

Study of the Preparation and Catalytic Performance of Molybdenum Carbide Catalysts Prepared with C₂H₂/H₂ Carburizing Mixture

Tiancun Xiao, Haitao Wang, Jianwen Da, Karl S. Coleman, and Malcolm L. H. Green¹

The Wolfson Catalysis Centre, Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QR, United Kingdom

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A series of molybdenum carbide catalysts were prepared using 10% C₂H₂/H₂ to carburize molybdenum trioxide at different temperatures. Their catalytic performance was evaluated using methane partial oxidation to synthesis gas as the model reaction. The structure of the catalysts treated under various conditions was characterized using X-ray diffraction, laser Raman spectroscopy, and scanning electron microscopy. The results show that MoO₃ is first converted into MoO₂ and MoC_{1-x}. With the rise of the carburization temperature, MoO₂ is converted into MoC_{1-x} and the catalyst crystallites tend to be very small. However, the catalyst surface remains coated by MoO₃ or MoO₂. When the carbides are heated in N₂ to 850°C, they are converted into MoC_{1-x} and β-Mo₂C. Interestingly, all the catalyst samples show high CH₄ conversion and CO selectivity in partial oxidation of methane, although the pretreatment has some effect on the preliminary activity and selectivity. The catalyst is partly oxidized and there is a small amount of carbon deposition after the activity test. Acetylene is therefore a good carburizing agent for preparing molybdenum carbide catalyst at low temperature for the partial oxidation of methane. © 2002 Elsevier Science (USA)

Key Words: molybdenum carbide catalysts; preparation using acetylene; partial oxidation of methane.

INTRODUCTION

Since 1973, when Levy and Boudart reported that WC displayed reactivity similar to Pt for neopentane isomerization (1), there has been considerable interest in the catalytic properties of metal carbides, particularly of the group VI transition metals, for a variety of reactions (2, 3). The main problem with using metal carbides as catalysts has been the difficulty in obtaining materials with sufficiently high surface area for catalytic applications. To overcome this difficulty, efforts have been focused on ways to prepare high-surface-area carbide catalysts, among which the method of temperature-programmed reduction (TPR) using hydrocarbon is most widely used

(4–11). Catalysts prepared in this way have a surface area as large as 200 m²/g. These carbide catalysts have shown promise for a number of reactions, including hydrodenitrogenation (HDN) and hydrodesulfurization (HDS) (12–15), hydrocarbon isomerization (16–20), CO hydrogenation, and Fischer–Tropsch synthesis (21–23). Recently, it has also been demonstrated that carbide catalysts show extremely high activity in methane partial oxidation to synthesis gas (syngas) (24). It has also been shown that the different structural types of molybdenum carbides have different performances in a range of chemical reactions. For example, the metastable α-phase of molybdenum carbide, α-MoC_{1-x}, whose structure is face-centered cubic (fcc), possesses catalytic performance properties which differ from those of stable hexagonal close packed (hcp) β-phases in the hydrogenolysis of ethane (25). The detailed properties of the molybdenum carbides with different structures were summarized by Oyama, and it is pointed out that the structures of the carbides are determined by two intimately connected factors, geometry and electronics (26).

In the carbide catalyst preparation using the TPR method with hydrocarbon, a range of carburizing agents are available. It has been shown that the choice of hydrocarbon has a reasonable effect on the catalytic performance of the catalyst (27–29). Using a hydrocarbon with a high carbon number decreases the phase transformation temperature from molybdenum oxide to carbide. To date, most of the work has focused on the use of mixtures of hydrogen and methane or ethane as carburizing agents. These gas mixtures are relatively unreactive and require the use of high temperatures to effect carburization. The carbide products are limited to high-temperature phases only. There have been some reports of the use of higher alkanes as carbon sources, and generally these show greater reactivity as carburizing agents than CH₄ and C₂H₆. Butane and ethylene have been used to prepare carbide catalysts (27, 29), but no work has been reported on the use of acetylene for carbide preparation. Herein, we report the preparation of series of molybdenum carbide catalysts using acetylene and their catalytic performance for methane partial oxidation.

¹ To whom correspondence should be addressed. Fax: +44-1865-272690. E-mail: malcolm.green@chem.ox.ac.uk.



EXPERIMENTAL

The catalyst preparation was carried out as follows. About 0.8 g MoO_3 (Alfa, 99.995%) was loaded in a 9-mm (o.d.) silica tube held with silica wool at the two ends. A flow of 100 ml/min of 10% $\text{C}_2\text{H}_2/\text{H}_2$ (vol) was passed over the MoO_3 , and the temperature was raised by $1^\circ\text{C}/\text{min}$ to different target temperatures and held for 4 h. The volume ratio of C_2H_2 to H_2 was chosen so the exposure of the MoO_3 to carbon was equivalent to 20% CH_4/H_2 , which is known to afford the highest surface area in molybdenum carbide catalysts. Afterward the reactor was quenched to room temperature under flowing argon by removing the tube from the furnace. Before exposure to air, the samples were passivated in flowing 1 vol% O_2/Ar (20 ml/min). The samples were carburized to final temperatures of 450, 500, 550, and 630°C . The resultant carbides are denoted as MoC-450, MoC-500, MoC-550, and MoC-630, respectively.

The crystalline structure of the materials was measured by X-ray diffraction (XRD) using a Philips PW1710 diffractometer with $\text{Cu } K\alpha$ radiation. A chosen amount of sample was loaded in a glass or aluminum sample holder, and the XRD pattern was recorded under ambient atmosphere. Occasionally an aluminum sample holder was used as an internal standard. The morphology of the passivated samples was observed with scanning electron microscopy (SEM) on a Hitachi S-520 microscope operated at 20 kV and 40 mA.

