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# Effect of sulfur on the performance of molybdenum carbide catalysts for the partial oxidation of methane to synthesis gas

Tian-Cun Xiao, Hai-Tao Wang, Andrew P.E. York and Malcolm L.H. Green *

*Wolfson Catalysis Centre, Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QR, UK*

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Molybdenum carbide was tested as a catalyst for the partial oxidation of methane to syngas in the presence of $H_2S$. The fresh and used catalysts have been characterized using XRD, laser Raman and SEM-TEM. It is suggested that $H_2S$ concentration higher than 0.1 wt% in the feedstock results in conversion of the carbide phase to sulfide, and also promotes the oxidation of the carbide catalyst surface; the combined effect is catalyst deactivation. At low $H_2S$ concentration in the feedstock (<0.1 wt%) the structure of the carbide catalyst was unchanged, but the rate of carbon deposition over the reactor wall and in the catalyst bed increased, again leading to the catalyst deactivation.

**KEY WORDS:** sulfur poisoning; molybdenum carbide catalyst; partial oxidation of methane; syngas.

## 1. Introduction

The discovery of similarities between the catalytic behavior of group VI transition metal carbides and the noble metals has generated considerable interest [1]. This is due to the possibility of replacing expensive metals, such as Pd, Pt and Rh, with relatively abundant group VI metals [1–7]. To date there have been many studies on the preparation, structure and catalytic performance of transition metal carbide catalysts. Oyama *et al.* showed that molybdenum carbide catalysts were superior to conventional sulfide catalyst systems in HDS and HDN [8,9], and it has also been shown that transition metal carbide catalysts are stable and active for hydrodechlorination [10–12]. Recently, transition metal carbide catalysts, especially molybdenum carbide, have been tested for methane reforming to synthesis gas; the materials tested were active, selective and highly resistant to thermal sintering in synthesis gas production, performing as well as some noble metal catalysts [13–15].

Sulfur compounds, such as $H_2S$, are almost always present in fuel feedstocks, and are effective poisons for the noble metal catalysts often used in catalytic processes. Therefore, there have been a lot of studies on the sulfur poisoning of noble metal catalysts, their stabilization to deactivation, and regeneration [16–20]. It has been proposed that carbide catalysts have a high ability to resist sulfur poisoning, although there have been few studies concerning the effect of sulfur on the performance of carbide catalysts [21]. In this work, the effect of different $H_2S$ concentrations on the performance of a molybdenum carbide catalyst for methane partial oxidation to synthesis gas has been studied.

## 2. Experimental

*Catalyst preparation*: Molybdenum oxide, $MoO_3$ (200 mg) (Alfa, purity: 99.999%) was placed in a 9 mm (o.d.) silica tube plugged with silica wool at both ends. Carburizing reagent, 20% $CH_4/H_2$, was passed over the molybdenum oxide at a flow rate of $100\,ml\,min^{-1}$, and the temperature ramped at $1\,K\,min^{-1}$ to 750 °C and held for 30 min. The reactor was then cooled down to room temperature in flowing $H_2$. After cooling, the $H_2$ was stopped and the carbide sample passivated in 1% $O_2/He$ ($40\,ml\,min^{-1}$).

*Catalyst activity test*: The catalyst sample (generally 0.2 g) was placed between two quartz wool plugs in the centre of a 4-mm-i.d. silica tube, which was placed inside a steel tube and sealed at both ends with rubber "O"-rings to ensure that no gas could pass into the space between the two tubes. The reactor was inserted into a vertical Severn Science tube furnace, heated to 750 °C under $CH_4/H_2$, and then the gas was switched to flowing Ar while the temperature was further increased to the required reaction temperature (900 °C). The well-mixed reactants ($8\,ml\,min^{-1}$ $CH_4$ (including the desired concentration of $H_2S) + 19.8\,ml\,min^{-1}$ air (giving a $CH_4/O_2$ ratio = 2)) were passed to the reactor and the back pressure set to 8 bar. A sulfur trap was installed to capture sulfur in the exit gas before it entered the on-line GC. The products were analyzed in a GC (HP 5890A) equipped with TCD and FID detectors.

