

Effect of Sulfur on Properties of Mo₂C and Pt/Mo₂C Catalysts

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Introduction

Early transition metal carbides have been demonstrated to be active for a variety of chemical reactions [1], and recently methods have been developed to support metals directly onto their surfaces. The resulting carbide supported catalysts possessed extraordinary catalytic activities and selectivities [2]. Some carbides are also sulfur tolerant [3]. Research described in this paper examined the effects of sulfur on the activities of carbide and carbide supported catalysts for the water gas shift (WGS) and methanol steam reforming (MSR) reactions. These reactions are important for the production of hydrogen. While sulfur can be in reformat feed to the water gas shift, it is not typically in the feed for methanol steam reforming. Nevertheless, adding sulfur to this relatively simple steam reforming reaction can provide insights into the effect of sulfur on carbide-based metals in more complicated reactions.

Materials and Methods

The Mo₂C catalysts were prepared by temperature programmed reduction of (NH₄)₆Mo₇O₂₄·4H₂O (Alfa Aesar) at 590 °C for four hours. The Pt/Mo₂C catalysts were prepared by wet impregnation of the Mo₂C support with H₂PtCl₆·6H₂O (Sigma-Aldrich) and subsequent reduction in H₂ at 450 °C for four hours. The resulting materials were passivated for five hours using a mixture of 1% O₂/He. The catalyst compositions were determined using inductively coupled plasma (ICP) spectroscopy. The reactions were carried out at atmospheric pressure and temperatures between 180 °C and 240 °C. For WGS, the feed stream consisted of 9% CO, 30% H₂O, 39% H₂, 6% CO₂, and 16% N₂, and the GHSV was 125,000 h⁻¹. For MSR, the feed stream consisted of 13% methanol, 13% H₂O, and 71% N₂, and the GHSV was 50,000 h⁻¹. Hydrogen sulfide was introduced to the feed in concentrations up to 100 ppm. The materials were characterized with X-ray diffraction (XRD), BET surface area analysis, and X-ray photoelectron spectroscopy (XPS) at various stages of exposure to sulfur. Thermogravimetric analysis (TGA) was used to measure the sulfur uptake rates for a H₂S/He stream with H₂S concentrations ranging from 5 to 500 ppm.

Results and Discussion

Hydrogen production rates for the Mo₂C and Pt/Mo₂C catalysts reached pseudo-steady state levels for WGS and MSR after approximately 15 hours on stream. After reaching pseudo-steady state, 5 ppm H₂S was added to the feed stream. As shown in Figure 1, the hydrogen production rates for Mo₂C decreased for both reactions. For WGS, nearly 99% of the pseudo-steady state activity was lost in less than 30 minutes of sulfur exposure. The activity could not be recovered by simply removing H₂S from the feed stream. For MSR, approximately 50% of its activity was retained. Again the activity could not be recovered by removing H₂S from the feed. After regenerating the Mo₂C catalyst in 15% CH₄/H₂ for four hours, approximately 10% of the pseudo-steady state WGS activity was recovered while 100% of the pseudo-steady state MSR activity was recovered.

The Pt/Mo₂C catalyst was also completely deactivated on exposure to H₂S during WGS, but retained approximately 10% of its activity for MSR. After regeneration in 15% CH₄/H₂ for four hours, the catalyst remained inactive for WGS, but recovered 10-30% of its pseudo-steady state MSR activity.

Sulfur uptake rates for the Mo₂C and Pt/Mo₂C catalysts were measured during exposure to 5 ppm H₂S/He at the same temperature and flow conditions used for the kinetics studies. After 18 hours, the Mo₂C and Pt/Mo₂C catalysts gained between 7 and 10 wt %; this corresponds to 1.7 to 2.4 monolayers of sulfur incorporation. X-ray diffraction patterns for the spent TGA samples did not indicate the presence of bulk sulfide phases, therefore the sulfur is assumed to primarily remain on the surface of the catalyst. The XPS spectra for the fresh, spent, and sulfur exposed catalysts indicated the presence of adsorbed sulfur on Mo, MoS₂, and SO₂ species. For WGS, sulfur species were identified on all spent catalysts even after regeneration, however, the peak intensity was much higher for the spent Pt/Mo₂C catalyst than for the Mo₂C catalysts suggesting a stronger interaction of sulfur with Pt than with Mo₂C. Following MSR, no sulfur species were distinguishable on the spent Mo₂C catalysts; however, sulfur species were present on the surface of Pt/Mo₂C.

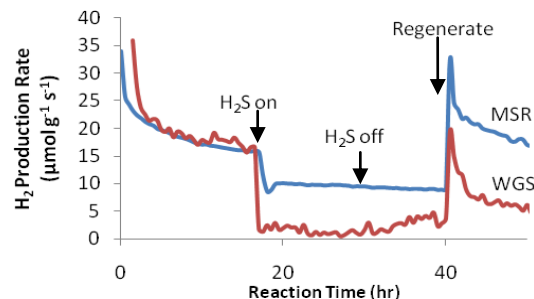


Figure 1. Hydrogen production rates during WGS and MSR for Mo₂C catalysts at 240 °C prior to and after the introduction of 5 ppm H₂S. After 12 hours of sulfur exposure, the H₂S was removed from the feed stream. After another 10 hours, the catalysts were treated with 15% CH₄/H₂ at 590 °C for four hours.

Significance

The effect of sulfur on the WGS and MSR rates for Mo₂C and Pt/Mo₂C catalysts has been examined. These reactions are important for the production of hydrogen. The results provide important insights into the sulfur tolerance of metal carbides and carbide supported metals.

References

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