Low-temperature water-gas shift reaction over Mn-promoted Cu/Al$_2$O$_3$ catalysts

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Water-gas-shift reaction was carried out over a series of Mn-promoted Cu/Al$_2$O$_3$ catalysts in the temperature range of 448–533 K. The catalysts were characterized suitably by various techniques. The catalyst containing 8.55 wt% Mn was found to be the most active one among five catalysts tested. A maximum CO conversion of 90% was obtained over this catalyst at 513 K with a CO space-time of 5.33 h. The catalysts were found to be structure sensitive for the low-temperature water-gas shift reaction. A detailed kinetic study was performed for the reaction under investigation over the best catalyst. The kinetic data were fitted to two different models and the redox model was found to be the better one than the other. From the estimated kinetic constant, the activation energy was determined to be 81 kJ/mol for the water-gas shift reaction in the temperature range of 448–463 K.

KEY WORDS: water–gas shift reaction; fuel cell; hydrogen production; Mn-promoted Cu/Al$_2$O$_3$ catalysts; kinetics; redox model.

1. Introduction

With the recent development and beginning of commercialization of polymer electrode fuel cells (PEFCs), the demand of CO-free hydrogen has increased to a great extent. In fact, development of a technology for the production of pure hydrogen (with little or no CO) conveniently and at a low cost is one of the challenges posed to the hydrogen-energy sector. Conventionally, water-gas shift (WGS) reaction, CO + H$_2$O = CO$_2$ + H$_2$, is applied in most hydrogen production facilities to decrease the concentration of CO (and to increase simultaneously the production of hydrogen). The shift reaction is desirable even for the removal of a large amount of CO since it is moderately exothermic ($\Delta H_{298}^\circ = -41.1$ kJ/mol) and the reaction temperature is easy to control. However, the equilibrium conversion of CO is dependent largely on the reaction temperature, lower temperature being favored for higher conversion of CO. Again the reactant gases are not active enough to reach the chemical equilibrium at lower temperatures. Copper-based catalysts are generally more active for WGS reaction. The present work is concerned with the development of manganese promoted Cu/Al$_2$O$_3$ catalysts for low-temperature water-gas shift reaction.

Generally, bimetallic catalyst systems are used for water-gas shift reaction. Two important industrial catalysts for water-gas shift reaction are: high-temperature shift catalyst, FeCr, and low-temperature shift catalyst CuZn [1]. Interestingly, copper-based catalysts are also used for methanol synthesis [2] and methanol steam reforming reactions [3,4], where the water-gas shift reaction plays an important role. Though copper-based catalysts have been the subject of extensive studies for the water-gas shift reaction ever since they were introduced in the early 1960s, some important aspects of the reaction over these catalysts have not yet been addressed properly. For example, the nature of active sites for copper-based shift catalysts is a topic of controversy. Some studies indicate that metallic copper is active for reaction [5], but the relative importance of metallic copper and Cu$^{2+}$ sites is not clear.

The concept of structure sensitivity is widely used to describe the nature of catalytically active sites for the shift reaction. For structure sensitive catalysts, the specific activity (or the turnover frequency) of the reaction under consideration is strongly dependent on the catalyst parameters (e.g., catalyst composition, crystallite size distribution, nature of support, catalyst preparation parameters, etc. Lloyd et al. [1] had correlated the water-gas shift activity with the metallic copper surface area. According to them, the more the dispersion of metallic copper on the catalyst surface, the more active is the catalyst and a constant specific activity (or turnover frequency) is observed. Studies conducted by other researchers have also indicated that the turnover frequency is essentially constant over a wide range of metallic copper dispersions [6]. These studies seem to indicate that the catalyst parameters, like amount of copper dispersion, have no effect on the turnover frequency. Thus the water-gas shift reaction is structure insensitive on copper-based catalysts. On the other
hand, Kuijpers et al. [7] have proposed that the shift reaction is a structure sensitive reaction on silica supported copper catalysts, since the reaction takes place only on copper crystallites of size less than 20 nm.