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* To whom correspondence should be addressed.
E-mail: malcolm.green@chem.ox.ac.uk

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*Catalyst characterization*: The crystalline structure of the materials was measured by X-ray diffraction (XRD) using a Philips PW1710 diffractometer with Cu $K_\alpha$ radiation. The sample was loaded in a glass sample holder, and the XRD pattern recorded under ambient atmosphere. 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 backscattered confocal arrangement. 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.

## 3. Results and discussion

The partial oxidation of methane (containing 0.6% $H_2S$) to syngas using air over 0.2 g $Mo_2C$ catalyst was carried out at 900 °C and 8 bar, as the transition metal carbide catalyst is unstable for partial oxidation at ambient pressure [16]. The initial $CH_4$ conversion was 77%, the selectivity to CO was 90%, and the $H_2/CO$ volume ratio was around 1.98; these values are close to the thermodynamic equilibrium. However, after 1 h, $CH_4$ conversion and CO selectivity had dropped to 70% and 82% respectively, and the $H_2/CO$ ratio had decreased rapidly to 1.74. Meanwhile, the $CO_2$ selectivity increased. This suggests that the onset of catalyst deactivation by sulfur poisoning was occurring; deactivation by other routes can be dismissed since it has been shown that molybdenum carbide has been stable for >100 h for the partial oxidation of methane (containing no sulfur) to syngas under similar conditions to those used here. In the initial 5 h of the reaction, the catalyst activity and selectivity to CO and $H_2$ decreased rapidly, followed by a gradual decrease later; the $CO_2$ selectivity was seen to increase in parallel. These results indicate that sulfur further poisoned the catalyst with time on stream. It is believed that surface carbon in the molybdenum carbide takes part in the methane partial oxidation reaction. Therefore, it is possible that the high concentration of $H_2S$ (0.6 wt% in $CH_4$) can convert the carbide surface into sulfide, which would account for the catalyst deactivation, both by removing carbon from the surface, which would normally take part in the reaction, and by reducing the catalyst activity (sulfide is less active than carbide).

When the $H_2S$ concentration in $CH_4$ was decreased to 0.4%, the initial $CH_4$ conversion and CO selectivity were 77% and 80% respectively. In the first hour, the CO and $CO_2$ selectivity and the $H_2/CO$ ratio were quite stable, although a slow decrease in $CH_4$ conversion was observed. After 2 h time on stream, the $CH_4$ conversion was decreasing gradually, while almost no change in CO selectivity could be seen. However, the $H_2/CO$ ratio quickly decreased to 1.58. This result can be explained by the initial sulfurization of the catalyst surface, suppressing the rate of $CH_4$ decomposition over the catalyst, thus affecting the function of the catalyst for $H_2$ production. It is interesting to note that during the 10 h time on stream, the selectivity to CO was almost constant, but that $CH_4$ conversion decreased gradually. It has been pointed out that the mechanism of methane partial oxidation to syngas is the combination of methane total combustion followed by reforming and water-gas shift with the $CO_2$ and $H_2O$ products [17,18]. It is clear that in the $CH_4$ reforming reaction using $CO_2$ the thermodynamic equilibrium $H_2/CO$ ratio is 1, while in $CH_4$ reforming with steam, the $H_2/CO$ theoretical ratio is 3. The overall theoretical $H_2/CO$ ratio in the partial oxidation reaction is 2, but, as seen in figure 1(b), the $H_2/CO$ ratio decreased rapidly with the time on stream, while the CO selectivity was almost constant. This suggests that 0.4% $H_2S$ in $CH_4$ may be suppressing the methane-steam reforming reaction.

