Molybdenum carbide catalysts for water–gas shift

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Molybdenum carbide (Mo_2C) was demonstrated to be highly active for the water–gas shift of a synthetic steam reformer exhaust stream. This catalyst was more active than a commercial Cu–Zn–Al shift catalyst under the conditions employed (220–295 °C and atmospheric pressure). In addition, Mo_2C did not catalyze the methanation reaction. There was no apparent deactivation or modification of the structure during 48 h on-stream. The results suggest that high surface area carbides are promising candidates for development as commercial water–gas shift catalysts.

Keywords: water–gas shift, molybdenum carbide, novel catalysts, PEM fuel cells

1. Introduction

The water–gas shift (WGS) is the reaction of CO with H_2O to form CO_2 and H_2. This reaction is used industrially to produce H_2 for petroleum refining, chemicals production, and in processes that require synthesis gas with high H_2/CO ratios. Since the reaction is exothermic, the equilibrium CO conversion is highest at low temperatures. Consequently, a two-stage process is often used [1]. In industrial reactors, Fe–Cr catalysts are used for the high-temperature shift and Cu–Zn–Al catalysts are used for the low-temperature shift.

An emerging application for the WGS reaction is on-board purification and production of H_2 for fuel cell powered vehicles. Fuel cells are being developed to enable the commercialization of cleaner, more fuel-efficient vehicles. The fuel cell technology favored by most vehicle manufacturers is proton exchange membrane (PEM) cells operating with H_2 from hydrocarbon steam reforming or partial oxidation. Recently, a Peer Review Committee of the National Research Council reported that the fuel processor performance is the critical technical barrier to achieving the Partnership for a New Generation of Vehicles (PNGV) efficiency targets for fuel cell vehicles [2]. The WGS reaction is a critical step during fuel processing since CO severely and irreversibly poisons the PEM electrocatalyst. Shift reactors, charged with currently available commercial catalysts, constitute about a third of the mass, volume, and cost of the fuel processor system [3]. The PNGV has set a goal to reduce the weight of the shift reactors by at least 75% [4].

The goal of the research described in this paper was to evaluate the feasibility of using high surface area Mo carbides for the WGS reaction. These materials possess excellent catalytic activities for a variety of reactions [5–8], exceptional thermal and chemical stabilities [9] and good tolerance to poisons like sulfur [10]. Early transition metal carbides have also been reported to have catalytic properties that resemble those of noble metals [11,12], materials that are excellent WGS catalysts. Properties of the molybdenum carbides were compared to those of a commercial Cu–Zn–Al WGS catalyst.

2. Experimental and results

The precursor to the molybdenum carbide catalyst was ammonium paramolybdate (Alfa, ACS grade). This salt was first dissolved in warm distilled water. The liquid was slowly evaporated and the remaining solid was calcined in dry air for 3 h at 500 °C and sieved to retain material with a mesh size of 60/230. The calcination temperature was determined via thermal gravimetric analysis (TGA) using a Cahn Instruments TG-171.

The oxide was carburized in a temperature-programmed manner using an equimolar mixture of CH_4 and H_2 flowing at 150 $cm^3\,min^{-1}$. Approximately 1.5 g of the oxide was loaded onto a quartz wool plug in a quartz straight tube reactor. Because graphitic carbon can block catalytically active sites, special care was taken to minimize deposition of excess carbon. The appropriate temperature program was devised based on results from TGA in conjunction with X-ray diffraction (XRD), carried out on a Rigaku Rotaflex diffractometer. The TGA pattern for carburization of the oxide is shown in figure 1. The first event produced a feature at ∼580 °C. The weight loss associated with this event (12.2%) was consistent with the theoretical conversion of MoO_3 to MoO_2 (12.1%). The second event yielded a plateau starting at ∼610 °C. The total weight loss up to 615 °C (28.1%) was very close to the theoretical value for the conversion of MoO_3 to Mo_2C (29.1%). Diffraction patterns for solids isolated by quenching the reaction at various temperatures confirmed that MoO_2 was an intermediate during conversion of the oxide to Mo_2C. For temperatures

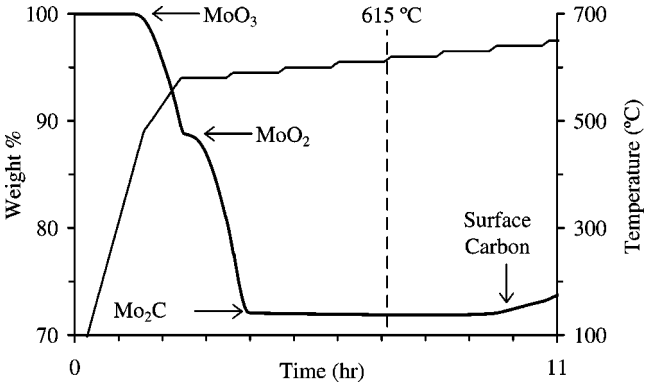

Figure 1. Thermal–gravimetric analysis of the reaction of MoO_3 with an equimolar mixture of CH_4 and H_2.

