

Molybdenum Carbide and Oxycarbide Hydrogen Production Catalysts: Preparation, Characterization, and Evaluation.

Robert O. Savinelli, Jun Li, Ram Seshadri, and Susannah L. Scott*

University of California, Santa Barbara, Ca 93106 (USA)

*sscott@engineering.ucsb.edu

Introduction

The catalytic properties of transition metal carbides are similar to some precious metals due to d-electron band contractions cause by lattice expansion upon the introduction of carbon atoms into the metal framework [1, 2]. Molybdenum and tungsten carbides may substitute for precious metals in the hydrodenitrogenation, hydrogenation, water-gas shift,[3, 4] Fischer-Tropsch, hydroisomerization, and methane reforming reactions, as well as use as fuel cells electrodes [1, 5]. The advantages to this work come from the high abundance and lower cost of transition metals as compared to precious metals. Metal carbide catalysts have not been widely accepted in industry due to deactivation issues.

Materials and Methods

Mo₂C catalysts were prepared from ammonium paramolybdate heated to temperatures between 570 °C and 900 °C in a flowing (1:1) mixture of hydrogen and methane [3]. This process was monitored by thermo-gravimetric analysis (TGA) [6] and by mass spectrometry (MS) of the gas phase products [7]. Additional characterization was performed using electron microscopy (SEM) and (TEM), nitrogen adsorption isotherms (BET), X-ray photoelectron spectroscopy (XPS), and powder X-ray diffraction (XRD). Catalysts were evaluated for water-gas shift (WGS) activity in a quartz tube microreactor, monitoring CO, CO₂, H₂ and H₂O concentration by MS before and after activation in pure H₂ at 600 °C for 1 h. CO conversion is compared at 250 °C in a flowing mixture of CO and H₂O, 3.0% and 4.5% respectively and a space velocity of 17,200 hr⁻¹, Table 1.

Results and Discussion

The carbon-rich mixture of CH₄ and H₂ used during Mo₂C synthesis was selected to increase surface carbon deposition. Catalysts prepared under slow ramp conditions (0.2 °C/min) appear to have rougher surfaces in SEM micrographs than samples brought to the final temperature rapidly, Figure 1. C 1s XPS spectra of catalysts ramped slowly have a higher ratio of graphite (g-C-C) to amorphous (a-C-C) carbon near the surface than those heated rapidly. BET surface areas were between 1 and 52 m²/g. The surface area of samples with more a-C-C and g-C-C were lower indicating that elevated surface areas are a result of the Mo₂C structure and not the surface carbon. XPS spectra indicate that there is an increase in g-C-C after air exposure. Catalysts (A) and (B) were prepared using different temperature programs, Table 1. (A) and (B) have similar surface areas (ca. 39 m²/g) and crystallite sizes (ca. 14 nm). (A) is a mixture of MoO₃ and Mo₂C bulk phases and has ca. 70% less a-C-C and g-C-C near the surface than (B), Figure 1. The bulk structure of (B) is Mo₂C.

Catalysts (A) and (B) are inactive at temperatures below 250 °C prior to H₂ activation, and showed little improvement at 450 °C, where CO conversions were 25% and 7% respectively. WGS activity at 250 °C was enhanced after the Mo₂C surfaces were activated with H₂, Table 1.

WGS activity was observed below 200 °C in (B) but not in (A). CO conversions were 75% with (A) and 90% with (B) at 450 °C. The activity of (B) improved considerably more than (A) upon the removal of excess surface carbon. These results indicate that fully carburized Mo₂C is better suited for water-gas shift catalysis than some partially carburized samples despite the presence of more a-C-C and g-C-C near the surface which must be removed prior to catalysis.

Table 1. Water-gas shift catalyst comparison at 250 °C

	Catalyst (A)	Catalyst (B)
Temperature program	2 °C/min, 630 °C, 0.25 h	0.2 °C/min, 650 °C, 5 h
CO conversion before H ₂	0	3
CO conversion after H ₂	17	76

Significance

Understanding the role of carbon deposition on the deactivation of Mo₂C water-gas shift catalysts is critical for improving the overall viability of transition metal carbide catalysts. Many industrial catalysts are also deactivated by carbon deposition. Advances in surface carbon analysis will benefit these heterogeneous systems as well.

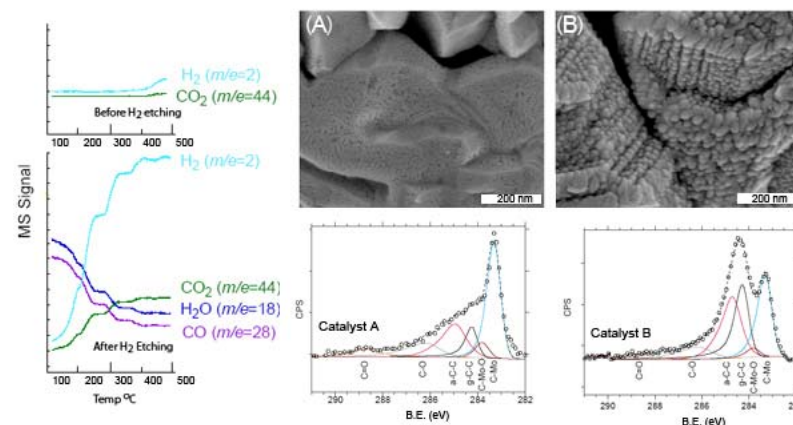


Figure 1. Water-gas shift reaction with catalyst (B), SEM micrographs and C 1s XPS spectra of catalysts (A) and (B) prior to H₂ activation or exposure to reaction conditions.

References

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