Effects of Passivation on Synthesis, Structure and Composition of Molybdenum Carbide Supported Platinum Water-Gas Shift Catalysts

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Abstract

High surface area molybdenum carbides are attractive for use as catalysts and supports. Due to their pyrophoricity, carbides are typically passivated prior to use. Research described in this paper compared the synthesis, structural and compositional properties, and water gas shift activities of catalysts produced by depositing Pt onto unpassivated and passivated Mo₂C. Passivation had a profound effect on the character of interactions between the Pt precursor salt (H₂PtCl₆) and Mo₂C. Nanoscale Pt metal particles were deposited onto the unpassivated Mo₂C while very large Pt particles were deposited onto the passivated Mo₂C (p-Mo₂C). *In situ* X-ray absorption spectroscopy revealed reduction of Pt⁴⁺ on contact with the unpassivated Mo₂C with commensurate oxidation of Mo. Water-gas shift activities were significantly higher for the Pt/Mo₂C compared to the Pt/p-Mo₂C catalyst. Overall, the results indicate that the passivation of Mo₂C prior to metal deposition had deleterious effects on the Pt loadings, structures, and activities.

Keywords: Platinum-Molybdenum carbide catalysts; water-gas shift; surface passivation; redox; *in situ* x-ray absorption spectroscopy

Introduction

Supports play a critical role with regard to the performance of heterogeneous catalysts. The most important function of the support is typically to facilitate dispersion of the active phase although the support can also participate in the reaction [1,2] and/or alter the electronic structure of the active phase [3,4]. A variety of supports have been investigated for catalytic applications (e.g., Al_2O_3 , SiO_2 , C and zeolites) [5-8]. Early transition-metal carbides and nitrides offer unique properties as supports for both electrochemical [9] and chemical catalysts [10-12]. These materials can be synthesized with high surface areas ($>100\text{m}^2/\text{g}$) [13] and can have catalytic properties that resemble to those of platinum group metals (e.g., Pd, Ru, Pt) [14]. Nitride- and carbide-supported metal catalysts have been reported to be active for chemical reactions including, but not limited to, hydrodenitrogenation and hydrodesulfurization [10,15], selective hydrogenations [12,16,17], Fischer-Tropsch Synthesis [18,19], methanol steam reforming [20,21], and water-gas shift [11,22], as well as electrochemical reactions such as the hydrogen evolution [9,23] and hydrogen oxidation reactions [24].

A practical challenge associated with the use of carbides and nitrides is their pyrophoricity; consequently prior to exposure to air, these materials are typically treated to form a passivation layer that prohibits bulk oxidation. As a result, most carbide- or nitride-supported metal catalysts reported in the literature were prepared by deposition or impregnation of the metal onto the passivated carbide or nitride surface [12,15-19,23]. Because the passivation layer is oxygen rich and metal at the surface of the carbide or nitride is oxidized [22], interactions between the passivated material and the deposited metal could be quite different from those for the native carbide or nitride. To date, there have been few reports of metal deposition onto unpassivated, native carbide or nitride supports [11,20,25]. These reports indicate that properties of the resulting materials can be somewhat unusual. Schweitzer et al. observed the formation of “raft-like” Pt particles on a Mo_2C support with the resulting catalyst exhibiting water-gas shift activities that were superior to those for Pt supported on oxides, catalysts that are among the most active known [11]. Schaidle et al. investigated the deposition of a variety of late transition metals onto

unpassivated Mo₂C [25]. They reported that some metal precursors (e.g., Pt⁴⁺, Pd²⁺, Cu²⁺) were spontaneously reduced during deposition/interaction with the native Mo₂C surface, suggesting the presence of surface redox chemistry (likely through oxidation of Mo). The possibility of redox chemistry is not surprising given that the carbides and nitrides are in a highly reduced state. The presence of a passivation layer should inhibit or prohibit this redox chemistry. Shou et al. reported effects of the passivation layer on Rb-promoted Mo₂C-based CO hydrogenation catalysts [26]. The authors focused on defining effects of the presence of the passivation layer during reaction as opposed to during catalyst synthesis, noting that the “fresh” (unpassivated) Rb/Mo₂C/Al₂O₃ performed similarly to its passivated counterpart. However, Rb⁺ is very difficult to reduce ($E^\circ = -2.93\text{V}$) and would likely not be spontaneously reduced upon interaction with Mo₂C as observed with Pt⁴⁺, Pd²⁺, and Cu²⁺ ($E^\circ = 0.74, 1.13, \text{ and } 0.34$, respectively) [27].