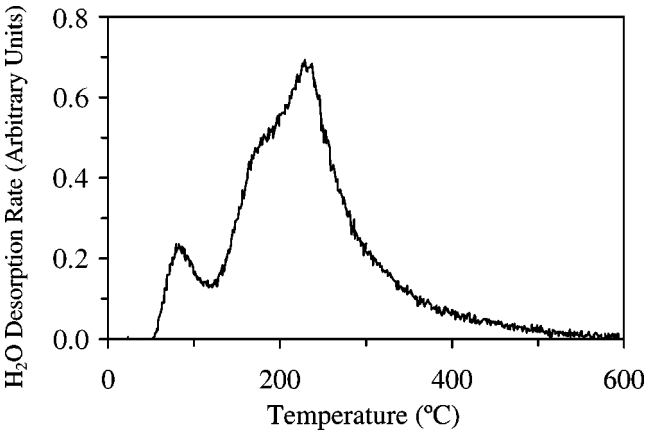

Figure 2. Water desorption rate during the temperature-programmed reduction of Mo_2C.

in excess of ∼650 °C, there was evidence of the deposition of excess carbon on the carbide.

The temperature program for carburization consisted of linearly heating the oxide at a rate of 600 °C h^{-1} to 300 °C, then at 60 °C h^{-1} to 615 °C. Following a 2 h soak period at the final temperature, the product was quenched to room temperature and passivated for 4 h in a mixture of 1% O_2 in He flowing at 30 $cm^3\,min^{-1}$. This passivation step was necessary to prevent pyrophoric oxidation of the carburized material upon contact with air. The XRD pattern indicated that the product was phase-pure Mo_2C.

The proper reduction temperature for activation of the catalyst was determined via temperature-programmed reduction (TPR) in H_2. An Altamira AMI-M, retrofitted with a Fisons Sensorlab 200D mass spectrometer, was used to perform the TPR experiments. A 100 mg sample of the Mo_2C catalyst was heated to 600 °C at 600 °C h^{-1} in a mixture of 5% H_2 in Ar while the composition of the effluent was monitored. Figure 2 shows the water desorption rate as a function of temperature. The first peak was due to physisorbed water and the other peaks correspond to the reduction of oxygen in the passivation layer. The results suggested that a reduction temperature of 400 °C was adequate.

Microstructural properties of the catalysts were characterized by N_2 physisorption. A Micromeritics ASAP 2010 sorption analyzer was used to produce isotherms, calculate the BET surface areas and determine the pore size distributions based on density functional theory. Table 1 provides a summary of the results. Surface areas for the Mo_2C and Cu–Zn–Al catalysts were within experimental error, although a substantial fraction of the surface area for the Mo_2C catalyst was associated with micropores.

Table 1
Surface areas, average pore sizes, and pore size distributions for the water–gas shift catalysts.

Catalyst	Surface area ($m^2\,g^{-1}$)	Average pore size (nm)	Pore size (vol%)		
			Micropore	Mesopore	Macropore
Mo_2C	61	3	22	65	13
Cu–Zn–Al	60	14	3	78	19

The WGS reaction rates and product selectivities were measured using a synthetic methane steam reformer exhaust stream. A 0.15 g sample of catalyst was diluted with ∼0.1 g silica gel (Aldrich, high purity grade, 70–230 mesh) to attain a bed volume of 0.34 cm^3. The Mo_2C catalyst was reduced at 400 °C for 4.5 h in H_2. The Cu–Zn–Al catalyst was reduced at 200 °C in a mixture of 2% H_2 in N_2 for 4.5 h per recommendations from the manufacturer. Rates were measured at atmospheric pressure and temperatures between 220 and 295 °C. The reactant contained 62.5% H_2 (99.99% pure), 31.8% deionized H_2O and 5.7% CO (99.5% pure). The gases were delivered by mass flow controllers and H_2O was fed by a Rainin Rabbit HPLC pump. The reactant was preheated prior to contacting the catalyst bed and the flow rates were adjusted to achieve gas hourly space velocities greater than 10,000 h^{-1}. An SRI model 8610C gas chromatograph equipped with Porapak Q and molecular sieve columns and a thermal conductivity detector was used to determine the effluent composition. A blank run of the silica gel bed (0.34 cm^3) showed no WGS activity.

