

Zirconia supported molybdenum carbide catalysts exhibited much higher activity for CH_4–CO_2 reaction than unsupported Mo_2C. By lowering the loading amount on ZrO_2, deactivation was suppressed completely under the reaction condition of higher CH_4/CO_2 ratios and excellent activity was maintained. Transmission electron microscopic observation as well as XPS analysis demonstrated that molybdenum carbide was highly dispersed on ZrO_2 with strong electronic interaction. Isotopic exchange reaction between CH_4 and CD_4 showed that the dissociation of methane was significantly retarded by supporting Mo_2C on ZrO_2, which could be the main reason of high activity and durability of supported catalysts.

Keywords: Methane; CO_2 reforming; Molybdenum carbide; Zirconium oxide; Deactivation

1. Introduction

Reforming of methane by carbon dioxide has received great attention, since it can convert two of the cheapest carbon containing materials into useful chemical products, those are, CO and H_2. Group VIII metals such as Ni, Rh and Pt are very active for this reaction at elevated temperatures, but have the problem of deactivation due to the carbon accumulation. In spite of this disadvantage, CH_4–CO_2 reforming process provides several advantages compared to steam reforming of methane, such as the production of synthesis gas with a low H_2–CO ratio, which is suitable for use in Fischer–Tropsch synthesis for higher hydrocarbons.

Two mechanisms have been proposed for the CH_4–CO_2 reforming reaction over group VIII metal catalysts [1,2]. One is the Eley–Rideal type mechanism in which methane is adsorbed and decomposed on the metallic sites to form H_2 and surface carbon. This carbon species reacts directly with CO_2 from the gas phase to form CO. In the alternative mechanism methane is decomposed on the metal to yield a surface CH_X species and hydrogen [3,4]. Carbon dioxide is also adsorbed on the metal or on the interface of the metal and support oxide dissociatively to CO and adsorbed oxygen or surface OH group. These oxygen species react with CH_X to form CO and H_2. A large number of recent researches suggest that both mechanisms can be operative, which greatly depends on the nature of metals as well as supports [5–8].

On the other hand, Green and co-workers [9] have proposed another reaction mechanism for CH_4

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reforming reaction over high surface area molybdenum and tungsten carbide catalysts, synthesized by the temperature programming reduction of the relevant metal oxide with methane/hydrogen. Their activities were found to be comparable to those of group VIII metal catalysts, but deactivated at ambient pressures in all the processes, due to the oxidation of the catalyst to MO_2. On the other hand, operation at elevated pressure (8 bar) resulted in stabilization of the carbide and no catalysts deactivation for the duration of the experiments. According to their proposal, there are two possible competing mechanisms for the formation of synthesis gas and their deactivation. The first is the cycling or redox mechanism and the second is a noble metal type mechanism, which has been described in the previous paragraph. In the redox type mechanism, it was proposed that after dissociative adsorption of CO_2, the formed oxygen species reacts with carbon in the carbide surface to leave a vacancy, which is then filled with either adsorbed carbon species from methane, remaining the carbide, or oxygen species, a first step in the oxidation to MO_2. The oxygen species in the vacancy, however, can also react with carbon formed from the dissociation of methane, instead of carbon from the carbide, which is the basis of the second, noble metal type mechanism.

We have also studied the CO_2 reforming reaction of methane over molybdenum carbide catalysts unsupported and supported over SiO_2, Al_2O_3, ZrO_2, TiO_2, CeO_2 and active carbon [10] and found that their activity was very sensitive to the particle sizes of metal carbides as well as the property of the supports employed. Among the supported catalysts, zirconia supported Mo_2C exhibited the highest TOF for syngas formation, whose activity was 5–6 times higher than unsupported Mo_2C catalysts. As for the particle size effect, we have investigated the dependence of the activity in the reforming of CH_4 with CO_2 upon the loading amount of Mo_2C, and 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.

In the present study we have investigated the CH_4–CO_2 reaction mechanism over unsupported and zirconia supported Mo_2C catalysts as well as their deactivation process from the kinetical analyses and an isotopic tracer technique tighter with catalyst characterization. We found that zirconia support played important roles for the enhancement of activity and durability of this reaction.

