Effects of passivation on synthesis, structure and composition of molybdenum carbide supported platinum water–gas shift catalysts

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A B S T R A C T

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 Mo_2C. Passivation had a profound effect on the character of interactions between the Pt precursor salt (H_2PtCl_6) and Mo_2C. Nanoscale Pt metal particles were deposited onto the unpassivated Mo_2C while very large Pt particles were deposited onto the passivated Mo_2C (p-Mo_2C). *In situ* X-ray absorption spectroscopy revealed reduction of Pt^{4+} in contact with the unpassivated Mo_2C with commensurate oxidation of Mo. Water–gas shift activities were significantly higher for the Pt/Mo_2C compared to the Pt/p-Mo_2C catalyst. Overall, the results indicate that the passivation of Mo_2C prior to metal deposition had deleterious effects on the Pt loadings, structures, and activities.

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1. 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 m^2/g) [13] and can have catalytic properties that resemble 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 Mo_2C [25]. They reported that some metal precursors (e.g., Pt^{4+}, Pd^{2+}, Cu^{2+}) were spontaneously reduced during deposition/interaction with the native Mo_2C 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 Mo_2C-based CO hydrogenation catalysts [26]. The

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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) $Rb/Mo_2C/Al_2O_3$ performed similar to its passivated counterpart. However, Rb^+ is very difficult to reduce ($E° = -2.93$ V) and would likely not be spontaneously reduced upon interaction with Mo_2C as observed with Pt^{4+}, Pd^{2+}, and Cu^{2+} ($E° = 0.74$, 1.13, 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 Mo_2C 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/Al_2O_3 catalyst, allowing a connection with the broader literature regarding water–gas shift catalysis.

2. Experimental methods

2.1. Catalyst synthesis

Molybdenum carbide was synthesized via temperature-programmed reaction (TPR) as previously reported [11,22,25]. Approximately 1.3 g 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 H_2 flow (400 mL/min) at a heating rate of 5 °C/min followed by a 12 h soak at this temperature. Following the soak step, 15% CH_4/H_2 gas was introduced (400 mL/min) and the material was heated to 590 °C at 2.67 °C/min followed by a 2 h 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 glove box without air exposure (referred to as Mo_2C), (2) surface passivation (material referred to as p-Mo_2C), (3) Pt deposition onto Mo_2C followed by reduction and passivation (to produce Pt/Mo_2C), or (4) Pt deposition onto p-Mo_2C followed by reduction and passivation (to produce Pt/p-Mo_2C). To passivate the surface, the material was exposed to 1% O_2/He flowing at 20 mL/min for at least five hours. To obtain the unpassivated Mo_2C, 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 Mo_2C and N_2 support via a wet impregnation method previously reported in detail for Mo_2C [25]. In brief, the unpassivated or passivated Mo_2C was transferred from the quartz reactor (without exposure to air) into a deaerated, aqueous solution of chloroplatinic acid ($H_2PtCl_6·6H_2O$), 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 h. Following deposition, the catalyst was transferred back to the quartz reactor under argon blanket then reduced with H_2 at 450 °C for 4 h. The material was then cooled and passivated as described above in order to inhibit bulk oxidation.

During the Pt deposition step, aliquots (1.3 mL) 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, Al_2O_3-supported Mo_2C materials were synthesized by dry impregnation of γ-Al_2O_3 (Alfa Aesar, 78 m^2/g, pore volume of 0.40 cm^3/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.

2.2. Materials characterization

Surface areas and pore size distributions of the resulting catalysts were obtained using N_2-physisorption (Micrometrics ASAP 2010). Surface areas were calculated using the Brunner–Emmett–Teller method while micropore and mesopore size distributions were obtained by applying the Horváth–Kawazoe (HK) and Barrett–Joyner–Halenda (BJH) methods, respectively. X-ray diffraction analysis was performed using a Rigaku Miniflex XRD with Cu Kα radiation and a Ni filter ($λ = 1.5418$ Å). An air-tight sample holder was used to obtain the diffraction pattern for unpassivated Mo_2C. The $2θ$ range ($10° < 2θ < 90°$) was scanned at a rate of 5°/min with a 0.02° step size. The final Pt loadings were determined by using a Varian 710-ES following digestion of 15 mg of the catalyst in aqua regia (3:1 $HCl:HNO_3$).

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% CH_4/H_2 (70 mL/min) at 590 °C for 4 h followed by a 0.5 h 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 Mo_2C and p-Mo_2C was 500 m^2/L; the Mo_2C-based catalyst weight was maintained at approximately 40 mg 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 MoO_2 (∼4 m^2/g), 500 mg 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 (20,000 eV) and Pt L3 (11,653 eV) edges were analyzed during separate deposition studies.

To conduct the *in situ* experiments, pellets of the unpassivated Mo_2C and Mo_2C/Al_2O_3 were prepared and secured in the XAS cell, which was subsequently purged with N_2. A spectrum of the Mo K or Pt L3 edge was obtained prior to introduction of the $H_2PtCl_6·6H_2O$ solution. The deaerated solution was then introduced through a septum and XANES spectra were continuously collected over five hours. The Mo_2C pellet and the final precursor solution were retained for subsequent elemental analysis. A more