The aim of the research described in this paper was to systematically compare the compositional, structural and functional properties of unpassivated and passivated Mo₂C supported Pt catalysts. In particular, we report similarities and differences in Pt deposition trends for these supports, results from characterization of the materials using techniques including *in situ* X-ray absorption spectroscopy (XAS), and their water gas shift activities. The water-gas shift reaction rates are compared to those for a commercial Cu-ZnO/Al₂O₃ catalyst, allowing a connection with the broader literature regarding water gas shift catalysis.

Experimental Methods

Catalyst Synthesis

Molybdenum carbide was synthesized via temperature-programmed reaction (TPR) as previously reported [11,22,25]. Approximately 1.3g of ammonium paramolybdate (125-250 μm) was loaded into a quartz flow-through reactor, supported by a bed of quartz wool, and secured in a vertical furnace. The precursor was heated from room temperature to 350°C under H₂ flow (400 mL/min) at a heating rate of

5°C/min followed by a 12 hr soak at this temperature. Following the soak step, 15% CH₄/H₂ gas was introduced (400mL/ min) and the material was heated to 590 °C at 2.67 °C/min followed by a 2 hr soak. Upon completion of the reaction, the reactor was removed from the furnace and allowed to cool to room temperature.

When the reactor had cooled to below 30°C, the material was treated in one of four ways: (1) transfer into an inert atmosphere glovebox without air exposure (referred to as Mo₂C), (2) surface passivation (material referred to as p-Mo₂C), (3) Pt deposition onto Mo₂C followed by reduction and passivation (to produce Pt/Mo₂C), or (4) Pt deposition onto p-Mo₂C followed by reduction and passivation (to produce Pt/p-Mo₂C). To passivate the surface, the material was exposed to 1% O₂/He flowing at 20mL/min for at least five hours. To obtain the unpassivated Mo₂C, the reactor was sealed and transferred into an inert atmosphere glove box without exposure to air. The third and fourth treatments involve the deposition of Pt onto the unpassivated or passivated Mo₂C support via a wet impregnation method previously reported in detail for Mo₂C [25]. In brief, the unpassivated or passivated Mo₂C was transferred from the quartz reactor (without exposure to air) into a deaerated, aqueous solution of chloroplatinic acid (H₂PtCl₆•6H₂O), which was continuously sparged with Ar. The target Pt loading (approximately 4 wt%) was selected to be consistent with previous work [11,21]. The Pt was allowed to deposit for up to 8 hrs. Following deposition, the catalyst was transferred back to the quartz reactor under argon blanket then reduced with H₂ at 450°C for 4 hr. The material was then cooled and passivated as described above in order to inhibit bulk oxidation.

During the Pt deposition step, aliquots (1.3mL) of the metal precursor solution were taken at discrete time intervals and filtered (Fisher, Sterile Nylon filters, 0.2 µm pore size) prior to elemental analysis. A Varian 710-ES Inductively Coupled Plasma spectrometer was used to determine the concentration of Pt in solution and produce the deposition profiles.

To improve the surface-to-bulk ratio for Mo for the XAS experiments, Al₂O₃-supported Mo₂C materials were synthesized by dry impregnation of γ-Al₂O₃ (Alfa Aesar, 78 m²/g, pore volume of 0.40

cm³/g) with ammonium paramolybdate followed by carburization of the resulting material via temperature-programmed reaction using conditions described earlier. These materials were then transferred directly into an inert glove box and pelletized for use in the X-ray absorption experiments.

Materials Characterization

Surface areas and pore size distributions of the resulting catalysts were obtained using N₂ physisorption (Micrometrics ASAP 2010). Surface areas were calculated using the Brunauer-Emmett-Teller method while micropore and mesopore size distributions were obtained by applying the Horváth-Kowazoe (HK) and Barrett-Joyner-Halenda (BJH) methods, respectively. X-ray diffraction analysis was performed using a Rigaku Miniflex XRD with Cu K α radiation and a Ni filter ($\lambda = 1.5418 \text{ \AA}$). An air-tight sample holder was used to obtain the diffraction pattern for unpassivated Mo₂C. The 2θ range ($10^\circ < 2\theta < 90^\circ$) was scanned at a rate of $5^\circ/\text{min}$ with a 0.02° step size. The final Pt loadings were determined by using a Varian 710-ES following digestion of 15mg of the catalyst in aqua regia (3:1 HCl:HNO₃).

