Embedded structure catalyst: a new perspective from noble metal supported on molybdenum carbide

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Abstract:

An embedded structure of noble metal (Pt) in situ supported on molybdenum carbide was found for the first time, which hindered Pt sintering at high temperature, and promoted the interaction between Pt and molybdenum carbide. This structure exhibited an excellent and stable catalytic activity for water gas shift reaction at low temperature.

Keywords: Noble metal, Molybdenum carbide, Embedded structure catalyst.

1. Introduction

Transition-metal carbides (e.g. molybdenum carbide) have attracted considerable attention due to their unique surface properties and outstanding physicochemical properties. Molybdenum carbide can serve as a catalyst support, and in this case, some unique catalytic properties resulting from the interaction between the doped metal and the molybdenum carbide were generated, which benefit the supported metal dispersion[1-4]. In the present study, Pt was doped on molybdenum carbide using the Temperature Program Reaction (TPRe) method. Based on characterizations, a new embedded structure was found for the first time, and when it was used for the Water gas shift (WGS) reaction, excellent and stable catalytic properties were exhibited at very low temperatures.

2. Experimental

Oxide precursors of Pt modified molybdenum carbides (Pt-MoO_3) with Pt/Mo initial molar ratios of 1.6/98.4 was prepared using a mixture of aqueous solutions of $H_2PtCl_6·6H_2O$ and $(NH_4)_6Mo_7O_{24}·4H_2O$. The chemicals were dissolved in distilled water at 25 °C under stirring for 4 h at first, which produced a viscous mixture, and then the mixture solution was continuously stirred in oil bath at 80 °C until dried. After the solid product was dried at 110 °C overnight, it was calcined in air at 500 °C for 4 h. Carburization of the Pt-MoO_3 was carried out in a fixed-bed quartz micro-reactor with an inner diameter of 8 mm. The carburization was performed in CH_4/H_2 (20 vol% CH_4) gas flow with a successive temperature-programmed process: the carburization temperature was increased from the room temperature (RT) to 300 °C with a heating rate of 5 °C/min, and then raised to 700 °C with a heating rate of 1 °C/min, and finally remained at 700 °C for 2 h. For comparison, MoO_3 powder was obtained by using the same method as the above to obtain Mo_2C catalyst.

3. Results and discussion

XRD patterns of Pt/Mo_xC_y catalysts synthesized at different carburization temperatures are shown in Figure 1 (a-b). From the Figure 1(b), one can see that with increased the carburization temperature, the carbide phase was formed. When the carburization temperature was increased to 700 °C (Pt-Mo-700 °C), the peaks at 2θ of 34.8° and 39.8° are attributed to the presence of a hexagonal β-Mo_2C. From the figure 1(b), one can see that with the increase in the carburization temperature, the Pt position shifted from 39.6° to 40°. This indicated that with the increase in the degree of carburization, the Pt crystal structure was changed or a solid mixture was formed during the carburization process. STEM and HR-TEM images of Pt/MoO_3 and Pt/Mo_xC_y are show in Figure 1 (c-f), respectively. It is obvious that Pt particles are located on the surface of MoO_3 with the largest particle size of about 17 nm. However, after the carburization process, as shown in

Figure 1(f), it is obvious that almost all Pt particles are surrounded by the molybdenum carbide. Such a kind of nanostructure (embedded structure) could enhance the interaction between the Pt and molybdenum carbide.