Raman spectra were recorded with a resolution of 2 cm^{-1} using an Yvon Jobin Labram spectrometer with an Ar^+ laser (514.5 nm) running on a back-scattered confocal arrangement. The samples were pressed on a microscope slide and the scanning time was set to 60 s. The scanning range was 90 to 2500 cm^{-1} . The catalyst surface areas were determined from N_2 BET isotherms on a Sorptomatic 1990. The carbon and nitrogen contents of the samples were measured with a CHN analyzer in the Inorganic Chemistry Laboratory, University of Oxford.

The catalytic partial oxidation of methane to syngas was carried out by continuously passing a gaseous feed containing methane (>99.95%) and air (CH_4/O_2 , ratio: 2.03) over the catalyst (0.2 g) packed in a 9-mm (o.d., i.d. 6 mm) quartz reactor kept in a tubular furnace (i.d. 25 mm). The reactor was heated under flowing Ar or CH_4 to 860°C , a well-mixed reactant (CH_4 and air) was conducted to the reactor bed at 860°C , and the pressure was raised to 5 bar. The reaction temperature was controlled to within 5°C . The gaseous products were passed to the GC-MS through a heated pipeline and analyzed by an online gas chromatograph using a spherocarb column and detected with TCD and FID. CH_4 conversion for the reaction refers to the ratio of converted CH_4 to the feeding CH_4 . During the reaction, CO and CO_2 were obtained as the main carbon oxide products. Selectivity to CO refers to the ratio of CO yield in the product to the amount of converted CH_4 .

RESULTS AND DISCUSSION

Characterization of the As-Prepared Molybdenum Carbides

The XRD patterns of the as-prepared molybdenum carbides are shown in Fig. 1. Three main peaks at 26.0 , 37.0 , and 53.4° were seen in the XRD pattern of MoC-450, which are characteristic of MoO_2 (30); no peaks due to molybdenum carbide were seen (31). This suggests that C_2H_2 is not able to reduce MoO_3 to carbide at 450°C . The formed MoO_2 resulted from the hydrogen reduction of MoO_3 (27). The sample color changed from light green to black after attempted carburization at 450°C . However, no carbon was detected by XRD, suggesting that the carbon deposit is highly dispersed in the sample or amorphous.

When the carburization temperature was raised to 500°C , the amount of MoO_2 present decreased rapidly; however, no peaks in the XRD corresponding to molybdenum carbide were observed, suggesting that carburization of MoO_3 with 10% $\text{C}_2\text{H}_2/\text{H}_2$ to 500°C does not afford carbide. In the XRD patterns of MoC-550 and MoC-630, the peaks due to MoO_2 were no longer observed, and new peaks at 37.0 , 42.0 , and 62.3° were present, which can be assigned to the diffraction of MoC_{1-x} (32). This also shows that carburization of MoO_3 with 20% $\text{C}_2\text{H}_2/\text{H}_2$ may be a new method to produce MoC_{1-x} . In the XRD pattern of MoC-630, besides the peaks of MoC_{1-x} , relatively sharp peaks at 38.4 and 44.6° were observed, which correspond to the diffraction of aluminum sample badge. These results therefore suggest that during the carburization of MoO_3 with 10% $\text{C}_2\text{H}_2/\text{H}_2$ the oxide is first reduced to MoO_2 by H_2 , which is then converted to MoC_{1-x} . Comparison of the XRD patterns of carburized MoO_3 using 10% $\text{C}_2\text{H}_2/\text{H}_2$, 10% $\text{C}_2\text{H}_6/\text{H}_2$ (26), and 5% $\text{C}_4\text{H}_{10}/\text{H}_2$ (27) suggests that the sample prepared using 10% $\text{C}_2\text{H}_2/\text{H}_2$ has the weakest diffraction peak, while that prepared using 10% $\text{C}_2\text{H}_6/\text{H}_2$ has the strongest diffraction

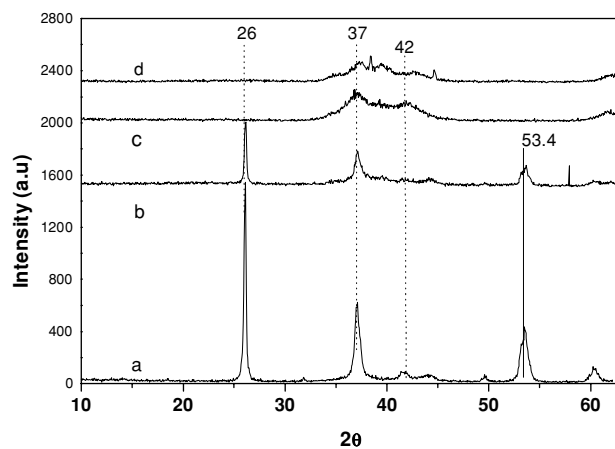


FIG. 1. XRD patterns of molybdenum oxide carburized with 10% $\text{C}_2\text{H}_2/\text{H}_2$ to different temperatures: (a) 450, (b) 500, (c) 550, and (d) 630°C .

