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On the preparation of molybdenum carbide-supported metal catalysts

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ABSTRACT

Carbide-supported metal catalysts have been demonstrated to be highly active for a number of reactions including water gas shift and electrochemical hydrogen evolution. Their activity appears to be a consequence of intimate interactions between the metal and support. These interactions as well as the structures and compositions depend on the conditions used during preparation. The objective of research described in this paper was to define key aspects regarding the adsorption and reaction of metal precursor complexes with unpassivated, high surface area Mo_2C powders during wet impregnation. The rate of metal deposition and the final state of the metal were functions of the nature of the precursor (i.e., counter ion), electrostatic interactions, and red–ox reactions with the Mo_2C surface. The deposition rate decreased in the following order: $H_2PtCl_6 \sim Pd(NH_3)_4(NO_3)_2 \sim CuCl_2 \sim Cu(NO_3)_2 > Co(NO_3)_2 \sim Ni(NO_3)_2 \gg CoCl_2 \sim NiCl_2 \sim FeCl_2 \sim Fe(NO_3)_3$. The observed adsorption and red–ox behavior suggest that supporting metals onto native carbide surfaces could result in properties that are significantly different from those for metals supported on oxidized carbide surfaces.

1. Introduction

Most heterogeneous catalysts consist of an “active species” dispersed on a high surface area support. The active species directly influences the catalytic rates and selectivities, while the support typically affects the size and morphology of the active species domains [1]. For some systems, the support can also modify electronic properties of the active species and/or participate directly in the reaction as a co-catalyst. Oxides such as alumina and silica are commonly used as supports for heterogeneous catalysts; however, new types of supports are being investigated to drive old and new reactions more efficiently. Early transition metal carbides are promising candidates for use as catalyst supports [2–5]. These materials can be produced in high surface form [6] and have catalytic properties that can resemble those of platinum group metals [6,7]. Carbide-supported metal catalysts have been reported to be active for reactions including Fischer–Tropsch Synthesis [8,9], hydrodenitrogenation and hydrodesulfurization [10], methanol steam reforming [2,5] and water gas shift [3,4]. These materials are also active for electrocatalytic reactions [11–16]. For example, Espositio et al. [11] reported that a monolayer of Pt supported on WC exhibited hydrogen evolution rates comparable with that for bulk Pt.

A number of methods have been used to prepare carbide-supported metal catalysts including thermal evaporation in a vacuum environment [11], atomic layer deposition [13], and wet impregnation [8–10]. In most cases, the carbides were in their passivated forms prior to deposition of the metal. Like other highly reduced nanoscale materials, high surface area early transition metal carbides are often passivated before exposure to air to avoid deep oxidation of the materials. While the resulting materials can be highly active, they are best described as metals supported on oxycarbide or oxide surfaces. Setthapun et al. [2] and Schweitzer et al. [4] used a wet impregnation method to deposit metals directly onto high surface area carbide supports. The resulting materials tended to be more active than those prepared using passivated supports [17]. The deposition of Pt directly onto a native Mo_2C surface produced Pt/Mo_2C catalysts with thin “raft-like” Pt particles and very high Pt dispersions [4]. Water gas shift activities for these catalysts exceeded those for oxide supported Pt catalysts by in some cases more than an order of magnitude. The high activities were attributed to a high density of active sites at the interface between the raft-like Pt particles and Mo_2C support. Motivated by observations like this, we have been examining the nature of interactions between late transition metals and early transition metal carbide surfaces.

The objective of the research described in this paper was to investigate the kinetics and mechanism(s) involved in the deposition of metals on native Mo_2C surfaces during wet impregnation with aqueous metal precursor solutions. Like other types of heterogenous processes [18], the preparation of supported catalysts involves multiple steps including transport of the metal ion/complex to the support surface, adsorption of the ion/complex, and possibly reaction at the support surface. There are a number of factors that could affect interactions of the metal precursors with the support surfaces: the nature of the support (e.g., point of zero charge),

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solution pH, and chemistry of the metal precursors including their ionic strengths [19]. Brunelle was among the first to report that electrostatic interactions can play a role in the adsorption of metal complexes on supports [19]. Electrostatic adsorption is governed by double layer theory [20] and has been investigated in depth by Regalbuto et al. [21–23]. According to the electrostatic model, the solution pH, the charge of the metal complex in solution, and the point of zero charge (PZC, pH at which the surface of the material has a net zero charge) of the support are the key parameters affecting metal adsorption [19,21–23]. Electrostatic binding does not, however, account for the adsorption of all metals on supports [20,24], so more complex theories have been developed. These include the triple layer theory, specific site adsorption, and ligand exchange mechanisms [20].

In addition to transport and adsorption, the metal precursor could react with the support surface. These reactions can produce mixed molecular species that remain on the surface of the support [20]. One example is the formation of layered nickel silicate structures during the adsorption of nickel(II) ammine complexes on silica [25,26]. The metal precursors can also be involved in red–ox reactions with the support surface. The synthesis of bimetallic metal particles is often accomplished via the direct red–ox reaction of a parent metal and a second metal in oxidized form [24,30–31]. Since transition metal carbides behave like metals (band structure of carbides is metallic-like, that is, the d-band of the metal is situated around the Fermi level and there is no bandgap) [27–29], red–ox reactions could be involved in interactions between the metals and carbide surfaces.

