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Water–gas shift catalysis over transition metals supported on molybdenum carbide

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ABSTRACT

We report here that WGS rates per total surface area at 120 °C, 7% CO, 22% H_2O, 8.5% CO_2, 37% H_2 for Pt, Au, Pd and Ni supported over Mo_2C were 4–8 times higher than those of the commercial $Cu/ZnO/Al_2O_3$ catalyst. In agreement with previous literature, the WGS rate per total moles of Pt over Pt/Mo_2C at 120 °C has been shown to be higher than on any Pt/Metal oxide catalyst. We have made use of systematic changes in the apparent kinetic parameters with various admetals (decrease in apparent CO order and apparent activation energy and increase in apparent H_2O order compared to unpromoted Mo_2C) to conclude that the function of the rate-promoting admetals is to enhance the relative surface concentration of the adsorbed CO, thereby leading to a promotion in the WGS rate per total surface area of the catalyst. Temperature programmed desorption of CO was used to show that the CO adsorption properties of Mo_2C were modified by the various admetals by creating new metallic sites. *In situ* X-ray absorption on Pt and Au and STEM–EELS experiments showed that the supported Au nanoparticles over Mo_2C decrease in average particle size from ~9 nm to 3 nm after a 600 °C carburization pretreatment. Pt was also shown to have assumed a stable structure at 600 °C in the form of a Pt–Mo alloy. We suggest that Mo_2C can be used to synthesize thermally robust supported metal catalysts.

1. Introduction

Transition metal carbides (TMCs) such as Mo_2C, WC, and TiC are formed by the incorporation of carbon atoms into the metal lattice. These materials have been shown to display intriguing catalytic properties. In one of the early observations of the catalytic activity of molybdenum carbide (Mo_2C), Sinfelt and Yates [1] reported that during the process of ethane hydrogenolysis, the carburization of the molybdenum catalyst led to an increase of the reaction rate over time, and the formation of the molybdenum carbide was confirmed by X-ray diffraction. Numerous studies have shown that carbides of molybdenum and tungsten exhibit catalytic activities for several chemical reactions, viz. ammonia synthesis [2], carbon monoxide hydrogenation [3], methane reforming [4], and hydrodesulphurization [5]. The turnover rates for such reactions under reducing environments were equal to or greater than those on oxide supported metals such as Pt, Pd and Ru, and these materials were deemed to be cheaper replacements for the noble metal catalysts.

This study was followed by a number of investigations. Patt et al. [6] studied the water–gas shift (WGS) reaction ($CO + H_2O \rightarrow CO_2 + H_2$) over unsupported Mo_2C and reported that the WGS reaction rates normalized by the amount (mass or surface area) of catalyst for Mo_2C were comparable to those for the commercially used low temperature WGS catalyst, $Cu/ZnO/Al_2O_3$. Schweitzer et al. [7] used high surface area Mo_2C as a supporting material for Pt nanoparticles to study WGS catalysis. It was shown that the WGS reaction rate normalized by total moles of Pt was higher compared to the most active oxide supported Pt catalysts such as Pt/CeO_2 and Pt/TiO_2. Also, the WGS rate per gram of catalyst for Pt/Mo_2C at 240 °C was shown to be 4–5 times higher than that of the unsupported Mo_2C. This study has laid the groundwork for the potential application of Mo_2C as a support for making WGS

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catalysts with reaction rates per mole of noble metal higher than other known noble metal catalysts.

In light of the work performed by Schweitzer et al. [7], we have explored the modifications in the WGS kinetics by addition of various transition metals to unsupported Mo_2C with the objective of understanding the role of the admetals for promotion of the WGS rates. To gain insights into the high WGS rates over Mo_2C and metals supported over Mo_2C, we have performed kinetic and spectroscopic investigation of several Metal/Mo_2C systems. Passivated, unsupported Mo_2C, synthesized via temperature programmed carburization in the presence of a CH_4/H_2 mixture, was used as a support for making supported Pt, Pd, Au, Ni, Cu and Ag catalysts. Variation in the WGS reaction orders with admetals was studied and the role of the rate-promoting admetals is suggested to be the creation of alternative sites for CO activation, thereby increasing the availability of active CO. Similar to the study by Schweitzer et al. [7], the superiority of the Metal/Mo_2C systems over the oxide supported catalysts has been confirmed. We have performed *in situ* X-ray absorption spectroscopy (XAS) to observe the working state of the catalysts during WGS reaction. Additionally, high resolution Scanning Transmission Electron Microscopy (STEM) combined with Electron Energy Loss Spectroscopy (EELS) was used to understand the morphology and qualitatively determine the composition of the supported metal particles. From the kinetics and structures of the catalyst a bifunctional active site for WGS is proposed.

2. Experimental methods

2.1. Catalyst preparation

The unsupported Mo_2C was synthesized by temperature programmed carburization of an ammonium heptamolybdate precursor ($(NH4)_6Mo_7O_{24}\cdot 4H_2O$; 81–83% as MoO_3) from Alfa Aesar in a fixed bed reactor system with 0.5 g of the precursor loaded in a quartz reactor tube over a quartz wool plug. The precursor was exposed to pure H_2 (75 sccm), and the temperature was ramped to 350–370 °C at 4 °C min^{-1} and then held at that temperature for 10 h. The temperature was further ramped to 600 °C at 3 °C min^{-1} after the gas was switched to a 15% CH_4/H_2 (75 sccm) mixture. The reactor was maintained at this temperature for 3.5–4 h. It was then cooled to RT under the flow of Ar, and then the catalyst was passivated in a flow of 1% O_2/Ar. The oxygen concentration in the passivation mixture was progressively increased to 20% and the Mo_2C support was ultimately exposed to air. Passivation was performed in order to avoid the spontaneous combustion of the freshly synthesized Mo_2C upon exposure to the ambient air. The passivated Mo_2C was used as a support for the synthesis of Metal/Mo_2C catalysts.