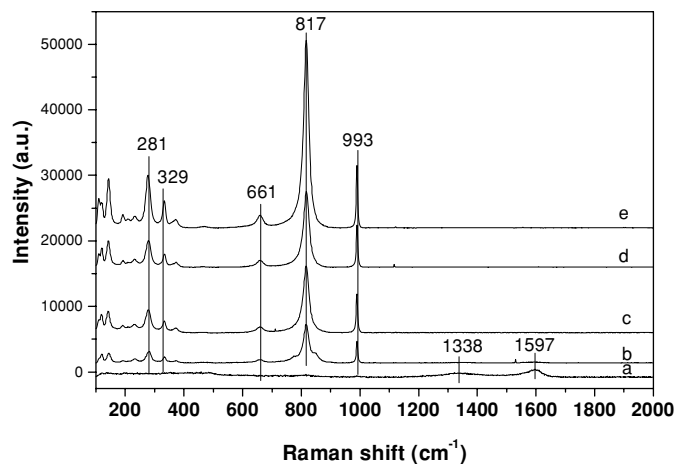


FIG. 2. LRS of the molybdenum carbides prepared by carburizing MoO_3 with 10% $\text{C}_2\text{H}_2/\text{H}_2$ to different temperatures: (a) 450°C point 1, (b) 450°C point 2, (c) 500, (d) 550, and (e) 630°C.

peaks. This indicates that carburization with $\text{C}_2\text{H}_6/\text{H}_2$ gives molybdenum carbide with the largest crystallites, whereas carburization with $\text{C}_2\text{H}_2/\text{H}_2$ produces molybdenum carbide with small crystallites. This may be related to the stability of the carburizing agent.

The laser Raman spectra (LRS) of the acetylene-carburized samples are shown in Fig. 2. Because the spectrometer enables us to do microanalysis, the Raman spectra were recorded at different points of the sample. As a consequence, the surface of MoC-450 was known not to be uniform. At one point, peaks at 1338 and 1597 cm^{-1} were observed on the catalyst surface. The band at 1338 cm^{-1} is attributed to the vibration of disorder-induced carbon and is called the D line, whereas the peak at 1597 cm^{-1} is related to the crystallized carbon, known as the G line. (32, 33) At this sample point, the two peaks are the main peaks, and almost no peaks due to molybdenum oxides are seen, suggesting at this point the surface is completely covered by a carbon deposit (Fig. 2, line a). However, another point in the sample shows Raman peaks at 993, 817, 661, 329, and 281 cm^{-1} (Fig. 2, line b), which can be assigned to MoO_2 in the sample. In combination with the XRD results, this sug-

gests that the bulk and surface of MoC-450 are composed of MoO_2 , although some carbon deposit covers the surface. The carbon deposit may arise from the thermal decomposition of C_2H_2 over the catalyst. The surface of MoC-500, -550, and -630, however, is uniform, with the LRS at different points in the sample all the same as shown in Fig. 2, lines c, d, and e. No carbon deposit is present on the catalyst surface, and the peaks attributed to MoO_2 become increasingly intense with the increase in carburization temperature. In MoC-500, because the main phase is MoO_2 , the surface gives a Raman spectrum of MoO_2 as expected. MoO_2 was also detected in the Raman spectra of MoC-550 and -630, which may be a result of the passivation step after the carburization was complete.

The composition and surface areas of the prepared samples are given in Table 1. The carbon contents in MoC-450, -500, -550, and -630 are 8.72, 4.89, 5.69, and 8.55 wt% respectively. MoC-450 has the highest carbon content, and although this is present in the form of carbon deposit due to the thermal decomposition of C_2H_2 , no molybdenum carbide was formed. The lower carbon content in MoC-500 may result from the hydrogenation of the carbon deposit over MoO_2 at higher temperature. With the rise of carburization temperature to 550 and 630°C, the carbon content increases again, which is due to the formation of molybdenum carbide because carbide formation is faster than carbon deposition.

The surface areas of MoC-450, -500, -550, and -630 are 18.6, 22.4, 26.6, and 36.2 m^2/g , respectively. The surface area increases with increase of the carburization temperature and the formation of carbide. The morphologies of the molybdenum carbides prepared with acetylene were studied by SEM, the results of which are shown in Fig. 3. It is interesting that all the materials have similar crystal shapes. They are all rectangular, although there is a significant difference of particle size. The particle size of MoC-450 is about 10 μm , and there are fewer smaller particles of MoC-450. The particles become smaller in MoC-500, and the particles range from 3 to 10 μm . In MoC-550, the particles become smaller still and are thinner with some needle-like particles also present. In MoC-630, the molybdenum carbide particles are only 6 μm long, and more square in shape.

TABLE 1

Composition and Surface Area of Molybdenum Carbide Prepared Using 10% $\text{C}_2\text{H}_2/\text{H}_2$ and Treated under Different Conditions

| Catalyst | MoC-450 | | | MoC-500 | | | MoC-550 | | | MoC-630 | | |
|------------------------------------|-------------|---------------------------|--------------------|-------------|---------------------------|--------------------|-------------|---------------------------|--------------------|-------------|---------------------------|--------------------|
| | As prepared | Treated with N_2 | After POM reaction | As prepared | Treated with N_2 | After POM reaction | As prepared | Treated with N_2 | After POM reaction | As prepared | Treated with N_2 | After POM reaction |
| Carbon content (wt%) | 8.72 | 4.35 | 5.49 | 4.89 | 4.79 | 6.74 | 5.69 | 3.98 | 5.65 | 8.55 | 4.01 | 6.55 |
| Nitrogen content (%) | n.d. | 0.36 | n.d. | n.d. | 0.41 | n.d. | n.d. | 0.32 | n.d. | n.d. | 0.25 | n.d. |
| Surface area m^2/g | 18.6 | 20.4 | 23.5 | 22.4 | 23.2 | 19.8 | 26.6 | 23.1 | 25.2 | 36.2 | 25.1 | 23.1 |