Carbon monoxide chemisorption results were obtained using a Micromeritics Autochem 2910 instrument equipped with a thermal conductivity detector and a Pfeiffer Quadstar GSD 300 mass spectrometer. The catalysts (~100 mg) were pretreated in 15% CH₄/H₂ (70 mL/min) at 590°C for 4 hr followed by a 0.5 hr purge step in He at 600°C to remove methane or hydrogen from the surface. The sample was then cooled to 35°C. The catalyst was exposed to pulses of a mixture of 5% CO/He until surface saturation was observed. CO chemisorption capacities for these materials were calculated by comparing the area of the initial injection peaks to areas when the catalyst surface had been saturated.

Scanning electron micrographs of the catalysts were obtained using FEI Nova Nanolab Dualbeam (FIB/SEM). The materials were supported on sample holders using copper tape and were gold sputter coated to improve conductivity. Elemental analyses of specific micrographs were obtained using Energy Dispersive X-ray Spectroscopy (EDX).

The point of zero charge (PZC, measured by pH) measurements were carried out using procedures described in the literature [25,28,29]. The desired surface loading for PZC determination of Mo₂C and p-Mo₂C was 500m²/L; the Mo₂C-based catalyst weight was maintained at approximately 40mg per solution. The pH of the starting solution (deionized water purged with Ar) was adjusted using concentrated hydrochloric acid or ammonium hydroxide to meet a target starting pH value. The catalyst sample was added to the solution, and the pH was recorded as a function of time until it stabilized at a final pH value. Due to the low surface area of MoO₂ (~4 m²/g), 500mg of material was used in order to maintain the desired surface loading.

To analyze the dynamic deposition and spontaneous reduction (previously reported by Schaidle et al. [25]) of Pt, *in situ* X-ray absorption experiments were conducted at the Advanced Photon Source at Argonne National Laboratory. A custom cell (see Supporting Information) was designed to allow for the *in situ* analysis; both the Mo K (20,000eV) and Pt L3 (11,653eV) edges were analyzed during separate deposition studies.

To conduct the *in situ* experiments, pellets of the unpassivated Mo₂C and Mo₂C/Al₂O₃ were prepared and secured in the XAS cell, which was subsequently purged with N₂ flow. A spectrum of the Mo K or Pt L3 edge was obtained prior to introduction of the H₂PtCl₆•6H₂O solution. The deaerated solution was then introduced through a septum and XANES spectra were continuously collected over five hours. The Mo₂C pellet and the final precursor solution were retained for subsequent elemental analysis. A more detailed description of the custom cell and *in situ* experiments can be found in the SI. Spectra were analyzed using the Demter software package [30]. The Pt and Mo oxidation states were determined based on spectra obtained for metal standards (Pt: H₂PtCl₆, Pt⁰; Mo: MoO₃, MoO₂, Mo⁰) using linear combination fitting.

Water-Gas Shift Activity Measurements

The water-gas shift activities were determined using a flow reactor equipped with a GC-TCD (SRI 8610, Carboxen 1000). Prior to obtaining the activity data, all of the Mo₂C-based catalysts were

pretreated in 15% CH₄/H₂ at 590°C for 4hr (10°C/min heat rate) to remove the passivation layer. The commercial Cu-ZnO/Al₂O₃ was pretreated in 4% H₂/N₂ at 200°C for 4 hr (3°C/min heat rate) per vendor specifications. The reactant feed consisted of 11% CO, 21% H₂O, 6% CO₂, 43% H₂, and 19% N₂ (262 mL/min, 125,000 hr⁻¹) to simulate commercial reformat streams and the temperature was varied between 200 and 240°C. Prior to injection into the GC, the effluent stream flowed through a condenser, held at 0°C to remove water from the stream.

Differential conditions were maintained by limiting the conversions to 10%; this was accomplished by adjusting the catalyst weight. The catalyst was diluted with low surface area SiO₂ (Alfa Aesar, 99.995% metals basis) in order to maintain a constant bed height and volume. Hydrogen production rates were determined by monitoring the consumption of CO; mass balance closure was confirmed by quantifying the formation of CO₂. Direct measurement of H₂ was not possible because we used He as the carrier gas. Arrhenius plots for the turnover frequencies (TOF, s⁻¹), CO consumption rates normalized by CO uptakes, are reported for each of the catalysts.