The $Mo_2C$ catalyst was more stable in the partial oxidation of methane containing 0.2% $H_2S$, although the $CH_4$ conversion and CO selectivity did decrease gradually. However, the $H_2/CO$ ratio again dropped much faster than either the $CH_4$ conversion or CO selectivity. Indeed, after 10 h time on stream, the $CH_4$ conversion decreased from the initial 78.5% to 76%, and the CO selectivity from 83.8% to 80%, whereas the $H_2/CO$ ratio decreased from the initial 2.0 to 1.68. These results show that 0.2% $H_2S$ in $CH_4$ feedstock leads to only a very slow deactivation of $Mo_2C$.

Further decreasing the $H_2S$ concentration in $CH_4$ to 0.1% resulted in almost no change in the $CH_4$ conversion after 10 h time on stream, while the CO selectivity and $H_2/CO$ showed only minor changes from the initial values of 90% and 2.04 to 87% and 2 respectively, after the same period. These results reveal that 0.1% $H_2S$ in $CH_4$ feedstock has almost no effect on the catalyst effectiveness for $CH_4$ conversion, and a minor but nevertheless observable influence on CO selectivity. In fact, although the catalyst appeared to be fairly stable for the duration of the experiment, the back-pressure of the reactor increased very quickly after 30 h, and after the activity test a thick layer of carbon was present in the pre-catalyst zone of the reactor. This suggests that a large amount of carbon deposited on the reactor walls. Therefore, even though the lower $H_2S$ concentration does not affect the intrinsic $Mo_2C$ catalyst activity significantly, it does accelerate carbon deposition in the pre-catalyst zone, thus detrimentally affecting the catalytic reaction.

The changes in $CH_4$ conversion and CO and $H_2$ selectivity with percentage $H_2S$ concentration in the $CH_4$ feedstock, are shown in figure 2. In the reaction system with $H_2S$ higher than 0.4%, the $H_2/CO$ ratio increased very slowly with decreasing $H_2S$ concentration, suggesting that the high $H_2S$ content may be suppressing the steam reforming reaction. When $H_2S$ in methane was lower than 0.4%, the $H_2/CO$ ratio increased rapidly