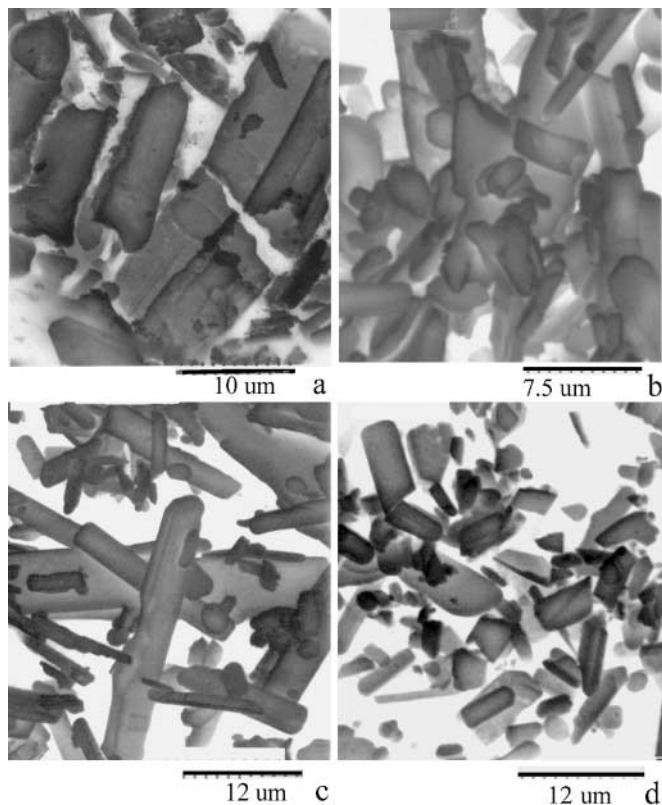


FIG. 3. SEMs of the molybdenum carbide carburized using 10% C_2H_2/H_2 to (a) 450, (b) 500, (c) 550, and (d) 630°C.

The carburized samples have a morphology similar to that of their parent oxide, suggesting that the carburization of MoO_3 with acetylene is a topotactic process (11). This process is similar to the carburization with ethane or butane (27), but different from the carburization using methane. These results are in keeping with the increase in surface area as the carburization temperature is increased.

Thermal Treatment of the Molybdenum Carbide under N_2

It was shown in the preceding section that there is carbon deposit present in the carbide prepared with acetylene. To study the structural changes of the carbide catalysts and the pretreatment effect on the catalyst performance, the as-prepared molybdenum carbides (after passivation and exposure to air for 1 day) were heated to 850°C under flowing nitrogen, and then cooled down to room temperature and passivated with 1% O_2/Ar . The XRD patterns of the treated samples are shown in Fig. 4. The N_2 -treated MoC-450 has diffraction peaks at 25.8, 34.7, 37.6, 39.8, and 43.2° respectively, among which the peaks at 25.8 and 37.6° are assigned to the diffraction of MoO_2 in the sample (30), and the new peaks at 34.7 and 39.8° are assigned to the diffraction of Mo_2C (31). The peaks at 37.6 and 43.2° are attributed to the diffraction of MoC_{1-x} (34). This suggests that the thermal treatment of MoC-450 in N_2 causes the carbon de-

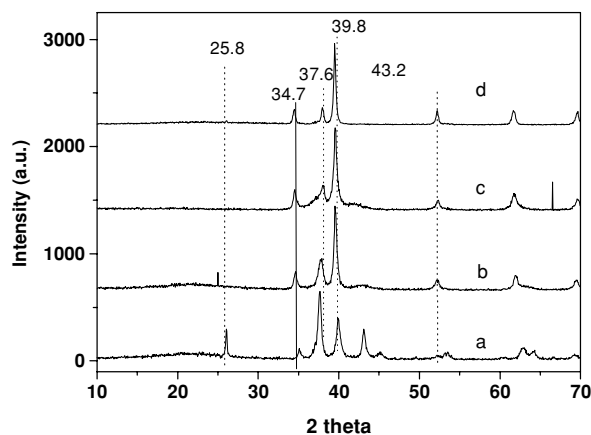


FIG. 4. XRD patterns of MoC prepared by carburizing MoO_3 with 10% C_2H_2/H_2 at (a) 450, (b) 500, (c) 550, and (d) 630°C. The carbides were then heated to 850°C at 5°C/min under N_2 for 2 h.

posit and MoO_2 , which are present in the sample, to react together to form Mo_2C and MoC_{1-x} carbides. In the XRD pattern of MoC-500 after N_2 thermal treatment, the peaks corresponding to MoO_2 that were originally present have disappeared, and only peaks at 34.7, 37.6, and 39.8° are seen, which are attributed to the XRD of Mo_2C . The XRD patterns of MoC-550 and MoC-630 after N_2 thermal treatment at 850°C are similar to that of N_2 -treated MoC-500. This reveals that N_2 thermal treatment causes MoC-500, -550, and -630 to transform from fcc to hcp carbides. In all the samples, no molybdenum nitride was detected.

The laser Raman spectra of the thermally treated samples under N_2 are shown in Fig. 5. In the thermally treated MoC-450, the peaks at point 1 appear at 838 and 790 cm^{-1} , which are assigned to the vibration of Mo–O. At point 2, main Raman peaks were seen at 993 and 817 cm^{-1} and

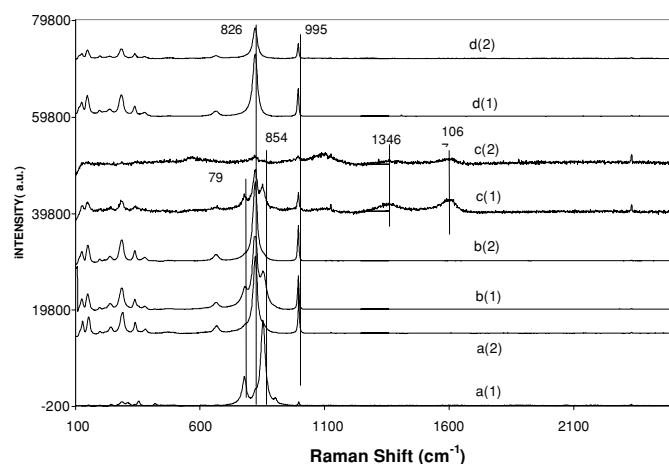


FIG. 5. LRS of MoC prepared by carburizing MoO_3 with 10% C_2H_2/H_2 at (a) 450, (b) 500, (c) 550, and (d) 630°C. The carbides were then heated to 850°C at 5°C/min under N_2 for 2 h.