2. Experimental

Supported MoO_3 were prepared by impregnating a $(NH_4)_6Mo_7O_{24}\cdot4H_2O$ precursor onto ZrO_2 support, which were transformed into supported carbide catalysts by direct carburization with the mixed gases of CH_4 and H_2 in a flow type micro reactor (quartz tube: 7 mm diameter), operated at atmospheric pressure. For comparison, unsupported catalysts were also prepared by the same procedure as mentioned above starting from molybdenum oxide powder. The formed carbide catalysts were characterized by TEM, EDX, XRD and XPS, as well as CO chemisorption at room temperature to estimate the TOF of CH_4–CO_2 reaction.

The reaction was carried out in the same flow type micro reactor at ambient pressures and the gas composition was analyzed by gas chromatography and mass spectrometer. The amount of employed catalysts was 0.3–0.5 g. The composition of feed gases was usually $CH_4{:}CO_2 = 1{:}1$ and the flow rate was 27 μmol/s (40 cm^3/min: SV = 5100 h^{-1} for unsupported and 1500 h^{-1} for supported catalysts). The isotopic exchange reaction of CH_4 and CD_4 was carried out over Mo_2C/ZrO_2 catalysts after the curburization of MoO_3/ZrO_2 in a closed gas circulation system with the same procedure as the flow system, and the products were analyzed by quadrupole mass spectrometer.

3. Results and discussion

Fig. 1 demonstrates the time courses of CO_2 reforming of CH_4 over unsupported and 1 and 5 wt.% ZrO_2 supported Mo_2C catalysts at 1123 K. The characteristic feature of the reaction is that the conversion of CO_2 is a few times larger than that of CH_4, and at the same time the rate of CO formation is considerably larger than that of H_2 formation (not shown in the figure). The mass balance analysis suggested the occurrence of the reverse water gas shift reaction taking place during CH_4 reforming with CO_2. The initial activity of unsupported Mo_2C was not so different from that of zirconia supported catalyst, but decreased abruptly within 1 h. This deactivation

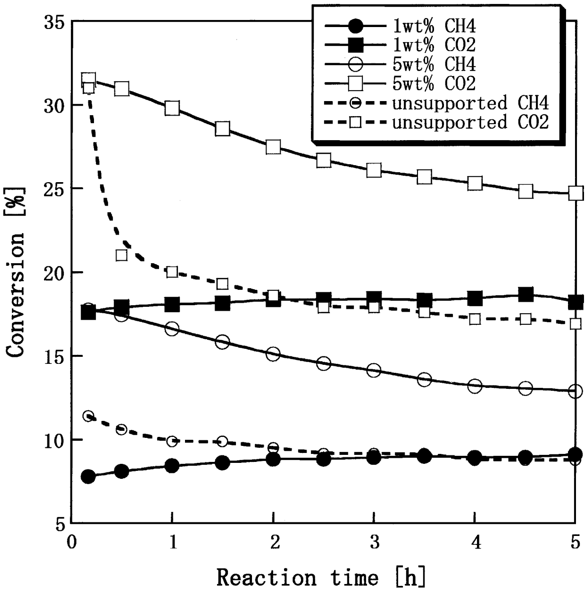

Fig. 1. Time courses of CH_4–CO_2 reaction over unsupported Mo_2C and 1 and 5 wt.% Mo_2C/ZrO_2 at 1123 K (CH_4:CO_2 = 1:1).

corresponds to the transformation of carbide into MoO_2, which could be detected by XRD. The activity of 5 wt.% Mo_2C/ZrO_2 catalysts were rather stable and after 16 h the conversion was decreased to about 90% of the initial one. No such deactivation was observed in the case of 1 wt.% catalysts, and the conversions of CH_4 and CO_2 stayed almost constant for more than 20 h. Green and co-workers needed elevated pressure to maintain the constant high activity for 72 h, while their activity dropped abruptly after 7 h in the reaction at ambient pressure. According to the Green's reaction mechanism mentioned above, the latter noble metal type mechanism may be predominant instead of redox type one, over highly dispersed Mo_2C catalysts.