The reaction rates reached steady state after approximately 1 h on-stream and were reproducible to within 10% during subsequent runs. There was no evidence of methanation activity for the Mo_2C or Cu–Zn–Al catalysts under the conditions employed. Steady-state gravimetric reaction rates for the Mo_2C catalyst were higher than those for the commercial Cu–Zn–Al catalyst over the temperature range explored (see figure 3). The CO conversion ranged from 2 to 30%. The areal reaction rate for the Mo_2C catalyst was 0.22 $\mu mol\,m^{-2}\,s^{-1}$ at 295 °C. Using the active surface area reported by the manufacturer (11 $m^2\,g^{-1}$), the Cu–Zn–Al catalyst had an areal reaction rate of 0.69 $\mu mol\,m^{-2}\,s^{-1}$ at 295 °C. Apparent activation energies for the Mo_2C (17 ± 2 kcal mol^{-1}) and Cu–Zn–Al (17 ± 2 kcal mol^{-1}) catalysts were similar. There was no decrease in the activity for the Mo_2C catalyst during ∼48 h on-stream. In addition, there was no apparent modification of the bulk phase structure. Figure 4 compares diffraction patterns for the Mo_2C catalyst before and after use at 270 °C.

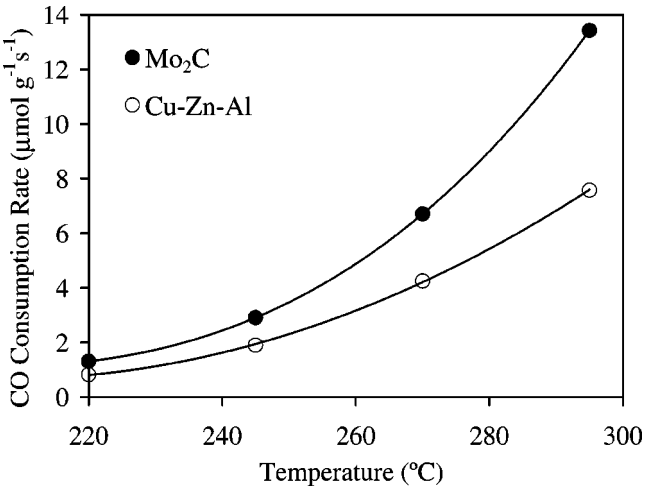

Figure 3. Carbon monoxide consumption rates for the Mo_2C (61 $m^2\,g^{-1}$) and commercial Cu–Zn–Al (60 $m^2\,g^{-1}$) catalysts.

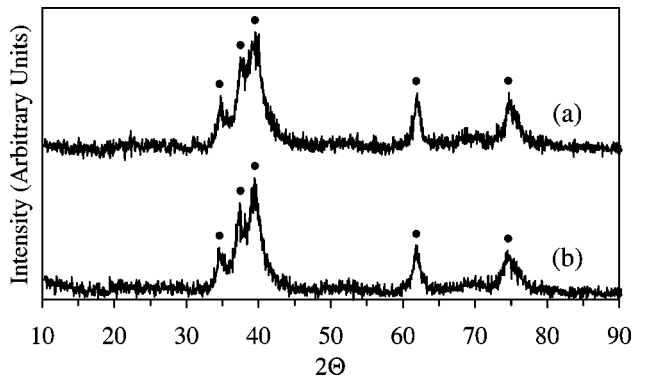

Figure 4. X-ray diffraction patterns for the Mo carbide catalyst (a) before and (b) after use for 48 h at 270 °C. The material was phase-pure Mo_2C (●).

Results presented in this paper demonstrate that high surface area molybdenum carbide is a very active WGS catalyst. In addition to its high activity and durability, the Mo_2C catalyst was 25% more dense than the Cu–Zn–Al catalyst and it has been reported to be sulfur tolerant [10]. The higher densities associated with the carbides could result in smaller reactor bed volumes. Further development of these materials could lead to substantial reductions in the size, weight and cost of WGS reactors.

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