were assigned to the vibration of Mo–O in polycrystalline MoO₂. This suggests that the surface of molybdenum oxide is present in different states after thermal treatment under nitrogen. This could be due to the trace oxygen passivation or the incomplete reaction of some MoO₂ with carbon in the as-prepared sample. The surface states of MoC-500 were changed by the thermal treatment under N₂, although the surface was still dominated by the molybdenum oxide states. At point 1 in MoC-500, the sample surface shows Raman peaks at 993, 849, 817, and 776 cm⁻¹, which are characteristic of polycrystalline MoO₃ (35). However, the peaks at 993 and 817 cm⁻¹, attributed to MoO₂, are observed at point 2. The Raman bands in different positions on sample MoC-550 and -630 after thermal treatment under N₂ are similar to the as-prepared sample. These results are in agreement with the XRD results and show that some of the MoO₂ present in MoC-450 and -500 reacts with the carbon deposit to form molybdenum carbide. The lack of uniformity in the sample surface may be a consequence of carbon deposit being unevenly distributed across the sample.

The SEMs of the molybdenum carbide after thermal treatment under N₂ are shown in Fig. 6. There is a signifi-

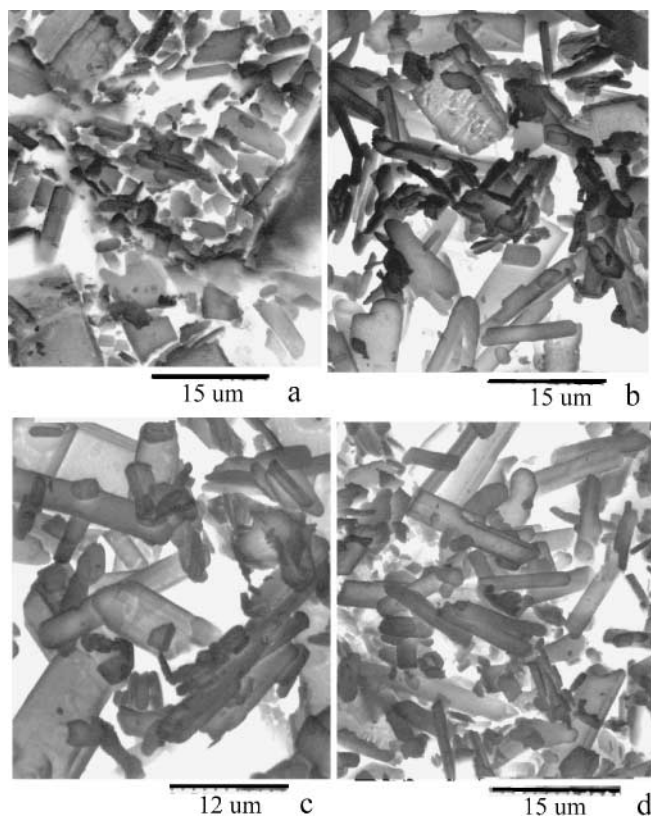


FIG. 6. SEMs of molybdenum carbide prepared by carburizing MoO₃ with 10% C₂H₂/H₂ at (a) 450, (b) 500, (c) 550, and (d) 630°C. The carbides were then heated to 850°C at 5°C/min under N₂ for 2 h.

cant variation in the particle size in the treated MoC-450, although the particles remain rectangular in shape. This suggests that the phase transformation of MoO₂ to carbide is a topotactic process. The morphology of MoC-500 after thermal treatment under N₂ similarly shows that some thinner rectangular crystals are present. Compared with the untreated sample, once again, the thinner crystals may be a result of the reaction of MoO₂ with carbon deposit resulting in formation of Mo₂C. The thermal treatment under N₂ also caused some of the MoC-550 and -630 particles to split into smaller crystals, although some large crystals were still present. However, all the crystals in the materials after thermal treatment under N₂ are rectangular. The small changes in morphology of the crystals are consistent with the change in carbide form, which is in agreement with XRD.

The composition and surface areas of the molybdenum carbides prepared with acetylene after thermal treatment under N₂ are shown in Table 1. The surface areas of the treated MoC-450 and -500 are increased slightly, but for MoC-550 and -630, the thermal treatment with N₂ causes the surface area to decrease. This may be due to the conversion of the main phase of MoO₂ in the as-prepared sample into carbide upon thermal treatment of MoC-450 and -500. However, in MoC-550 and -630, the thermal treatment with N₂ results in the formation of large particles, which may explain the decrease in surface area. The carbon content in the samples after thermal treatment under N₂ decreased and there was a trace quantity of nitrogen detected, suggesting a small amount of nitride was formed.

Catalytic Performance of the Molybdenum Carbides for Partial Oxidation of Methane

It has been shown that carbide catalyst is active for methane partial oxidation to syngas, and that the active phase is the lattice carbon in the molybdenum carbide (24, 36). Hence it is expected that passivation leading to the presence of surface oxygen is not beneficial to the catalyst performance and that pretreatment is needed to remove the surface oxygen and activate the passivated catalyst. It has been shown that all the forms of molybdenum carbide are converted into Mo₂C when the temperature is above 750°C (37) because molybdenum carbide catalysts are active and become stable only above 860°C and 4 bar for the partial oxidation of methane. It is believed that Mo₂C is the active component for the partial oxidation of methane to syngas. In the activity test in this study, the catalysts were treated under different conditions and the effect of pretreatment on the catalyst performance was studied.

