Active Species of Molybdenum Carbide Catalysts in Methane Reforming: η-Mo_3C_2

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η-Mo_3C_2 was the most active molybdenum carbide species for methane reforming, surpassing β-Mo_2C which has been reported previously. From the correlation of the TPR results, the amount of η-Mo_3C_2 was directly related to the methane decomposition rate, indicating the importance of this type of carbide for methane reforming.

Molybdenum carbide catalysts are reported to have high activity towards various reactions such as CO_2 hydrogenation,[1] isomerization of *n*-hexane,[2] and hydrogenolysis of ethane.[3] Recently, supported molybdenum carbide catalysts have been reported to be active for the reforming of methane, producing benzene in high selectivity.[4–6] Although molybdenum carbides are cited as the active species for this reaction, the specific type of carbide has not been specified due to the difficulty in determining the molybdenum carbide species of supported catalysts. Also, the differences arising from the various carbide structures have not been reported. In this study, unsupported molybdenum carbide catalysts were compared to determine the specific type of carbide active in methane reforming. By changing the pretreatment method, it is possible to prepare either α-Mo_2C, β-Mo_2C, or η-Mo_3C_2. This paper compares the activity of these three molybdenum carbide species and identifies the active species for the reforming of methane using temperature-programmed reaction (TPR) methods.

The unsupported molybdenum carbide catalysts were prepared in an atmospheric pressure flow reactor system following a temperature-programmed carbiding method. 0.2 g of the MoO_3 precursor was heated in 20% CH_4/H_2 flow utilizing a temperature ramp of 1 K min^{-1} at a gas flow rate of 4 L h^{-1}. After reaching the carbiding temperature of either 873, 923, or 973 K, the temperature was maintained for 3 h. Another pretreatment method involved nitriding of the oxide at 973 K using the same temperature ramp. The pretreatment gas was then switched to 20% CH_4/H_2, after which the catalyst was heated at either 973 K or 1173 K. To designate the pretreatment temperature, the following denotation will be used. 973 K-carbided denotes the catalyst carbided at 973 K in the CH_4/H_2 mixture, while nitrided/973 K-carbided denotes the catalyst nitrided at 973 K in NH_3 and carbided at 973 K. The reforming reaction and TPR experiments were carried out in-situ after preparation. The catalystic tests were conducted in CH_4 (15 mL min^{-1}) at 973 K with the reaction products detected by a quadrupole mass spectrometer connected on-line. TPR was carried out in-situ (H_2 flow rate: 15 mL min^{-1}, temperature ramp: 10 K min^{-1}) with the desorption peaks deconvoluted using commercial software.

The conversions of methane for the various molybdenum catalysts at 7 h time on stream are listed in Table1. The nitrided/1173 K-carbided catalyst showed the greatest methane disappearance rate of 2.57 mmol min^{-1} mol Mo^{-1}, followed by the 873 K-carbided catalyst. XRD analyses of the nitrided catalyst and nitrided/973 K-carbided catalyst before and after reaction revealed that the carbide phase changes from γ-Mo_2N and α-Mo_2C, respectively, to η-Mo_3C_2. Figure 1 shows the XRD patterns of the nitrided/973 K-carbided catalyst before and after reaction. Whereas the catalyst exhibited only the α-Mo_2C structure before reaction, the carbide phase changes to η-Mo_3C_2 after reaction, with a small peak of β-Mo_2C. For the catalysts without nitriding pretreatment, β-Mo_2C was the only carbide phase detected, and no change was observed as a result of the reaction.

Table 1. Activity data for various molybdenum carbides

Catalyst Nitrided at (K)	 Carbided at (K)	Conversion[a]	CH_4 disappearance rate[b]	XRD pattern b. r.[c]	 a. r.[d]
973	1173	0.5	2.57	η-Mo_3C_2	η-Mo_3C_2
973	973	0.4	2.01	α-Mo_2C	η-Mo_3C_2
—	973	0.4	2.00	β-Mo_2C	β-Mo_2C
—	923	0.3	1.66	β-Mo_2C	β-Mo_2C
—	873	0.5	2.19	β-Mo_2C	β-Mo_2C
973	—	0.4	1.96	γ-Mo_2N	η-Mo_3C_2

[a]%. [b]mmol min^{-1} mol-Mo^{-1}. [c]Before reaction. [d]After reaction.