In the case of unsupported Mo_2C catalysts, the transmission electron micrograph revealed the aggregation of small crystallites, whose diameters were several hundred angstroms. As demonstrated in Fig. 2(B), the TEM photo of 5 wt.% Mo_2C/ZrO_2 indicated the dispersion of a few hundred angstrom crystallites over ZrO_2 support. On the contrary, in the case of 1 wt.% Mo_2C/ZrO_2 we could not observe any crystalline particles of Mo_2C in the TEM photo in Fig. 2(A), suggesting the uniform dispersion of Mo_2C layer on ZrO_2 surface. XPS analyses of unsupported and ZrO_2 supported Mo_2C catalysts were also investigated before and after CH_4–CO_2 reaction. In the case of unsupported catalyst, the binding energies of $Mo3d_{5/2}$ and $Mo3d_{3/2}$ transitions shifted toward higher energy side from 227.5 and 230.8 to 228.5 and 231.5 eV after the reaction, indicating the oxidation

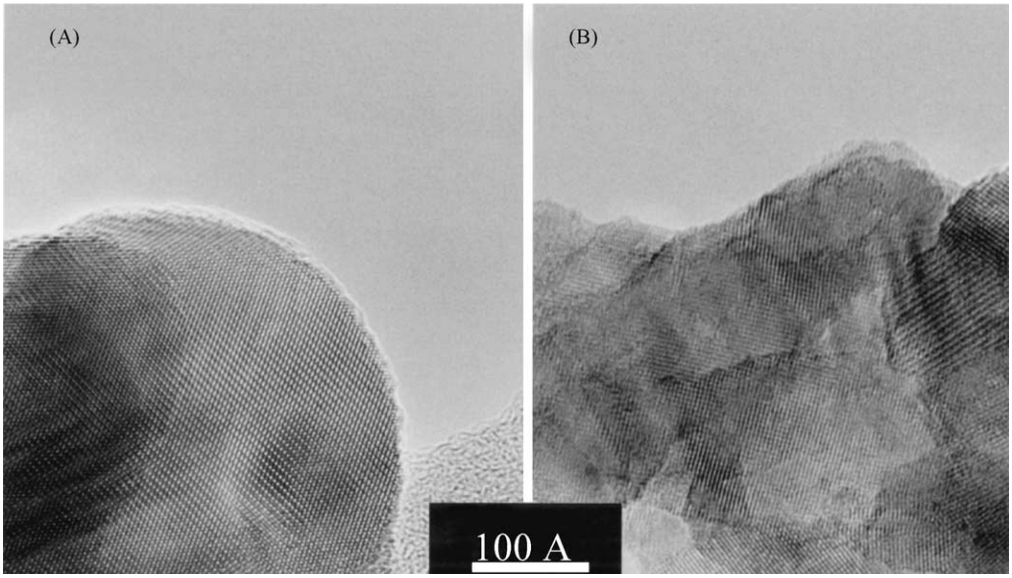

Fig. 2. TEM images of zirconia supported molybdenum carbide catalysts: (A) 1 wt.%; (B) 5 wt.%.

of Mo_2C. On the other hand, no such shift of binding energies was observed after the reaction in the case of Mo_2C/ZrO_2 catalysts, although their values were 1.0–1.5 eV higher than those of unsupported ones from the beginning. These results indicate that there is a certain strong electronic interaction between Mo_2C and ZrO_2 on the fresh Mo_2C/ZrO_2 catalyst, which is not disturbed much by the CH_4–CO_2 reaction.

Pressure dependence of the initial rates of H_2 and CO formation over unsupported and ZrO_2 supported catalysts were studied by changing the composition of CH_4 and CO_2 in the feeding gas at 1123 K. The empirical reaction orders of the initial rates of H_2 and CO formation over these three catalysts were estimated using the following rate equation: $V_{\mathrm{H_2\ or\ CO}} = kP_{\mathrm{CH_4}}^{\alpha} P_{\mathrm{CO_2}}^{\beta}$. The results are summarized in Table 1. The obtained reaction orders for the initial rates were the same over 1 and 5 wt.% supported catalysts, suggesting the similar reaction mechanism is operating on both catalysts, but quite different from those of unsupported catalysts. By supporting on ZrO_2, the reaction order of CH_4 for H_2 formation became very large, exceeding unity. This means that the rate determining step of H_2 formation shifts from the surface reaction of adsorbed species to the dissociation step of methane by supporting Mo_2C on zirconia.