The catalytic activities of the molybdenum carbide catalysts for methane partial oxidation to syngas were evaluated under different conditions; the results are shown in Figs. 7a–7e. To study the effect of pretreatment on the catalytic performance, samples of MoC-450 were heated to 860°C under N₂ and separately under CH₄. Then a mixture

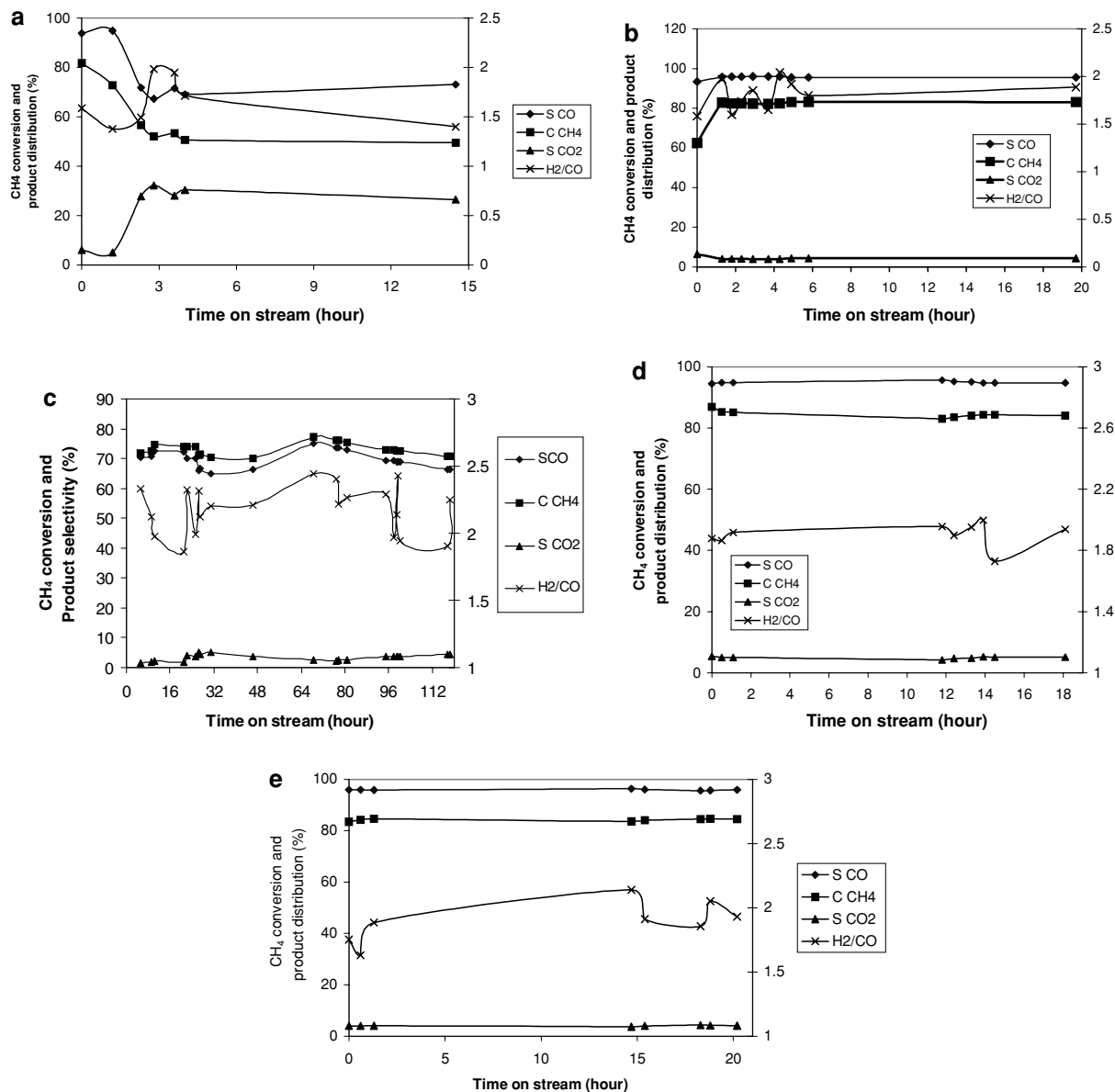


FIG. 7 (a) CH₄ conversion and product distribution in methane partial oxidation to syngas over 0.2 g MoC-450. The catalyst was heated under flowing N₂ to 860°C and switched to the mixture of CH₄ and air. (b) CH₄ conversion and product distribution in methane partial oxidation to syngas over 0.2 g MoC-450. The catalyst was heated under flowing CH₄ to 860°C and switched to the mixture of CH₄ and air. (c) CH₄ conversion and product distribution in methane partial oxidation to syngas over 0.2 g MoC-500. The catalyst was heated under flowing N₂ to 860°C and switched to the mixture of CH₄ and air. (d) CH₄ conversion and product distribution in methane partial oxidation to syngas over 0.2 g MoC-550. The catalyst was heated under flowing N₂ to 860°C and switched to the mixture of CH₄ and air. (e) CH₄ conversion and product distribution in methane partial oxidation to syngas over 0.2 g MoC-630. The catalyst was heated under flowing N₂ to 860°C and switched to the mixture of CH₄ and air. All reactions were carried out at 860°C and 5 bar. CH₄/O₂ ratio: 2.03.

of methane and air (CH₄/O₂ = 2.03) was passed over the catalyst and the catalyst performance was tested. The initial methane conversion was 80%, CO selectivity was 92%, and CO₂ selectivity was very low at 8%. However, after 3 h on-stream, CH₄ conversion dropped to 56%, and CO selectivity to 73%, but CO₂ selectivity increased to 31%, while the H₂/CO ratio was only 1.3 (Fig. 7a). These results suggest that MoC-450 preheated under N₂ is not stable for partial

oxidation of methane (POM) to synthesis gas. This can be explained by the small amount of Mo₂C present compared with MoO₃, which is not active in POM (24).