In this paper, we describe the preparation of Mo_2C-supported Pt, Pd, Cu, Co, Ni, and Fe catalysts using a wet impregnation method. Special precautions were taken to preserve the native carbide surface chemistry and structure by avoiding exposure of the materials to air; this allowed the metal precursors to interact directly with Mo_2C. Uptake of the metal was monitored as a function of time, and the resulting materials were characterized using X-ray diffraction (XRD), X-ray absorption spectroscopy (XAS), and X-ray photoelectron spectroscopy (XPS). The results were used to define key aspects of the mechanisms governing the deposition of metals onto Mo_2C and could help establish a scientific basis for the preparation of other carbide-supported metal catalysts.

2. Materials and methods

2.1. Catalyst preparation

The Mo carbide supports were synthesized using a temperature programmed reaction procedure [3,4]. Ammonium paramolybdate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$; 81–83% as MoO_3; Alpha Æsar) was crushed and sieved to retain particles with sizes between 125 and 250 μm. The powder (∼1.3 g) was then supported in a tubular quartz reactor with quartz wool and placed in a vertical furnace. The powder was exposed to H_2 flowing at 400 mL/min and heated to 350 °C at 5 °C/min and held at this temperature for 12 h. The gas was then changed to 15% CH_4/H_2 flowing at 375 mL/min, and the temperature was increased at 2.67 °C/min to 590 °C and held at this temperature for 2 h. The resulting materials were then cooled to room temperature in 15% CH_4/H_2. A single batch produced ∼0.75 g of Mo carbide.

Metals were deposited onto the supports via a wet impregnation method. Precursors containing different metals and ligands/counter ions were used. First, an appropriate amount of $Pd(NH_3)_4(NO_3)_2$, H_2PtCl_6, $Cu(NO_3)_2$, $CuCl_2$, $Co(NO_3)_2$, $CoCl_2$, $Ni(NO_3)_2$, $NiCl_2$, $Fe(NO_3)_3$, or $FeCl_2$ was dissolved in 70 mL of deionized water to produce solutions containing 2.27 mmol metal per liter. This metal concentration was chosen to achieve ∼10% coverage of the Mo_2C surface (surface area of ∼120 m^2/g) assuming complete deposition of the precursor. The nominal metal loading would be 1.76 μmol metal per m^2. The solution was purged with Ar gas for more than 15 min in order to remove any dissolved oxygen. The freshly synthesized Mo carbide powder was then transferred, under an Ar blanket, to the solution as it was continuously purged. For temporal analysis of the amount deposited, the support powder remained in the precursor solution for up to 45 h with continuous Ar purging and samples of the solution were extracted for elemental analysis via inductively coupled plasma-optical emission spectroscopy (ICP-OES). Finally, the resulting powders were transferred back into the quartz reactor tube, under an Ar blanket gas.

Some of the solid materials were dried in a He stream flowing at 20 mL/min at room temperature over night. The resulting materials were then stored in a glove box until analyzed by XAS. These materials are referred to as “dried.” Some of the solid materials were dried at 110 °C for 2 h in H_2 and then reduced in H_2 at 450 °C for 4 h. After reduction, the resulting materials were also transferred into a glove box for subsequent characterization. These materials are referred to as “reduced.” Materials not intended for XAS analysis were passivated in 1% O_2/He flowing at 20 mL/min at room temperature for 6 h after the synthesis.

2.2. Materials characterization

The PZC of the Mo carbide was determined according to the procedure described by Park and Regalbuto [32]. Eighteen milliliters of deionized water was purged with Ar, and the solution pH was adjusted to the desired value using either concentrated HCl or NH_4OH. After the pH stabilized, the unpassivated Mo carbide powder was transferred to the solution under an Ar blanket. The solution was continuously stirred, and the pH of the solution was recorded as a function of time. The surface loading was ∼5000 m^2/L, similar to the value used in Park and Regalbuto [32].

The metal loading was determined using one of two procedures. The first involved direct characterization of the powder product. Approximately 15 mg of catalyst was dissolved in 3 mL of aqua regia solution (75 vol.% HCl and 25 vol.% HNO_3). The solution was allowed to stabilize overnight. One milliliter of this solution was diluted with 13 mL of deionized water then analyzed using ICP-OES with a Varian 710-ES ICP Optical Emission Spectrometer. The second method involved analysis of the precursor solutions after contact with the support. For this method, 1 mL of the solution was diluted with 13 mL of deionized water then analyzed using ICP-OES. For each sample, the relative intensities were compared with those for standards of known concentrations.

X-ray diffraction analysis was performed using a Rigaku Miniflex Diffractometer with Cu Kα radiation and a Ni filter (λ = 1.540 Å). The 2θ range ($10° < 2\theta < 90°$) was scanned at a rate of 5°/min with a 0.02° step size. X-ray absorption spectroscopy was performed at the Argonne National Laboratory Advanced Photon Source beamline MR-CAT 10-ID-B. Spectra at the Fe K (7112 eV), Ni K (8333 eV), Cu K (8979 eV), Pd K (24,350 eV), and Pt L3 (11,564 eV) edges were collected in fluorescence mode using Ar ion chambers for detection. Materials for XAS characterization were prepared in a glove box to ensure that the materials were completely isolated from air so that neither the metal nor Mo carbide support was oxidized.

The XAS results were analyzed using free online software Athena utilizing standard analysis procedures. The background was removed by fitting the pre-edge data to a linear function and subtracting out the result. The curves were then normalized by fitting the post-edge data to a third-order polynomial and dividing the data by the extrapolated value at E_o, the energy at the step edge. Finally, the background of the post-edge data was removed using a cubic spline function. The *R*-space data were plotted by first