

Molybdenum Carbide and Oxycarbide Hydrogen Production Catalysts

Preparation, Characterization and Evaluation

Robert Savinelli, Jun Li, Ram Seshadri, Susannah L. Scott
University of California at Santa Barbara, Departments of Chemistry and Materials



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 hydrodenitrogenation, hydrogenation, water-gas shift, Fischer-Tropsch, hydroisomerization, and methane 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 its WGS activity. Metal carbide catalysts have not been widely accepted in industry due to deactivation issues. This study varies synthesis conditions, air exposure, and H₂-TPR activation 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 synthesis, handling, activation, and reaction conditions due to changes in the surface structure and composition. Evidence of these changes should be detected by XPS, BET, SEM, and TEM. XRD is a supplement to these techniques as it sensitive to changes in the bulk structure. The conditions to the right are varied in order to elucidate the catalyst activation and deactivation pathways.

Synthesis Procedure (TPC)

Temperature: 650 °C (300 °C)
Rate: 0.2 - 2 °C/min
Soak time: 0.1h - 4 h

Handling

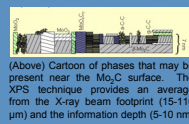
Air exposure: rapid, none (1% O₂)

Activation (H₂-TPR)

Temperature: 600 °C or 825 °C

Reaction flow rate: 120, 40, or 60 mL/min

Surface Structure by XPS



Mo 3d_{5/2} (V) (IV)(III)

Mo 3d

Component	B.E. (eV)	FWHM
Mo(V)	228.20	0.59
Mo(V)	229.25	1.22
Mo(V)	230.80	1.18
Mo(V)	232.60	1.28

B.E. Assignment

O 1s

(Left) Representative high-resolution Mo 3d spectra of Mo₂C catalysts. Mo(V) is the most prevalent molybdenum oxidation state. Mo(V) is detected in sample 1 and is the dominant oxidation state in the commercial Mo₂C.

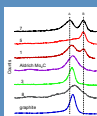
C 1s

(Left) Representative high-resolution O 1s spectra of Mo₂C catalysts. (Below) O 1s binding energy assignments.

Component	B.E. (eV)	FWHM
O-Mo	530.14	1.29
O-C-Mo	531.49	1.44
O-C	532.37	1.34
O-C	533.70	1.57
O-H	538.12	1.59

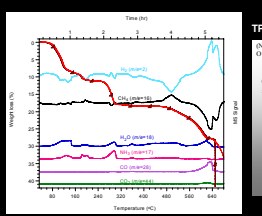
C 1s

(Above) Representative high-resolution C 1s spectra of catalysts as prepared. Feature A is a combination of amorphous and graphitic carbon. Feature B is carbide carbon. Catalyst 3 is similar to the C 1s spectrum for pure graphite. The C 1s spectra of catalyst 2 is similar to catalyst 8 and to the commercial Mo₂C. * 7 and 8 are not described in this poster.

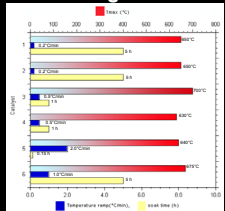


Temperature Programmed Carburization

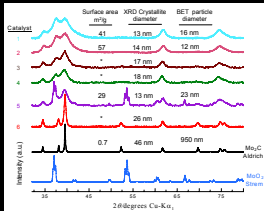
Mo₂C was prepared from ammonium paramolybdate heated to temperatures between 630 °C and 700 °C in a flowing (1:1) mixture of hydrogen and methane. This carbon-rich mixture was selected to increase surface carbon deposition. The carburization process was monitored by thermogravimetric analysis (TGA) and by mass spectrometry (MS) of the gas phase products. Typical TPC-MS and TGA results are shown to the right. TGA weight loss is shown as a red line with brown arrows. Intermediate phases are as the right of the TPC-MS plot.



Heating Profiles



XRD and BET

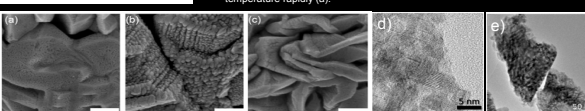


(Left) Particles sizes are estimated from surface areas using the spherical approximation and from XRD broadening using the Scherrer equation. * indicates that BET results were unavailable. Post H₂-TPR XRD patterns were also unavailable.