To confirm this point, CH_4–CD_4 isotopic exchange reaction was carried out over unsupported and supported catalysts. The initial rates of CH_3D formation were listed in Table 2 at various reaction temperatures. Over unsupported catalysts, the exchange reaction began to take place as low as 373 K. The reaction temperature, where similar initial rate of CH_3D formation was observed, increased with decreasing the loading amount. Over 1 wt.% Mo_2C/ZrO_2, the exchange reaction was observed at 793 K, which was close to the CH_4–CO_2 reaction temperature. These results clearly indicate that by dispersing on ZrO_2, CH_4 dissociation ability of molybdenum carbide is diminished significantly because of the strong electronic interaction with ZrO_2, as indicated in the XPS analysis. These results correspond well to the previous consideration that methane dissociation would be the rate determining step of CH_4–CO_2 reaction over supported catalysts.

Table 1
Reaction orders of the initial rates of product formation in CH_4–CO_2 reaction over unsupported and ZrO_2 supported Mo_2C catalysts at 1123 K $V_{\mathrm{H_2\ or\ CO}} = kP_{\mathrm{CH_4}}^{\alpha} P_{\mathrm{CO_2}}^{\beta}$

Catalysts	Products	Reaction orders	
		α	β
Unsupported Mo_2C	H_2	0.4	0.1
	CO	0.5	0.8
1 wt.% Mo_2C/ZrO_2	H_2	1.6	0.1
	CO	0.6	0.2
5 wt.% Mo_2C/ZrO_2	H_2	1.7	0.2
	CO	0.6	0.3

Table 2
Initial rates of CH_3D formation in CH_4–CD_4 isotopic exchange reaction over unsupported and ZrO_2 supported Mo_2C catalysts at various temperatures

Catalysts	Reaction temperature (K)	Initial rates of CH_3D formation (mol/min)
Unsupported Mo_2C	373	3.4×10^{-7}
5 wt.% Mo_2C/ZrO_2	473	1.6×10^{-7}
1 wt.% Mo_2C/ZrO_2	793	1.9×10^{-7}

Although the kinetical behavior of the initial rates were similar over 5 and 1 wt.% Mo_2C/ZrO_2, the catalytic behavior of deactivation process was different in both catalysts as mentioned already. To investigate the mechanistic difference of the deactivation process over these catalysts, the time courses of CH_4–CO_2 reactions with various CH_4/CO_2 ratios were observed. The results were summarized in Figs. 3 and 4. Under oxidative condition where CH_4:CO_2 ratio is 1:3, no deactivation was observed even over 5 wt.% catalysts. Consequently, oxidation of the Mo_2C is not significant over supported catalysts. On the other hand, under reductive condition, where CH_4:CO_2 ratio is 3:1, slight deactivation was observed even in 1 wt.% catalyst. Temperature programmed reduction of the steady state surface after CH_4–CO_2 reactions with various CH_4/CO_2 ratios was studied over 5 wt.% Mo_2C/ZrO_2 catalysts. The amount of formed methane under reductive condition was almost twice more than under oxidative condition mentioned above, although amount of formed H_2O was almost the same on both surfaces.

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 pressures over unsupported Mo_2C [1]. In our case, lower loading catalysts of Mo_2C on ZrO_2 with high CO_2/CH_4 ratio maintained

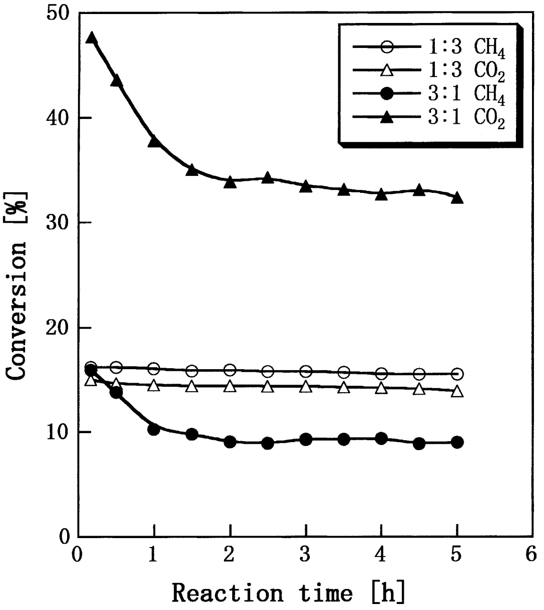

Fig. 3. Time courses of CH_4–CO_2 reaction over 5 wt.% Mo_2C/ZrO_2 at 1123 K under 1:3 and 3:1 CH_4/CO_2 ratios.