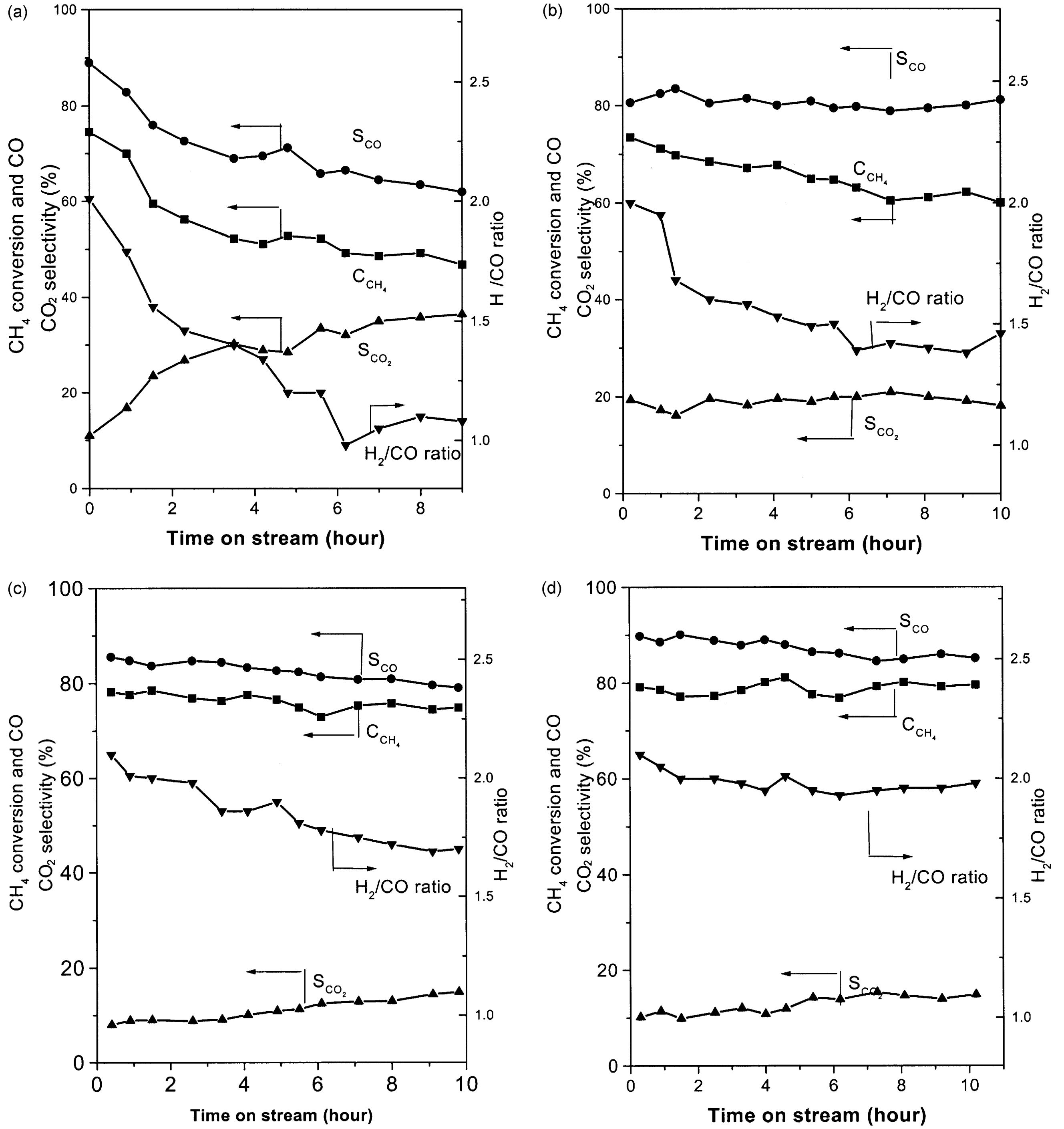


Figure 1. Partial oxidation of methane over the $Mo_2C$ catalyst (0.2 g catalyst, 900 °C, 8 bar, GHSV = 4200 ml $g^{-1}$ $h^{-1}$, $CH_4/O_2$ = 2.1). (a) 0.6% $H_2S$; (b) 0.4% $H_2S$; (c) 0.2% $H_2S$; and (d) 0.1% $H_2S$.

the decrease in $H_2S$ concentration, tending to stabilize with very low $H_2S$ concentrations (0.2–0%). When $H_2S$ is lower than 0.1%, the $H_2$/CO ratio is above 2, *e.g.*, more $H_2$ is produced than expected from thermodynamic equilibrium calculations. This is probably due to the decomposition of $CH_4$ over the carbide catalyst and on the reactor walls [19].

The XRD patterns of the molybdenum carbide catalysts after methane partial oxidation are shown in figure 3. According to ref. [20], the hexagonal $Mo_2C$ (P63/mmc) molybdenum carbide catalyst has diffraction peaks at 34.3, 37.9, 39.5 and 52.2°. After reaction, a new peak at 9.8° appeared, which is assigned to the diffraction of $MoS_2$ [22]. The peak at 26° is assigned to the diffraction of carbon deposits over the catalyst. The very intense peak indicates a large amount of carbon content in the catalyst sample. The carbide diffraction peaks after the reaction containing 1% $H_2S$ are very