Results

Material Characterization

X-ray diffraction patterns for the Mo_2C and $\text{p-Mo}_2\text{C}$ materials contained peaks characteristic for

Figure 1. X-ray diffraction patterns for the studied catalysts, including standards from ICDD ($\beta\text{-Mo}_2\text{C}$ [PDF #04-001-2151], $\alpha\text{-MoC}_{1-x}$ [PDF #04-001-2968], Pt [PDF #98-001-3679]).

$\alpha\text{-MoC}_{1-x}$ and $\beta\text{-Mo}_2\text{C}$ (Figure 1). For these catalysts, there was no evidence of oxide phases indicating that carburization was complete and that formation of the passivation layer was restricted to the surface, or that any other species were amorphous or below the detection limits for the diffractometer ($\sim 5\text{nm}$). The surface area decreased significantly from 162 to $103\text{ m}^2/\text{g}$ upon passivating the Mo_2C materials. This loss of surface area corresponds to the loss of micropores during passivation as observed in the pore size distributions (Figure 2); the mesopore densities are very similar.

Figure 2. Pore size distributions in unpassivated and passivated Mo₂C for (a) micropores determined using the Horvath-Kowazoe (HK) method and (b) mesopores determined using the Barrett-Joyner-Halenda (BJH) method.

Platinum Deposition

The deposition of Pt onto the Mo₂C and p-Mo₂C supports was quantified by monitoring the concentration of Pt in the supernatant solution as a function of deposition time. Figure 3 indicates very rapid deposition of Pt onto the Mo₂C surface. Conversely, Pt deposition onto the p-Mo₂C surface occurred in two stages. During the initial stage, the deposition of Pt approached an asymptote corresponding to ~25% of the Pt in the original solution. After approximately 150 min, additional Pt deposition occurred at a slower rate until essentially all of the Pt was removed from the solution. This deposition trend was reproducible for separate experiments with the discontinuity in the adsorption curve occurring at times between 120 and 180 minutes.

Coincident with changes in the Pt concentrations, there were distinct color changes for the aqueous solutions (see Supporting Information). During deposition of Pt onto Mo₂C, the metal precursor solution changed from yellow to clear. During deposition of Pt onto p-Mo₂C, the solution remained yellow for the first 120-180 min. Subsequently, the aqueous solution began to turn blue. Following deposition of Pt onto p-Mo₂C, the aqueous solution was dark blue. We believe the coloration was due to dissolution of some or all of the passivation layer, likely a molybdenum oxycarbide. Placing p-Mo₂C into deionized water (without H₂PtCl₆) also resulted in the formation of this blue color. The material that gave rise to the blue color was filtered out of the solution prior to elemental analysis to avoid introduction of any particulates into the ICP. Water was evaporated from this blue solution and the resulting solid was characterized. The material was x-ray amorphous and contained 62±7 wt% Mo; for comparison, MoO₃ contains 67 wt% Mo and MoO₂ contains 75 wt% Mo. The results are not inconsistent with the blue material being an oxycarbide.

Figure 3. Profiles for Pt deposition (H₂PtCl₆ precursor) onto Mo₂C (■) and p-Mo₂C (●).

Analysis of the resulting catalysts indicated that the Pt/Mo₂C catalyst contained 3.7wt% Pt and the Pt/p-Mo₂C catalyst contained 1.1wt% Pt. The actual Pt loading for the Pt/Mo₂C catalyst was within experimental error of the amount of Pt removed from the deposition solution (equivalent to 3.9wt% Pt). The Pt loading for the Pt/p-Mo₂C catalyst was significantly less than the amount of Pt removed from the

solution (equivalent to 3.8 wt%). The basis for this observation will be considered in the Discussion section.

Differences between Pt deposition profiles and compositions for the Mo₂C and p-Mo₂C supports suggest different deposition mechanisms. The deposition of Pt onto Mo carbides has been reported to proceed via electrostatic adsorption of the Pt ions followed by reduction on the Mo₂C [25]. The point of zero charge (PZC) is a useful metric with regard to the surface chemistry of materials in solution [28,29]. The PZC of a material characterizes the point at which surface functional groups (e.g. hydroxyl) equilibrate with the solution such that no net protonation or deprotonation of surface –OH groups occurs. Solutions of initial pH above or below the PZC will deprotonate and protonate surface hydroxyls, respectively, in an attempt to equilibrate the material-solution system. If the PZC of Mo₂C or p-Mo₂C lies sufficiently far above the pH of the metal precursor solution, the material surface will generate a positive surface charge; the [PtCl₆]²⁻ anion will then be attracted to the surface and adsorb electrostatically.