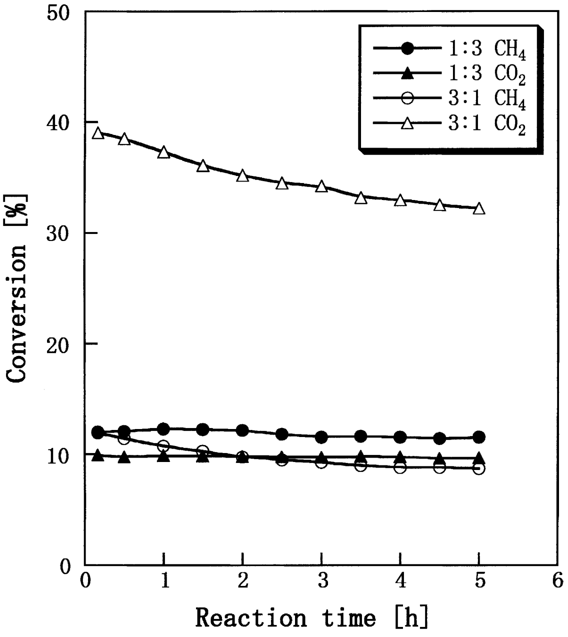

Fig. 4. Time courses of CH_4–CO_2 reaction over 1 wt.% Mo_2C/ZrO_2 at 1123 K under 1:3 and 3:1 CH_4/CO_2 ratios.

its high activity for more than 20 h even at ambient pressure. This result suggests that a different deactivation mechanism is operating over supported catalysts. Green and co-workers concluded that the oxidation of Mo_2C with O(a) formed by the dissociation of CO_2 as the main deactivation process over unsupported Mo_2C. From the results of pressure dependence, we would like to propose a different deactivation mechanism of inactive carbon accumulation rather than oxidation of Mo_2C over higher loading Mo_2C/ZrO_2 catalysts.

4. Conclusion

Deactivation of catalysts would be summarized as follows: over unsupported catalysts, both methane dissociation and CO_2 dissociation takes place on the surface of carbide itself. Accordingly there may be an equal chance for both the accumulation of inactive carbon and the oxidation of Mo_2C. On the other hand, over supported catalysts, CO_2 activation would takes place at the vicinity of Mo_2C and ZrO_2, and the chance for oxidation of carbide may decrease. Also the rate determining step would be the dissociation of methane, the chance of polymerization of inactive carbon may also decrease. These are the reasons that supported catalysts are more stable and durable for CH_4–CO_2 reforming reaction.

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References

[1] M.F. Mark, F. Maier, J. Catal. 164 (1996) 122.
[2] A. Erdohelyi, J. Cserenyi, F. Solymosi, J. Catal. 141 (1993) 287.
[3] M.C. Bradford, M.A. Vannice, Appl. Catal. A 142 (1996) 97.
[4] M.C. Bradford, M.A. Vannice, J. Catal. 173 (1998) 157.
[5] E. Ruckenstein, Y.H. Hu, J. Catal. 162 (1996) 230.
[6] A. Slagtern, Y. Schuurman, C. Leclercq, X. Verykios, C. Mirodatos, J. Catal. 172 (1997) 118.
[7] J.H. Bitter, K. Seshan, J.A. Lercher, J. Catal. 171 (1997) 279.
[8] J.H. Bitter, K. Seshan, J.A. Lercher, J. Catal. 176 (1998) 93.
[9] J.B. Claridge, A.P.E. York, A.J. Bruggs, C. M-Alvares, J. Sloan, S.C. Tsang, M.L.H. Green, J. Catal. 189 (1998) 85.
[10] Y. Tsuji, T. Miyao, S. Naito, Catal. Lett. 69 (2000) 195.