Supporting information

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

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1. Experimental section

1.1. Preparation of 3% Pt/Mo_xC_y and Mo₂C

Oxide precursors of Pt modified molybdenum carbides (Pt-MoO₃) with Pt/Mo initial molar ratios of 1.6/98.4 was prepared using a mixture of aqueous solutions of chloroplatinic acid ($H_2PtCl_6\cdot 6H_2O$; Sigma-Aldrich Co., 99%) and ammonium heptamolybdate ((NH₄)₆Mo₇O₂₄·4H₂O; Kojundo Chemical Laboratory Co., 99%). 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-MoO₃ was carried out in a fixed-bed quartz micro-reactor with an inner diameter of 8 mm, in which Pt-MoO₃ powder was placed on a porous quartz plate. The carburization was performed in CH₄/H₂ (20 vol% CH₄) 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. After the reactor was cooled down to RT in the CH₄/H₂ gas flow, the product was passivated in 1%O₂/Ar gas flow for 12 h at RT.

For comparison, MoO_3 powder was obtained by calcinations of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ at 500 °C for 4 h in air and then also carburized using the same method as the above to obtain Mo_2C catalyst.

1.2. Material characterization

Crystal structures of the catalysts before and after the reaction were determined by X-ray diffraction (XRD 610, Shimadzu, Japan) with a Cu K α radiation and an operating potential of 30 kV, a current of 30 mA, and a scanning rate of 4°/min; phase identification was determined through comparison of obtained XRD patterns with those of "Joint Committee on Powder Diffraction Standards (JCPDS)". Transmission

electron microscope (TEM) and scanning electron microscope (SEM) images were obtained using a Hitachi transmission electron microscope HF-3300 operating at 300kV. X-ray photoelectron spectroscopy (XPS) analysis was done with AXIS ULTRA DLD spectrometer using Al K α radiation (h ν =1486.6 eV) as the photon source, generation at 150 W. The binding energies of Mo 3d and Pt 4f were analyzed using the Shirley baseline correction.

1.3. Catalyst performance evaluation

Catalytic performances for the WGS reaction were evaluated in a micro-reactor with an inner diameter of 6 mm. Prior to the reaction, the catalyst was pretreated with 15% CH₄/H₂ gas flow at 590 °C for 2 h in order to reduce the oxide on the surface. The total amount of the catalyst used was 0.4 g, and a weight hourly space velocity (WHSV) of 9000 cm³ g⁻¹ h⁻¹ was selected in this study, the reaction gas composition was 21% H₂O-10.5% CO in Ar. Water flow rate was controlled by a syringe pump. It was vaporized in a pre-heater containing ZrO₂ beads maintained at 150 °C and carried by dry gas flow. Catalytic performance was tested in a temperature range of 150-400 °C in atmospheric pressure. A thermocouple was contacted with the catalytic bed for the reaction temperature control. A water-ice cold trap was set at the exit of the reactor to remove the unconverted water prior to the analysis of the gas compositions in the product. The products were analyzed using a gas chromatograph with TCD detectors (Agilent 7890A GC system). The outlet gas flow rate was determined by an inner standard method, in which CO and CO₂ were calculated based on the flow rate of the inner gas N₂ in the reaction system while H₂ was calculated based on the flow rate of the inner gas He in the reaction system.

Performances of the catalysts were characterized in terms of CO conversion, hydrogen production rate (µmol/g-cat/min). The CO conversion was defined as the molar ratio of the CO in the product stream to the feed CO, which is expressed as the followings:

$$X_{CO} = \frac{n_{CO,in} - n_{CO,out}}{n_{CO,in}} \times 100\%$$
(1)

where $n_{CO,in}$ and $n_{CO,out}$ are the flow rates of CO in the inlet and outlet, respectively.

2. Results and discussion



Fig. S1 Morphologies of Pt/MoO₃ and 3% Pt/Mo_xC_y: (a) SEM morphology of Pt/MoO₃ (inset: Pt diffraction), (b) SEM morphology of 3% Pt/Mo_xC_y (inset: Pt diffraction); (c) TEM morphology of Pt/MoO₃ (magnification of circle in (a)), (d) TEM morphology of 3% Pt/Mo_xC_y (magnification of circle in (b)).



Fig. S2 XPS spectra of Pt 4f of as-prepared Pt-Mo $_xC_y$ catalysts prepared at different carburization temperatures.

For investigated the interaction between Pt and molybdenum carbide, Mo 3d XPS analysis was also carried out to elucidate the surface chemical states of molybdenum carbide support. The binding energies of Mo 3d peaks obtained from 3% Pt/Mo_xC_y (700 °C) and Mo₂C catalyst are shown in Fig. S3 and the binding energies were summarized in Table S1. Herein, the double peaks should be a splitting of 3.13 eV with a Mo $3d_{5/2}$ to Mo $3d_{3/2}$ ratio of 3:2, and the distribution of Mo states was estimated by means of deconvolution [1, 2]. There are three molybdenum species on the 3% Pt/Mo_xC_y surface: one with $3d_{5/2}$ binding energy (BE) of 228.9 eV was attributed to Mo²⁺ species involved in Mo-C bonding, and other two with $3d_{5/2}$ binding energies of 229.9and 233.0 eV were identified as Mo⁴⁺and Mo⁶⁺, respectively, which involved Mo-O and Mo-O-C bondings. The existence of molybdenum oxide in the fresh molybdenum carbide should be attributed to the surface oxide formed during the passivation process [1-3]. In contrast, the Mo⁸⁺

species was detected in the Mo₂C sample. Comparing with the binding energies of the corresponding Mo 3d XPS peaks of the fresh β -Mo₂C, from the Fig. S3 and Table S1, one can see that Pt addition caused a change in the electronic band structure of Mo²⁺ species. The binding energy of Mo²⁺ shifted from 228.4 to 228.9 eV when Pt was doped on the molybdenum carbide surface.



Fig. S3 XPS spectra of Mo 3d of Mo_2C and 3% Pt/Mo_xC_y (700 °C) catalyst.

Table S1 Mo $3d_{5/2}$ binding energy of the fresh β -Mo₂C and Pt-Mo_xC_y catalysts.

	Mo 3d _{5/2} (eV)			
Catalysts	Mo	Mo ^{IV}	Μοδ	Мо ^{VI}
	(Mo_2C)	(MoO ₂)	(MoO_xC_y)	(MoO ₃)
3% Pt/Mo _x C _y	228.9	229.9		233.0
Mo ₂ C	228.4	229.4	231.7	232.8

XRD pattern of the spent catalyst of 3% Pt/Mo_xC_y after long-term stability test is shown in Fig. S4. No peaks corresponding to the molybdenum oxide were detected, indicating that the molybdenum carbide phase was very stable during the WGS reaction.



Fig. S4 XRD pattern of the spent 3% Pt/Mo_xC_y catalyst after the test shown in Fig. 5.

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