Results from the PZC experiments for the Mo₂C, p-Mo₂C, and MoO₂ materials are shown in Figure 4. The flat portion of each curve represents the point of zero charge. The PZC for Mo₂C is ap-

Figure 4. Point of zero charge determination for the Mo₂C, p-Mo₂C and MoO₂ materials.

proximately pH 5, while PZCs for the p-Mo₂C and MoO₂ materials are very similar and approximately pH 3. These results not only indicate that surface chemistries of the unpassivated and passivated Mo₂C surfaces are different, but that the charge of the p-Mo₂C surface in solution at a given pH resembles that of MoO₂. For completeness the PZC for MoO₃ was estimated and found to be approximately pH 3 in acidic solutions, but this result is not reported since MoO₃ dissolves in basic solutions.

In situ X-ray Absorption Spectroscopy

Schaidle et al. reported that during the preparation of Mo₂C supported metal catalysts, select metal ions (e.g., [PtCl₆]²⁻, [Pd(NH₃)₄]²⁺, Cu²⁺) were reduced on interaction with Mo₂C while others (e.g., Ni²⁺, Fe²⁺) were not [25]. They proposed that redox reactions occurred between the Mo₂C surface and metal precursor such that metal reduction was accompanied by Mo oxidation. To probe for evidence of redox reactions, the Pt (Pt L3 edge) and Mo (Mo K edge) chemical states were monitored by X-ray absorption spectroscopy during the interaction of aqueous solutions of H₂PtCl₆ with Mo₂C (see Figure 5). A small degree of Mo oxidation was observed during Pt deposition (13wt%, ~25% surface coverage assuming 10¹⁹ sites/m²) onto bulk, unpassivated Mo₂C as indicated by the edge shift from ~20008 to

Figure 5. (a) Pt L3 edge spectra for 14.3wt% Pt/Mo₂C following metal deposition as well as spectra for H₂PtCl₆ (blue line) and Pt⁽⁰⁾ (red line) standards. (b) Initial and final Mo K edge spectra for 14.3% Pt/Mo₂C following Pt deposition onto bulk Mo₂C as well as spectra for Mo metal (red line) and MoO₂ standards (blue line).

~20008.2 eV at a normalized $\mu(E)$ value of 0.5, while the Pt was reduced from Pt^{4+} (the formal oxidation state for Pt in H_2PtCl_6) to approximately $Pt^{0.4+}$ as evidenced by the loss of the strong white line signal present in oxidized Pt and an edge shift to lower energy. The average oxidation states of Mo and Pt were determined using linear combination fitting to known standards. By quantifying the electrons required to reduce the deposited Pt from Pt^{4+} to $Pt^{(0)}$ as measured by elemental analysis of the solution before and after deposition, the expected change in oxidation state of Mo was +0.20. The measured change in oxidation state derived from linear combination fitting was +0.18, in close agreement with the expected change. However, this change in oxidation state is relatively small. To enhance the signal to noise ratio, the experiment was repeated with Mo_2C dispersed onto $\gamma-Al_2O_3$. The use of Mo_2C/Al_2O_3 improves the surface to bulk ratio allowing for easier quantification of Mo oxidation. The chemistry of Mo_2C/Al_2O_3 has been reported to be comparable to those for bulk Mo_2C [31]. Platinum (6 wt% equivalent, based on the work by Wang et al. [31]) was deposited onto 20wt% Mo_2C/Al_2O_3 while recording spectra. The results of these experiments are shown in Figures 6 and 7. The Pt L3 edge XANES spectra (shown in Figure 6a) changed dramatically during Pt deposition. The results are consistent with the reduction of Pt^{4+} in H_2PtCl_6 to metallic Pt. Observing isosbestic points at 11.573 and 11.602 keV, it is evident that the spectra can be deconvoluted as a linear combination of at least two known standards (Pt metal and H_2PtCl_6 in this case). This deconvolution was used to estimate the average oxidation states as shown in Figure 7a. The Pt oxidation state decreased rapidly from +4 (H_2PtCl_6) to +0.5 after 4 hours of interaction with Mo_2C . Similar to results observed for the bulk Mo_2C support, the oxidation state did not reach zero, likely due to the presence of oxidized Pt remaining in solution (approximately 9% of the initial concentration as determined by elemental analysis of the final solution).