Au/Mo_2C was prepared using the deposition precipitation method. Chloroauric acid ($HAuCl_4\cdot 3H_2O$, Sigma) was added to deionized water along with the support material. An appropriate amount of 1 N Na_2CO_3 solution was added drop-wise to maintain a pH of 2.6 for 6 h of stirring. Additional Na_2CO_3 was then added to bring the pH near 6.6 and the solution was stirred for another 4 h. The mixture was then centrifuged, washed and dried. Atomic absorption spectroscopy was performed on each sample using an AAS, Perkin-Elmer AAnalyst 300 instrument. Prior to AAS measurements, the catalysts were digested in 2 mL/1 mL/100 mg = aqua regia/HF/catalyst in a Nalgene® amber high-density polyethylene bottle for at least 3 days, and this solution was then diluted to the desired concentration for the AAS measurement. Concentrations of Au were determined by comparing results to those of known standards.

Incipient wetness impregnation (IWI) was used for the preparation of Pt, Pd, Ni, Cu and Ag supported on passivated Mo_2C. The precursors used were aqueous solutions containing appropriate amounts of Chloroplatinic acid ($H_2PtCl_6\cdot 6H_2O$, Sigma), Tetraammonium palladium (II)nitrate ($Pd(NH_3)_4(NO_3)_2$, Alfa Aesar), Nickel nitrate ($Ni(NO_3)_2\cdot 6H_2O$, Sigma), Copper nitrate ($Cu(NO_3)\cdot 3H_2O$, Alfa Aesar) and Silver nitrate ($AgNO_3$, Alfa Aesar) for Pt, Pd, Ni, Cu and Ag respectively. The solutions were added drop-wise to the solid catalyst while it was stirred to enhance the mixing. The catalysts were then dried overnight at room temperature and reduced in the presence of pure H_2 at 450 °C for 3 h and passivated using the method mentioned above. All the metal loadings were kept between 1.5 and 2 wt%. The Cu/Zn/Al_2O_3 catalyst was obtained from Süd-Chemie in the form of pellets. The pellets were crushed and sieved to size between 125 and 250 microns before being loaded into the reactor.

2.2. WGS kinetic measurements

Our laboratory is equipped with a fully automated setup of four parallel plug flow reactors, a detailed description of which can be found elsewhere [8]. The WGS reaction rates were measured under differential conditions, i.e. CO conversion was kept below 10% and the products of the WGS reaction (CO_2 and H_2) were also co-fed. The appropriate amount of each catalyst was loaded so that the WGS kinetics could be measured at 120 °C for all the samples. Since the catalysts were prepared over the passivated Mo_2C, prior to the kinetic measurement, each catalyst was subjected to temperature programmed carburization up to 600 °C at 3 °C min^{-1} to bring the carbide surface back to its native form by the removal of oxygen from the surface. After this pretreatment, the reactors were cooled under Ar to 120 °C and were exposed to the WGS reaction mixture (standard conditions, 7% CO, 22% H_2O, 8.5% CO_2, 37% H_2, and balance Ar) with a flow rate of 75.4 sccm. The Cu/ZnO/Al_2O_3 catalyst was reduced using a previously reported procedure [9]. In 5% H_2/Ar, the temperature was increased to 150 °C at 3 °C min^{-1} and from 150 °C to 200 °C at 0.17 °C min^{-1} and was tested at 140 °C. The catalysts were stabilized for a period of ~20 h, which was enough for the initial deactivation of approximately 20–25% to occur and a stable CO conversion value to be reached. The apparent reaction orders were then measured over the stabilized catalysts by varying the partial pressures of one component at a time over the range of 4–21% CO, 5–25% CO_2, 11–34% H_2O, and 14–55% H_2. To determine the apparent activation energy, the temperature was varied from 110 to 140 °C, with the concentrations maintained at standard conditions. After the measurements were completed, the catalysts were passivated at room temperature.

2.3. Catalyst characterization

The bulk structures of the Mo_2C and Metal/Mo_2C catalysts were determined by X-ray diffraction (XRD) using a Scintag X2 diffractometer with Cu Kα radiation. Samples were scanned through 30–90° (2θ) with scanning rate 2° min^{-1}. The BET surface areas were measured using nitrogen adsorption isotherms (Micromeritics ASAP 2020). Samples were degassed at 250 °C for 5–6 h before N_2 adsorption.

CO Temperature programmed desorption (TPD) was performed over Mo_2C and Metal/Mo_2C catalysts using a Micromeritics Autochem 2920 II coupled with an Agilent 5975C mass selective detector (MSD). Prior to CO adsorption, all the samples were carburized in the presence of 15% CH_4/H_2 (50 sccm) at 600 °C (reached at 3 °C min^{-1}) for 4 h. The sample cell was then purged with Helium at 600 °C for 30 min. The pretreatment was followed by CO adsorption at RT by flowing a 5% CO/He (50 sccm) mixture for 1 h. The sample temperature was then linearly increased at 10 °C min^{-1} in the presence of He (30 sccm). The CO desorption response was recorded with the mass selective detector. The