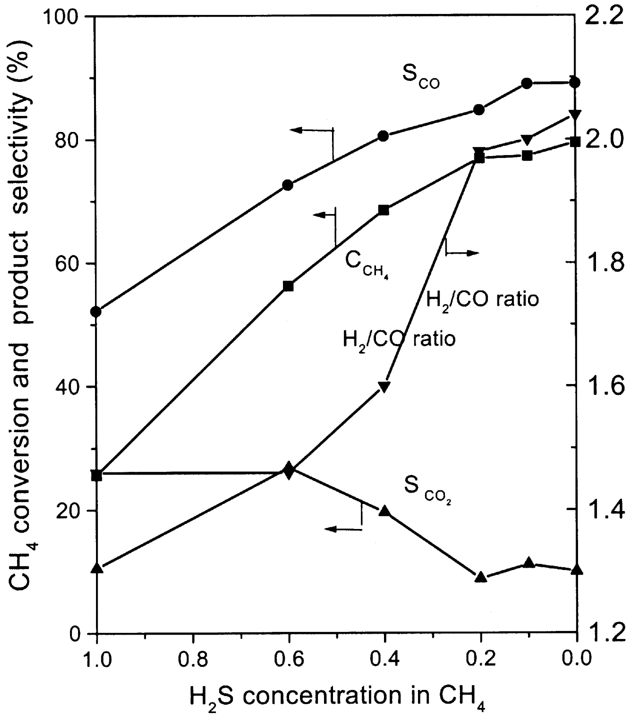


Figure 2. Effect of $H_2S$ concentration on the $CH_4$ conversion and product selectivity for methane partial oxidation over $Mo_2C$.

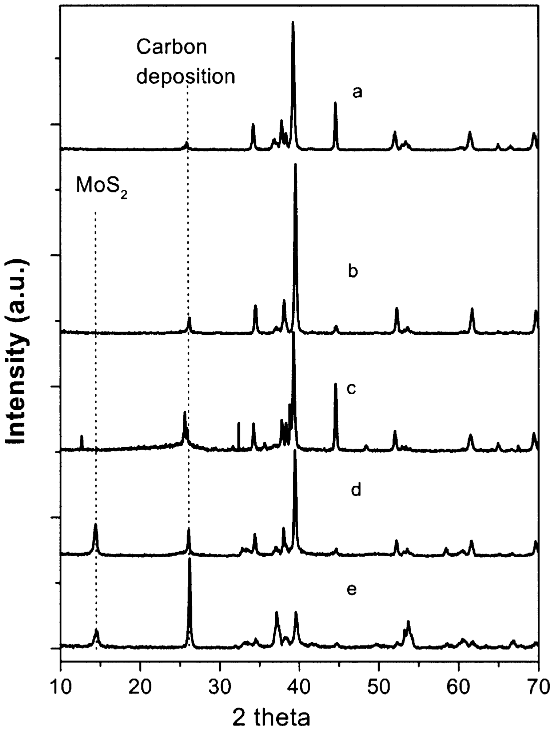


Figure 3. XRD patterns of the $Mo_2C$ catalysts before and after methane partial oxidation in the presence of hydrogen sulfide (reaction conditions as for figure 1). (a) 0.1% $H_2S$; (b) 0.2% $H_2S$; (c) 0.4% $H_2S$; (d) 0.6% $H_2S$; and (e) 1% $H_2S$.

weak, suggesting that less molybdenum carbide is present after the reaction. This is because some molybdenum carbide catalyst was converted into sulfide during the reaction.

Decreasing the $H_2S$ concentration in the methane feedstock to 0.6% also sulfurized the carbide catalyst and led to carbon deposits over the catalyst, as seen in figure 3(b); strong diffraction peaks due to $MoS_2$ and carbon were seen at 9° and 26° respectively. However, the diffraction peaks due to $Mo_2C$ are the strongest, suggesting that the main phase of the catalyst is carbide. Decreasing the $H_2S$ concentration to 0.4% in methane, the diffraction peaks due to molybdenum sulfide were further weakened, while the peaks due to carbon deposits were still obvious in the XRD pattern of the post-reaction catalyst. By further decreasing the $H_2S$ to 0.2% and 0.1% in methane, no molybdenum sulfide was seen in the spent catalysts by XRD, while the carbon deposits were ever present. This may give some explanation for the rapid decrease of catalyst activity in the reactions containing high $H_2S$ concentrations, and also suggests that sulfide is not active for the partial oxidation of methane to syngas. Although the low $H_2S$ concentration in the methane feedstock did not convert molybdenum carbide into the sulfide, carbon deposition in the catalyst bed was accelerated, which may lead to a slow decrease in the catalyst activity.

