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

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Introduction
Molybdenum carbide is polycrystalline powder with BET surface areas from 1 to 200 m²/g. Mo₂C may substitute for precious metal catalysts in the hydrogenation, dehydrogenation, and water-gas shift. Fischer-Tropsch, hydroisomerization, and methanol reforming reactions, as well as use as fuel cells electrodes. The H₂-producing water-gas shift (WGS) reaction is useful for fuel cells, ammonia synthesis, Fischer-Tropsch, and hydrocarbon reforming. This work studies the relationships between Mo₂C surface composition and WGS activity. Metal carbide catalysts have not been widely accepted in industry due to deactivation issues. This study varies surface conditions, gas exposure, and H₂-TPR activations to temperatures to generate a variety of surface compositions which are characterized using XPS prior to testing as WGS catalysts.

Hypothesis
The activity of Mo₂C catalysts are influenced by changes in surface composition and structure due to changes in the surface composition and structure. Evidence of these changes should be detected by XPS. BET, SEM, and TEM. XPS results are in agreement with the catalyst structure and composition.

Surface Structure by XPS

- Mo 2C surfaces are covered with carbon and oxygen atoms that were present during carburization.
- XPS results show that Mo₂C catalysts contain Mo(IV) and Mo(V) species.
- Mo 2C catalysts are more active in hydrogen production than MoO₂.

Hydrogen Production

- Catalysts were evaluated for hydrogen production in a quartz tube reactor using CO₂, Steam, and H₂ gas mixtures.
- CO₂ consumption increases with temperature and CO₂ partial pressure.
- CO₂ consumption decreases with increasing steam partial pressure.

Results and Conclusions

Carbon deposition is the major cause of Mo₂C catalyst deactivation. The type and quantity of carbon, blocking the active Mo₂C sites, influences the activity of the WGS reaction. Temperature, ramp rate, soot time, and air exposure. Catalysts prepared at higher temperatures have higher levels of carbon contamination. Slow heating rates result in rough surfaces with higher levels of graphite at the surface. Exposure to air increases the amount of graphitic and oxycarbide hydrogen. WGS temperatures above 750 °C were required to remove graphite deposits. BET surface areas were higher for catalysts with more graphitic carbon near the surface. WGS activity was highest in air-free catalysts which were slowly heated to 650 °C followed by H₂-TPR at 600 °C.