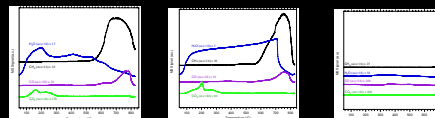
SEM and TEM Images

(Below) Electron micrographs of Mo₂C prepared under different conditions. (a) APM precursor heated at 2 °C/min. (b) APM precursor heated at 0.2 °C/min. (c) Mo₂C precursor heated at 0.2 °C/min. In A, B, and C the scale bar represents 200 nm. (d) TEM lattice image of Mo₂C illustrating lattice fringes from (321) planes. e) TEM image reveals nanoparticles in Mo₂C.

Catalysts prepared under slow ramp conditions (0.2 °C/min) appear to have rougher surfaces (b) in SEM micrographs than samples brought to the final temperature rapidly (a).



Temperature Programmed Reduction



H₂-TPR Catalyst 1, pure H₂ (250 mL/min), 825 °C, 0.5 h, 10 °C/min ramp
H₂-TPR Catalyst 2, pure H₂ (250 mL/min), 825 °C, 0.5 h, 10 °C/min ramp
H₂-TPR Catalyst 3, pure H₂ (250 mL/min), 825 °C, 0.5 h, 10 °C/min ramp

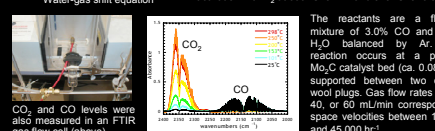
Mo₂C surfaces are covered with carbon and oxygen atoms that were present during carburization. These contaminants inhibit catalytic performance. The procedure for removing surface contaminants, prior to catalysts, is temperature programmed reduction in flowing H₂ (H₂-TPR) at temperatures >800 °C. H₂-TPR results depend on the composition of surface contaminants. Mo₂C and amorphous carbon contamination are reduced to CH₄ and H₂O between 500 °C and 700 °C. The Mo₂C catalyzed reduction of graphitic carbon is observed between 750 °C and 825 °C. Broad methane desorption peaks in catalysts 1 and 2 (above) are attributed to the presence of amorphous and graphitic carbon phases. The surface carbon on catalyst 3 is almost entirely graphitic carbon. H₂-TPR at 600 °C has little effect on graphitic carbon.

Water-gas shift Catalysis

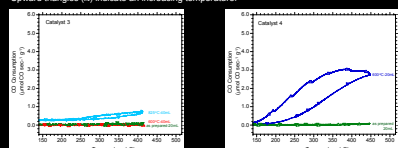
Water-gas shift (WGS) performance varies with surface area, crystallite size, and surface contamination. Low activity Mo₂C catalysts can form during temperature programmed carburization (TPC) if the maximum temperature is above 700 °C and the temperature ramp is slow. (20.5 °C/min). These conditions are conducive to the formation of larger Mo₂C crystallites and thick graphitic carbon layers.

Understanding the role of carbon deposition on the deactivation of Mo₂C 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.

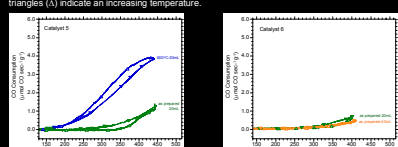
In the water-gas shift reaction, oxygen atoms "shift" from water to carbon monoxide. The energy barrier for this reaction is decreased in the presence of Mo₂C. Catalysts 1-6 were evaluated for catalytic activity before and after activation with H₂ at 600 °C for 1 h and 825 °C for 0.5 h.



Water-gas shift reaction monitored by MS using (catalyst 1, 98 mg, left) Mo₂C and (catalyst 2, 107 mg, right) in flowing 3% CO/Ar-3.4% H₂O (20, 40, 60 mL/min) ramped to 450 °C at 5 °C/min. Catalyst was treated for one hour at 600 °C or 825 °C under flowing H₂ 20 mL/min. Upward triangles (▲) indicate an increasing temperature.



Water-gas shift reaction monitored by MS using (catalyst 3, 92 mg, left) Mo₂C and (catalyst 4, 106 mg, right) in flowing 3% CO/Ar-3.4% H₂O (20 or 40 mL/min) ramped to 450 °C at 5 °C/min. Catalyst was treated for one hour at 600 °C or 825 °C under flowing H₂ 20 mL/min. Upward triangles (▲) indicate an increasing temperature.



Water-gas shift reaction monitored by MS using (catalyst 5, 75 mg, left) Mo₂C and (catalyst 6, 99 mg, right) in flowing 3% CO/Ar-3.4% H₂O (20 or 40 mL/min) ramped to 450 °C at 5 °C/min. Catalyst was treated for one hour at 600 °C or 825 °C under flowing H₂ 20 mL/min. Upward triangles (▲) indicate an increasing temperature.