Laser Raman spectra of the spent catalysts after methane partial oxidation in the presence of hydrogen sulfide are given in figure 4. The peaks at 785 and 984 $cm^{-1}$ are most likely due to the vibration of $MoO_3$, while the peaks at 1359 and 1582 $cm^{-1}$ are attributed to the vibration of carbon deposits [23]. It can be seen that after the partial oxidation of methane containing 1.0% $H_2S$, the peaks due to carbon deposits are very strong, suggesting that there is a lot of carbon in the catalyst bed. However, some $MoO_3$ is still present in the catalyst surface; this may be a transition state of the catalyst in the reaction. When the $H_2S$ concentration was decreased to 0.6% in methane, the spent catalyst appeared to contain less carbon. A further decrease in the intensity of the carbon peaks was seen with decreasing $H_2S$ concentration. The post-reaction catalyst used in the partial oxidation of methane containing 0.2% $H_2S$ had weak peaks for carbon, but the bands due to $MoO_3$ were very strong. This suggests that the $MoO_3$ in the used catalyst is not related to the concentration of $H_2S$ in the reaction system. Figures 4(e) and (f) are very similar, suggesting that 0.1% $H_2S$ in methane has even less effect on the catalyst surface. Indeed, less carbon was observed in the catalyst bed after the reaction, but a large amount of carbon deposit was seen on the reactor walls in the pre-catalyst zone. This is in agreement with XRD results.

In accordance with the XRD results, it is suggested that carbon deposition on the catalyst surface increases with increasing $H_2S$ in $CH_4$. However, the catalyst surface is also partly covered by oxygen and sulfur, suggesting that the surface is also oxidized and sulfurized. The Raman results also show that there is less carbon

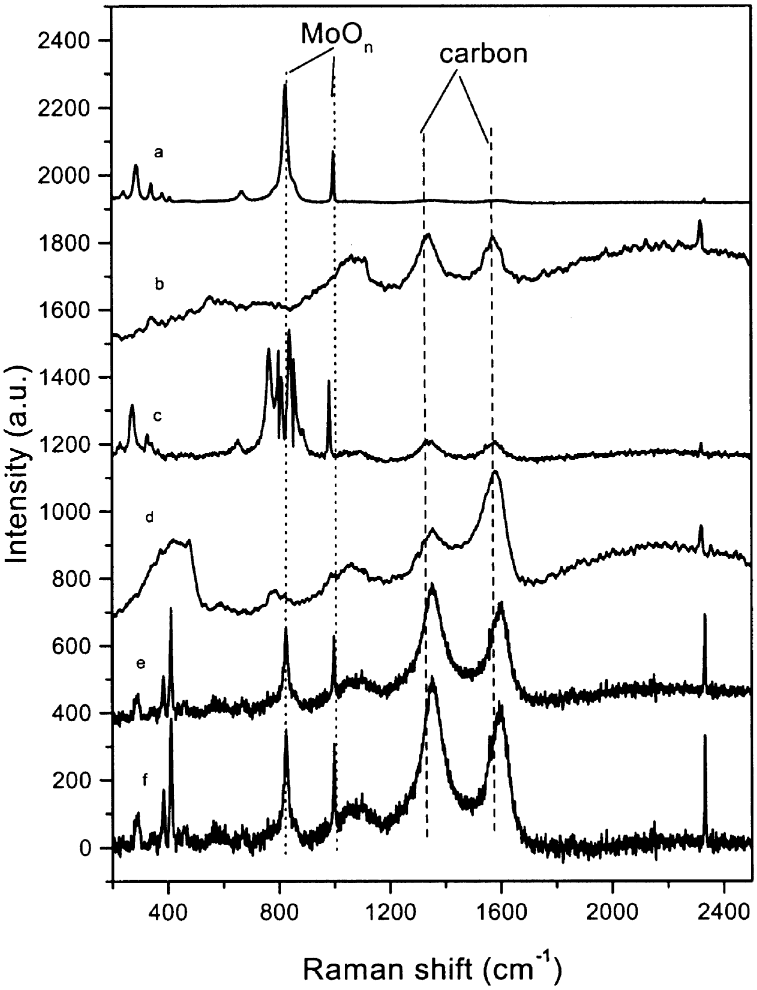
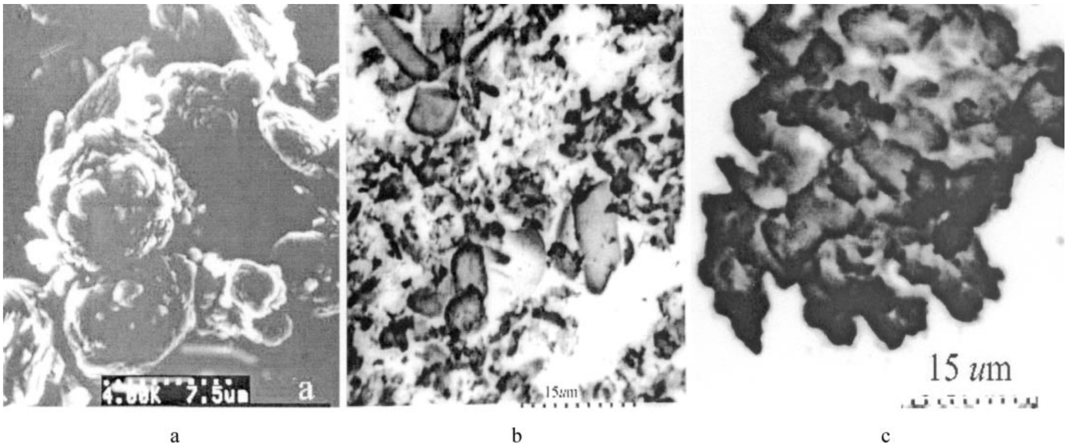