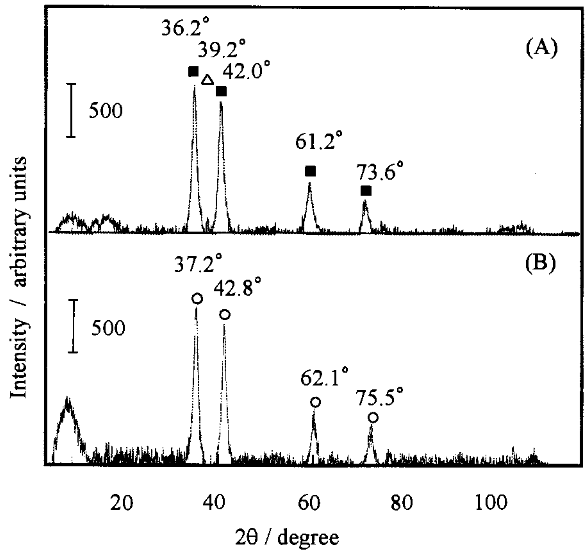

Figure 1. XRD patterns of nitrided/973 K-carbided catalyst before and after reaction. (A) After reaction and (B) before reaction.

The η-Mo_3C_2 catalyst retained this crystal structure throughout the reaction.

Along with XRD, the TPR results after 7 h time on stream also revealed that the surface compositions of the catalysts change as a result of the reaction. The various phases of molybdenum carbide can be distinguished through deconvolution of the methane desorption peak during TPR, as shown in a previous paper.[1] For the nitrided/973 K-carbided catalyst, the desorption products indicated predominance of α-Mo_2C on the catalyst surface, designated by the peak at 780 K, as shown in Figure 2. At 15 min time on stream, this desorption peak decreases, with an increase in the peak at 1083 K. This peak is assigned to η-Mo_3C_2.[1] After reaction, the catalyst surface is of η-Mo_3C_2 character, with a small peak at 881 K, which is assigned to β-Mo_2C. These results are in agreement with those obtained by XRD, which also showed the change from α-Mo_2C to η-Mo_3C_2, with traces of β-Mo_2C. Thus, methane reforming at 973 K changes the carbide species present on the catalyst surface to η-Mo_3C_2.

Correlating the amount of desorption for η-Mo_3C_2 as obtained from TPR with the results of the methane reforming reaction, a linear relationship was revealed. As the amount of η-Mo_3C_2 increased, the methane disappearance rate increased, as shown in Figure 3. This illustrates the importance of η-Mo_3C_2 for increased methane reforming activity. Thus, of the various types of molybdenum carbides, the η-Mo_3C_2 catalysts had the highest CH_4 decomposition rate, proving that η-Mo_3C_2 is the active species for the reforming of methane.

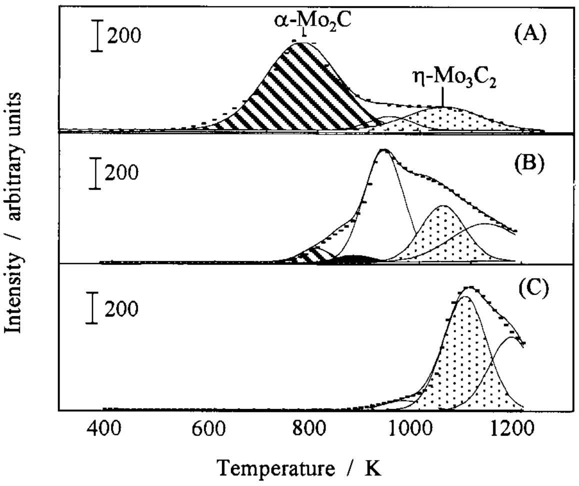

Figure 2. Peak deconvolution of CH_4 desorption peak during TPR of nitrided/973 K-carbided catalyst. (A) Before reaction, (B) 15 min into reaction, and (C) after reaction.

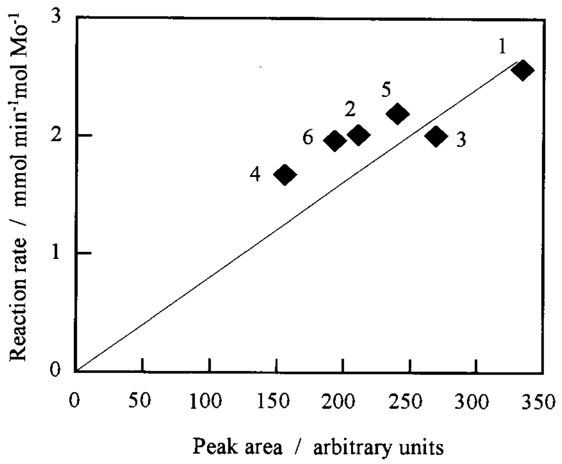

Figure 3. Reaction rate vs. amount of CH_4 desorption from TPR. (1) Nitrided/1173 K-carbided, (2) nitrided/973 K-carbided, (3) 973 K-carbided, (4) 923 K-carbided, (5) 873 K-carbided, and (6) 973 K-nitrided.

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