When MoC-450 was heated under flowing CH₄ to 860°C and evaluated for the reaction of methane partial oxidation to syngas, contrary to the performance of MoC-450 activated using N₂, CH₄ conversion and CO selectivity over MoC-450 activated using CH₄ are 82 and 93%, respectively,

with a H_2/CO ratio at around 2 (Fig. 7b). The catalyst shows an increased stability and higher selectivity. This may be due to the activation of the catalyst using CH_4 , which helps to convert the MoO_2 into Mo_2C .

For MoC-500 preheated under flowing N_2 , initial CH_4 conversion over the catalyst is 72%, selectivity to CO is 74%, and the H_2/CO ratio is around 2.2 (Fig. 7c). The excess of hydrogen may result from methane decomposition or the carburization of MoO_2 with CH_4 . With increasing time on stream, the H_2/CO ratio decreases, and the conversion of CH_4 and selectivity to CO increase. However, during an activity test over 5 days, a significant variation was observed, particularly in the H_2/CO ratio, and the CH_4 conversion and CO selectivity failed to reach the thermodynamic equilibrium values.

For the catalysts MoC-550 and -630 pretreated with N_2 to $860^\circ C$, CH_4 conversion and product distribution are all around the thermodynamic values in the methane partial oxidation to syngas (Figs. 7d and 7f). The catalyst performances were also found to be stable over 20 h. This result is in agreement with the main phase present being Mo_2C (XRD results), which is the active component for the catalytic reaction.

The XRD patterns of the spent catalysts from partial oxidation of methane are shown in Fig. 8. After POM reaction, the main dominant phase of MoC-450 is MoO_2 . After MoC-450 was activated with CH_4 to $860^\circ C$ and tested for POM reaction, MoO_2 and carbon deposition, along with Mo_2C , are present in the catalyst. This suggests that the dominant phase in MoC-450 activated with CH_4 is carbide. This may be the reason for the high activity and selectivity of the catalyst in the reaction. The spent MoC-500 activated with N_2 is composed of Mo_2C and MoO_2 , and the amount of Mo_2C is far greater than MoO_2 . However, carbon deposition also

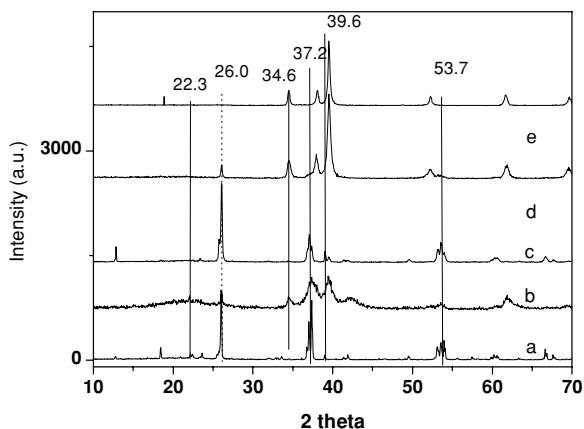


FIG. 8. XRD pattern of spent MoC catalysts for methane partial oxidation to syngas: (a) MoC-450 activated using N_2 to $860^\circ C$, (b) MoC-450 activated using CH_4 to $860^\circ C$, (c) MoC-500 activated using N_2 to $860^\circ C$, (d) MoC-550 activated using N_2 to $860^\circ C$, and (e) MoC-630 activated using N_2 to $860^\circ C$.

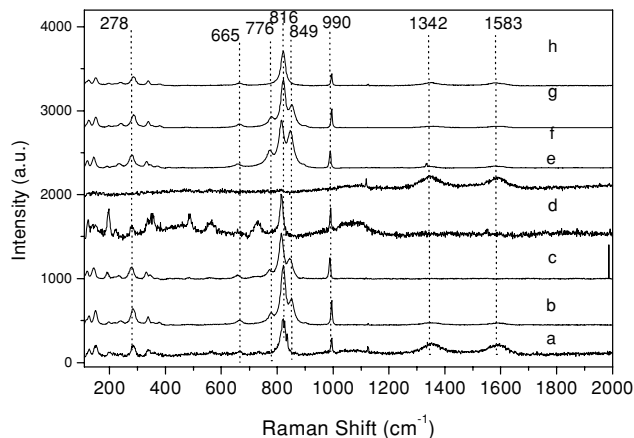


FIG. 9. Laser Raman spectra of MoC prepared using 10% C_2H_2/H_2 and after activity test for partial oxidation of methane at $860^\circ C$ and 5 bar; (a) MoC-450 point 1, (b) MoC-450 point 2, (c) MoC-500 point 1, (d) MoC-500 point 2, (e) MoC-550 point 1, (f) MoC-550 point 2, (g) MoC-630 point 1, and (h) MoC-630 point 2.

occurred over the catalyst; the carbon deposit is due to the long reaction period. In the XRD pattern of spent MoC-550 activated with N_2 , the dominant phase is Mo_2C ; however, a small peak at 26° is seen, which corresponds to MoO_2 , suggesting that there is a small amount of MoO_2 present in the catalyst. In the spent MoC-630 activated with N_2 , only peaks due to Mo_2C are seen, suggesting that MoC-630 is more stable than the other catalysts.