Figure 6. (a) Pt L3 edge XANES spectra during Pt (6wt%) deposition onto $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$. The spectrum for H_2PtCl_6 (blue) is at the top. The reference spectrum for metallic Pt is shown at the bottom (red). (b) Mo K edge XANES spectra of $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$ before and after Pt deposition. The inset represents a closer view of the edge shift. Metallic Mo (red line) and Mo (IV) oxide (blue line) are shown for reference.

Figure 6b illustrates the Mo K edge spectra before and after deposition. The change in Mo K edge was more subtle than that for Pt given the lack of a strong white line for Mo as is present for Pt. Nevertheless, an edge shift to higher energy was again observed indicative of oxidation. By

Figure 7. Average oxidation state of (a) Pt and (b) Mo in $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$ catalyst as a function of Pt deposition time. Open blue points in (B) represent the blank experiment (only deaerated water, no H_2PtCl_6).

deconvoluting the spectra using linear combination fitting, a dynamic profile of the average Mo oxidation state was obtained and is shown in Figure 7b. The Mo oxidation state increased from approximately 2.73 to 3.15 with most of the increase occurring at the beginning of the Pt deposition. The electrons required to reduce Pt deposited from the solution from Pt^{4+} to Pt^0 would result in an average Mo oxidation state increase from 2.73 to 3.31, which is in good agreement with the measured result. Elemental analysis of the initial and final H_2PtCl_6 solutions was performed to determine the extent of Pt deposition during these experiments ($\sim 90\%$ deposited for both experiments). To ensure that the observed oxidation of Mo resulted from interaction with the depositing Pt and not with H_2O , the $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$ material was exposed to deaerated H_2O while collecting XANES spectra on the Mo K edge. Negligible oxidation was observed, indicating that H_2O does not oxidize Mo_2C under these conditions, consistent with thermodynamics [11].

Structural and Surface Chemical Properties

No X-ray diffraction peaks were observed for Pt on either the Mo_2C or p- Mo_2C supports following Pt deposition, reduction, and passivation (see Figure 1). These results are consistent with low weight loadings or the presence of highly dispersed or amorphous Pt particles. Surface area and CO chemisorption uptakes for these catalysts are listed in Table 1. The surface areas for the Pt/ Mo_2C and Pt/p- Mo_2C were similar; the surface areas were also similar to that for p- Mo_2C indicating that the addition of

Table I: Summary of Physical, and Surface Chemical Properties and Water Gas Shift Activities.

Catalyst	Surface Area (m^2/g)	CO Chemisorption Uptake ($\mu\text{mol}/\text{g}$) ^c	N_2O Chemisorption Uptake ($\mu\text{mol}/\text{g}$)	CO Site Density (sites/ $\text{m}^2 \times 10^{18}$) ^d	TOF (s^{-1}) ^e	$E_{a,\text{App}}$ (kJ/mol)
Mo_2C^a	162	N/A	-	N/A	N/A	N/A
p- Mo_2C	103 ^b	404	-	2.36	0.16	68 ± 6
3.7% Pt/ Mo_2C	115 ^b	330	-	1.73	0.72	49 ± 4
1.1% Pt/p- Mo_2C	108 ^b	420	-	2.34	0.18	63 ± 15
Cu/ZnO/ Al_2O_3 [22]	60	-	192	1.93	0.38	42 ± 9

^a The pyrophoric nature of Mo_2C made extensive characterization of this material difficult

^b BET surface areas determined for the passivated catalysts

^c All catalysts pretreated in 15% CH_4/H_2 at 590°C for 4 hours prior to CO pulse chemisorption. Without the pretreatment step and removal of the passivation layer, CO chemisorption uptakes were very low (e.g. $6 \mu\text{mol}/\text{g}$ for p- Mo_2C).

^d Site densities were calculated based on the CO chemisorption and BET surface area results.

^e Turnover frequencies (TOF) were calculated by normalizing the CO consumption rates measured at 240°C by the number of sites estimated by CO chemisorption.