Figure 4. Laser Raman spectra of the $Mo_2C$ catalysts before and after methane partial oxidation in the presence of hydrogen sulfide (reaction conditions as for figure 1). (a) No sulfur; (b) 0.1% $H_2S$; (c) 0.2% $H_2S$; (d) 0.4% $H_2S$; (e) 0.6% $H_2S$; and (f) 1% $H_2S$.

deposition over the catalyst with $H_2S$ concentration below 0.4% in methane. This suggests that the lower $H_2S$ concentration has a less significant effect on the catalyst composition and structure; this has been confirmed in the activity tests.

The catalyst morphology after use under the different conditions was observed using SEM, and the results are shown in figure 5. Although activity test results show that 0.1% $H_2S$ in methane has less effect on the catalyst performance, the morphology of the post-reaction



a b c

Figure 5. SEM images of the $Mo_2C$ catalysts before and after methane partial oxidation in the presence of hydrogen sulfide. (a) Before reaction; (b) 0.1% $H_2S$; and (c) 0.4% $H_2S$.

catalyst had changed significantly. Some large rectangular particles, as well as very small powder particles, were observed; the rectangular particles are probably molybdenum oxide, which is from the oxidation of the catalyst during the reaction. The small powder particulates may be carbon deposits in the reactor. With $H_2S$ increasing to 0.4% in methane, the post-reaction catalyst showed signs of sulfurization (figure 5(c)), since the particles aggregated and the catalyst surface became dense [24].

## 4. Conclusions

Sulfur has a deleterious effect on the performance of the molybdenum carbide catalysts for partial oxidation of methane to syngas. High $H_2S$ content in the reactant accelerates carbon deposition over the catalyst bed and sulfurizes the catalyst, thus poisoning the catalyst. Lower $H_2S$ content in methane does not lead to obvious sulfurization of the catalyst but accelerates carbon deposition on the reactor wall; this would eventually result in blocking of the reactor. The morphology and catalyst surface compositions were changed after the reaction with reactants containing $H_2S$, which may also contribute to the observed catalyst deactivation.

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