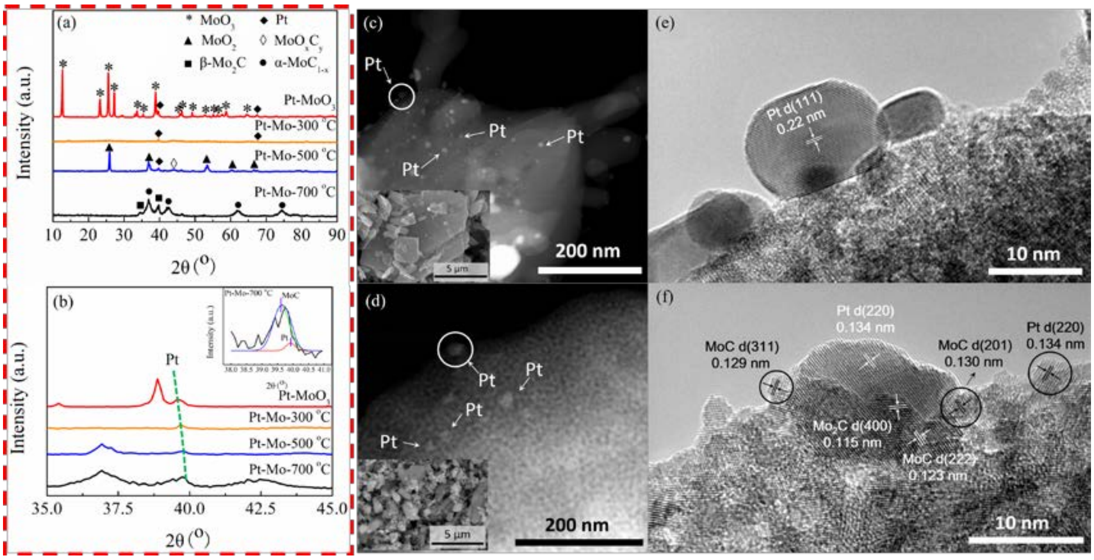

Figure 1. (a) and (b): XRD patterns for the Pt modified molybdenum carbides at different carburization temperature; (c) and (d): STEM morphology of Pt/MoO_3 and 3% Pt/Mo_xC_y, respectively; (e) and (f): HR-TEM of Pt/MoO_3 and 3% Pt/Mo_xC_y, respectively.

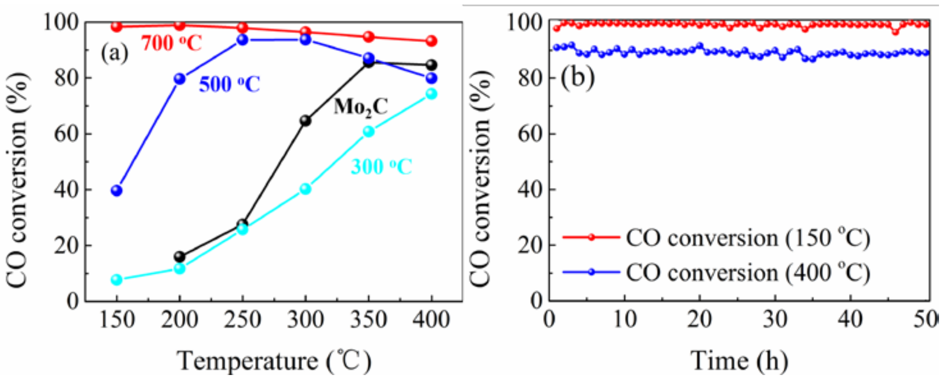

Figure 2. (a) Catalytic performances of 3% Pt/Mo_xC_y carburized at different temperatures for WGS reaction at different temperatures; (b) time-on-stream testing of 3% Pt/Mo_xC_y (700 °C) catalyst for WGS reaction at 150 °C and 400 °C.

As shown in Fig. 2(a), comparing with others, 3% Pt/Mo_xC_y carburized at 700 °C catalyst exhibited a much higher catalytic activity. One can see that with the increase in the degree of the carburization process, the embedded structure was formed, resulting in the increase in the catalytic activity. This indicates that the interaction between Pt and molybdenum carbide and the embedded structure are an important factor to promote the catalytic activity. A long-term stability test indicated that as-prepared 3% Pt/Mo_xC_y had excellent catalytic stability for the WGS reaction (Figure 2 (b)).

4. Conclusions

In conclusion, the Pt/Mo_xC_y catalyst with the embedded structure can be simply prepared by the in situ carburization of Pt doped molybdenum oxide (Pt/MoO_3) using a TPRe method. Such a new structure can hinder the sintering of a noble metal at high temperature, and exhibit excellent and stable catalytic properties. This embedded structure could be attractive for the practical applications of noble metal-based catalysts.

References

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