Pt had little effect on the surface area. The CO chemisorption capacities for the p-Mo₂C and Pt/p-Mo₂C catalysts, following recarburation, were comparable, while the chemisorption capacity was lower for the Pt/Mo₂C catalyst relative to Mo₂C. This decrease is likely a consequence of differences in the adsorption capacities of Pt and Mo₂C. Based on the surface areas, Pt surface coverages for the Pt/Mo₂C and Pt/p-Mo₂C were equivalent to 9.9 and 3.1% of a monolayer based on 10¹⁹ atoms/m², respectively. Differences between CO uptakes for the Pt/Mo₂C and Pt/p-Mo₂C catalysts could also be due to differences in the character or dispersion of Pt. This decrease following the addition of Pt has been observed previously [22].

Scanning electron micrographs and EDX mapping indicated very different morphologies for Pt on the Pt/Mo₂C and Pt/p-Mo₂C catalysts (Figure 8). Small particles of Pt were uniformly dispersed on the Mo₂C surface for the Pt/Mo₂C catalyst. Conversely, the Pt/p-Mo₂C catalyst contained very large agglomerates of Pt (19±6 μm, when averaged over 10 particles observed) randomly dispersed on the Mo₂C surface. EDX mapping confirmed that these agglomerates were Pt particles. The observation of large Pt particles on the Pt/p-Mo₂C catalyst is inconsistent with the XRD results. This discrepancy could

Figure 8. Scanning electron micrographs and corresponding EDX spectra for the a) Pt/Mo₂C and b) Pt/p-Mo₂C catalysts.

be a consequence of the low loading for this catalyst. We also note that, the most intense peak for Pt (39.8°, corresponding to (111) plane) is very close to that for β-Mo₂C (39.4°, corresponding to (121)

plane); this could lead to interference for the Pt/p-Mo₂C and Pt/Mo₂C catalysts. Nevertheless Pt morphologies for these catalysts were very different. The implications will be considered later.

Catalytic Activity

Water-gas shift (WGS) turnover frequencies, based on CO uptakes, for the Mo₂C-based and commercial Cu-ZnO/Al₂O₃ catalysts are shown in Figure 9. Turnover frequencies for the Pt/Mo₂C was significantly higher than those for the other materials including the Cu-ZnO/Al₂O₃ catalyst while the activation energy was lower than that for the Pt/p-Mo₂C and p-Mo₂C catalysts but comparable to that for the Cu-ZnO/Al₂O₃ catalyst (Table 1). The activation energies for the p-Mo₂C and Pt/p-Mo₂C catalysts were similar. Furthermore, activation energies for the p-Mo₂C, Pt/Mo₂C, and Cu-ZnO/Al₂O₃ catalysts are in agreement with those reported previously [11,22,32]. Interestingly, when normalized by the Pt content, activities for the Pt/p-Mo₂C (1.4 mol_{CO} mol_{Pt}⁻¹ s⁻¹) and Pt/Mo₂C (1.3 mol_{CO} mol_{Pt}⁻¹ s⁻¹) catalysts were similar. This similarity will be considered in the Discussion section. The Pt normalized rate for the Pt/Mo₂C catalysts matches closely with those reported by Schweitzer et al. (~1.4 mol_{CO} mol_{Pt}⁻¹ s⁻¹) [11].

Figure 9. Arrhenius plot illustrating turnover frequencies (normalized by CO uptake capacity) of the Mo₂C-based catalysts and the commercial Cu-ZnO/Al₂O₃.

Discussion

Results described in this paper revealed significant differences between the synthesis chemistries, structures and compositions of catalysts produced by depositing Pt onto unpassivated and passivated Mo₂C supports, and are consistent with the proposal by Schaidle et al. [25] that the deposition of Pt onto Mo₂C proceeded via electrostatic adsorption of an anionic Pt species onto the carbide surface, followed by reduction of Pt in that species. Shelimov et al. reported that [PtCl₆]²⁻ and [PtCl₅(H₂O)]⁻ are the dominant species in aqueous solutions of H₂PtCl₆ [33]. The pH of H₂PtCl₆ solutions used in our research was consistently ~2.2. Given this and literature regarding metal adsorption through electrostatic interactions [28,29,34,35], [PtCl₆]²⁻ and [PtCl₅(H₂O)]⁻ should be attracted to and deposited onto the Mo₂C surface (PZC ~5). With a PZC of 3, the electrostatic adsorption of [PtCl₆]²⁻ and [PtCl₅(H₂O)]⁻ would be less favorable for p-Mo₂C, nevertheless, some degree of adsorption should occur. For the Mo₂C material, the XAS results indicated that Pt⁴⁺ in [PtCl₆]²⁻ was reduced to ~Pt⁰ with concomitant oxidation of Mo, perhaps according to the reaction in Equation 1. This redox interaction likely facilitated the formation of highly dispersed Pt domains on the Mo₂C surface.