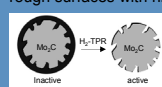
Hydrogen Production

Catalysts were evaluated for water-gas shift (WGS) activity in a quartz tube micro-reactor, monitoring CO, CO₂, H₂, and H₂O concentration by MS before and after activation in pure H₂ at 600 °C and 825 °C for 1 h. 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 57 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.

(Above) Typical water-gas shift reactant and product gases vs. temperature plot. CO conversions at 250 °C are between 30 and 80%. MS plots are corrected for fluctuations in total pressure and m/e 28 signal contributions from CO₂ fragments. The CO signals are reduced by 11% of m/e 44 signal.

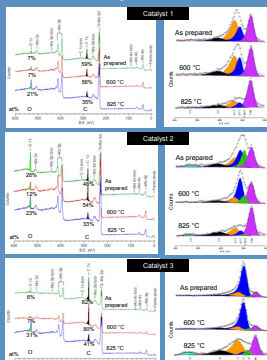
The overall performance of Mo₂C WGS catalysts are enhanced by H₂-TPR. CO consumption in catalysts 1 and 2 are highest when activated at 600 °C. In general, CO consumption increases with gas flow rate. The activity of catalyst 3 was unaffected by H₂-TPR at 600 °C due to the high g-C-C coverage (56%) remaining after H₂-TPR. The activity of catalyst 3 increased after H₂-TPR at 825 °C due to the decrease in g-C-C (5%). CO consumption measured with catalysts 4 and 5 increase after H₂-TPR 600 °C. Catalysts 5 and 6 had appreciable activity without activation due to low a-C-C and g-C-C content (<32% combined).

In general, WGS activity was higher during reactor cooling. This indicates that another catalytic activation pathway is present during the reaction. A possible explanation for this observation is the formation of more active oxycarbide sites during water-gas shift.



(Above) Carbon of catalyst activation by temperature programmed reduction in H₂.

XPS survey XPS C 1s

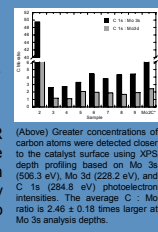


(Left) XPS survey and C 1s spectra of catalysts 1, 2, and 3 as prepared, after H₂-TPR-600 °C, and after H₂-TPR-825 °C. The O atomic percent (at%) is initially low in catalysts 1 and 3. The O at% decreases in catalyst 2 after H₂-TPR at 600 °C. This increase in all of the catalysts after H₂-TPR at 825 °C. This must be due to the exposure of sub-surface oxides and oxycarbides upon removal the graphite layer. Depth profiles of many Mo₂C powders prepared by TPC. (Below) indicate that the carbon at% is higher at shallow probe depths. The C at% is initially high in catalysts 3. It decreases in all spectra after H₂-TPR at 825 °C. The near surface carbide carbon (C-Mo) is highest in catalyst 1. Oxycarbide (C-Mo-O) is highest in catalyst 2. The C-Mo-O content decreased in catalyst 2 and increased in catalyst 3 after H₂-TPR. Amorphous carbon was formed from graphite during the H₂-TPR at 825 °C of catalyst 3.

(Right) C 1s XPS. A decrease in graphitic carbon (g-C-C) is observed after H₂-TPR at 825 °C. (Below) C 1s XPS. An increase in carbide carbon (C-Mo) is observed after H₂-TPR at 600 °C and 825 °C.

Results and Conclusions

Carbon deposition is the major cause of Mo₂C catalyst deactivation. The type and quantity of carbon, blocking the active Mo₂C surfaces, depend on synthesis temperature, ramp rate, and air exposure. Catalysts prepared at higher temperature have higher levels of carbon contamination. Slow heating rates result in rough surfaces with higher levels of graphite at the surface. Exposure to air increased the amount of graphitic and oxycarbide carbon. H₂-TPR temperatures above 750 °C were required to remove graphite deposits. BET surface areas were higher for catalysts with more carbide carbon atoms 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.



(Above) Greater concentrations of carbon atoms were detected closer to the surface by XPS depth profiling based on Mo 3s (606.3 eV), Mo 3d (228.2 eV), and C 1s (284.8 eV) photoelectron intensities. The average C : Mo ratio is 2.46 ± 0.18 times larger at Mo 3s analysis depths.