The Raman spectra of the spent catalysts after partial oxidation of methane reaction are given in Fig. 9. After reaction, MoO_2 and MoO_3 were produced over MoC-450 activated under N_2 . The difference in peak intensity of 816 and 849 cm^{-1} suggests different amounts of MoO_3 and MoO_2 over the catalysts. Although the XRD data for the spent MoC-450 activated under CH_4 show the bulk structure to be predominantly Mo_2C , the surface is still predominantly oxide. The surface oxide may arise from the reaction or during the passivation. When LRS was used to examine different areas of the postreaction samples of MoC-500, it was found that MoO_2 was present but there were some other areas where only carbon could be detected (38). In the Raman spectra of spent MoC-550, the Raman peaks corresponding to MoO_2 and MoO_3 appeared, and there was little difference between other positions on the sample, suggesting that the surface was mainly covered by molybdenum oxide. Peaks due to carbon deposition were very weak. The Raman spectra of the spent MoC-630 at different points on the surface were almost the same; only peaks due to MoO_2 were observed in this catalyst.

The SEMs of the four spent catalysts in Fig. 10 show that the particles in MoC-450 cracked and had more irregularities after the activity test. In the samples, some small particles ($<1\ \mu m$) are also present. In the spent MoC-550, smaller particles are seen, and the particle shape

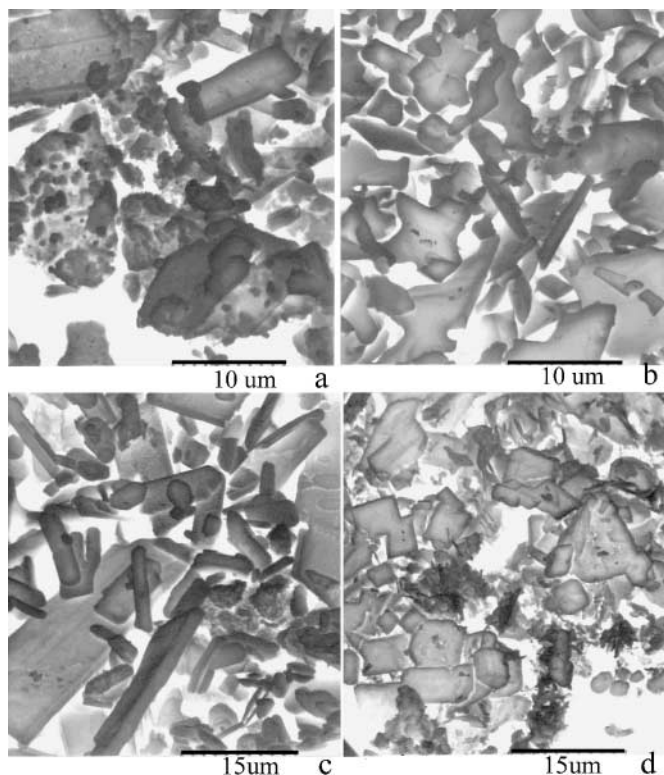


FIG. 10. SEMs of spent molybdenum carbide catalyst for methane partial oxidation prepared using 10% C_2H_2/H_2 at (a) 450, (b) 500, (c) 550, and (d) 630°C. The carbides were then heated to 850°C at 5°C/min under N_2 for 2 h.

is more irregular than the thermally treated sample under N_2 (Fig. 6b). No significant difference is present between the crystal morphologies of the thermally treated MoC-550 and spent MoC-550. However, in spent MoC-550, there are some very small particles, which may be carbon deposits or a new form of molybdenum carbide. The morphology of spent MoC-630 differs greatly from the carbide after thermal treatment under N_2 ; the particles are irregular and change from rectangular to square with some very fine particles present, which are probably carbon deposit.

The surface area of spent MoC-450 increases to 23.5 m^2/g , but the other spent catalysts have a lower surface area than their as-prepared samples. This may be due to the sintering or the oxidation of the catalyst during the reaction. The carbon content in the spent catalysts decreases in MoC-450, -550, and -630, which may be due to the reaction of the carbon deposit with oxygen. In MoC-500, the long catalyst run time may cause more coke to deposit on the catalyst, increasing the carbon content to 6.74 wt%.

CONCLUSIONS

Using 10% C_2H_2/H_2 as the carburizing agent, MoO_3 begins to convert into carbide when the carburization tem-

perature is above 500°C. Below this temperature, MoO_3 is converted into MoO_2 while the acetylene decomposes into carbon deposit. Carburization of MoO_3 into carbide is believed to be a topotactic process, because the morphology of the carbide is very similar to that of its parent oxide. C_2H_2 is therefore a potential agent for the preparation of molybdenum carbide at low temperatures.

Thermal treatment of the as-prepared samples under inert atmosphere causes the carbon deposit to react with MoO_2 and form the carbide. The molybdenum carbide with fcc structure is converted into Mo_2C with hcp structure, while the particle morphology is not changed significantly. The surface of the thermally treated carbide is covered by MoO_2 and MoO_3 .

Pretreatment has a significant effect on the catalytic performance of the carbide catalysts prepared using acetylene. MoC-450 activated under N_2 has a poor performance in POM to syngas, presumably because the main phase in the catalyst is MoO_2 . When activated under CH_4 , MoC-450 has a stable activity and selectivity for methane partial oxidation. The molybdenum carbides prepared using acetylene above 500°C show good performance in methane partial oxidation to syngas regardless of the activation methods.

In MoC-450 activated with CH_4 and MoC-550 and -630, the spent catalyst has hcp structure with Mo_2C , the main component, while the main component of MoC-450 and -500 activated with N_2 was found to be MoO_2 .

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