Schaidle et al. observed chlorine on the surfaces of the materials following the deposition of Pt from H₂PtCl₆ solutions [25]. It is likely that chloride anions complex with the surface following Pt reduction in order to balance the surface charge. Passivation, an oxidation of the Mo₂C surface from Mo^{~2+} to Mo⁴⁺/Mo⁶⁺, would be expected to inhibit redox chemistry with the Pt salts resulting in very different structural and compositional properties when compared to materials produced using the unpassivated materials. By oxidizing the Mo₂C surface (which serves as the reducing agent for Pt) prior to interaction with H₂PtCl₆, the driving force for redox chemistry is reduced or removed as, in a oxidized state, Mo is less willing to donate electrons to Pt. Regarding differences in catalyst compositions, we believe that the lower loading for the passivated Mo₂C was due to either removal of some of the deposited Pt

during the dissolution of the passivation layer or complexation between the dissolved oxycarbide and the Pt metal salt. These possibilities are being investigated.

The WGS rates and TOFs for the Pt/Mo₂C catalyst were higher to those for the Pt/p-Mo₂C catalyst despite being recarburized prior to the rate measurements. One might expect that recarburization of these materials would yield catalysts with similar performance characteristics including activation energies, however, this was not the case. This observation as well as details regarding synthesis of the materials illustrates the consequence of passivation prior to deposition of the Pt particles. Given the higher activities, depositing Pt directly onto the carbide surface is preferred.

Differences between TOFs and activation energies for the Pt/Mo₂C and Pt/p-Mo₂C catalysts suggest that active sites for these catalysts were different. Schweitzer et al. [11] proposed that the most active sites for WGS on the Pt/Mo₂C catalysts were at the interface between the Pt particle and Mo₂C surface. The results were consistent with H₂O activation on Mo₂C, producing oxygen for subsequent reaction with CO at the interface; the adsorption of CO was facilitated by the Pt. Given that rates, TOFs and activation energies for the Pt/p-Mo₂C and p-Mo₂C catalysts were nearly identical we believe that most of the activity was derived from the p-Mo₂C and that the Pt was relatively inactive. This is not inconsistent with the very large sizes for Pt particles on the Pt/p-Mo₂C catalyst, in particular when compared to those on the Pt/Mo₂C catalysts. Assuming 19 μm spherical particles, the Pt would account for $1.6 \times 10^{-4} \text{ m}^2$ or less than 0.001% of the surface area of the 1.1% Pt/p-Mo₂C catalyst. Finally we offer a comment about similarities between rates for the Pt/Mo₂C and Pt/p-Mo₂C catalysts when normalized by the Pt content. This similarity may have been a coincidence. For catalysts where the activity is dominated by the p-Mo₂C, mathematically, there will be one loading where the Pt normalized rates for the Pt/Mo₂C and Pt/p-Mo₂C catalysts should be identical. This possibility is being investigated.

Conclusions

Research described in this paper focused on determining the similarities and differences between structural, compositional and catalytic properties of materials produced by depositing Pt onto unpassivated and passivated Mo₂C. The results indicate that the catalytic and structural properties of the Pt/Mo₂C and Pt/p-Mo₂C catalysts were very different. Platinum deposition for the Pt/Mo₂C catalyst was governed primarily by redox reactions between the Pt precursor and Mo in Mo₂C with the Pt being reduced and the Mo being oxidized. This type of interaction was inhibited for the p-Mo₂C supported material due to the presence of the passivation layer. As a consequence, the Pt structures and catalyst compositions were impacted and the intrinsic water-gas shift activities of the Pt/Mo₂C and Pt/p-Mo₂C catalysts were very different. The Pt/Mo₂C catalyst was much more active than the Pt/p-Mo₂C catalyst. In conclusion, the results indicate that the passivation layer can have a larger impact on metal-support interactions than has been previously discussed and this should be considered during the synthesis of carbide- and nitride-supported metal catalysts.

ASSOCIATED CONTENT

Please see supporting information for additional content.

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Graphical Abstract for “Effects of Passivation on Synthesis, Structure and Composition of Molybdenum Carbide Supported Platinum Water-Gas Shift Catalysts”