The primary objective of this study was to develop Mn-promoted CuO/Al₂O₃ catalysts for low-temperature water-gas shift reaction. Catalyst characterization, experimental and kinetic studies were carried out on these catalysts to identify the active species, their role in the water-gas shift reaction activity and also to address the aforementioned points of controversy in the literature.

Although the WGS reaction involves only four small molecules, the reaction mechanism is quite complex. There are generally two reaction mechanisms proposed in the literature for the WGS reaction, associative and redox. In the first one, a formate species is formed which then decomposes to form CO₂ and H₂ [8–10]. On the other hand, the redox mechanism consists of a surface reduction (H₂O + * ⇒ H₂ + O*), followed by surface oxidation (CO + O* + CO₂ + *). Some studies have predicted that the redox mechanism is prevalent [1,5,11–13]. Grenoble et al. [9] proposed a reaction sequence based on an associative mechanism including formic acid as an intermediate in order to account for the apparent bi-functionality of the supported catalyst systems. They concluded that the WGS reaction occurs in two sites with the metal activating carbon monoxide and the support sites as the principal sites for water activation. Salmi et al. [10] studied the low-temperature water-gas shift reaction on industrial CuO-ZnO catalysts at 473 and 523 K. They found that the power rate law expression changed when the temperature of reaction was varied, indicating the complex nature of the WGS reaction mechanism. A part of the present study was devoted to establish a suitable mechanism for the reaction under investigation over the developed catalyst.

2. Experimental

2.1. Materials

ACS grade copper nitrate trihydrate [Cu(NO₃)₂·3H₂O] and manganese nitrate of 99.98% purity were obtained from Johnson Matthey Company, Ward Hill, MA, USA. Aluminum nitrate nonahydrate [Al(NO₃)₃·9H₂O] and sodium carbonate, both of purity >99.5%, were procured from BDH Chemicals Ltd., Toronto, ON, Canada.

2.2. Catalysts preparation

The catalyst was prepared in two major steps. In the first step, copper was loaded on alumina by co-precipitation technique from 105 g of a solution of copper nitrate trihydrate and aluminum nitrate nonahydrate having a copper/aluminum ratio of 0.52. Precipitation was brought about by adding this solution dropwise, with constant stirring, to 0.5 M sodium carbonate solution maintained at 40 °C in a 3 L flask. The quantity of sodium carbonate solution taken was 1.1 times the stoichiometric requirement. The resulting slurry (pH 7.5) was vigorously stirred for another 30 min. The precipitate was filtered and washed several times with warm water and finally with cold water and then dried at 383 K for 12 h in air. The dry coprecipitated precursor was designated as CA.

In the second step, the dried precipitate was pelletized in a hydraulic press under a compacting pressure of 680.5 atm, crushed and sieved into a pellet size range from −8 to +10 mesh (2.00–2.36 mm). These catalyst precursor pellets were then impregnated with manganese nitrate solutions having five different concentrations in the range of 0.2 to 2 M by an incipient wetness technique. The Mn-impregnated catalysts were dried first at 383 K for 12 h in an air oven and then calcined in a muffle furnace by raising the temperature slowly to 973 K and then keeping at this temperature for 3 h.

2.3. Catalyst characterization

The calcined promoted catalysts were characterized for various properties responsible for catalytic activity. The different techniques used for characterization include powder X-ray diffraction (XRD) with a Rigaku D/Max-RBX diffractometer (Rigaku, Tokyo, Japan), elemental analysis using inductively coupled plasma-atomic emission spectroscopy (ICP-AES) with a Thermo Jarrel Ash ICAP 61E Trace Analyzer (Thermo Instruments Canada Inc., Mississauga, ON, Canada), temperature programmed reduction (TPR) using ChemBET 3000 equipment (Quantachrome Corporation FL, USA), scanning electron microscopy (SEM) using Phillips SEM-505 scanning electron microscope, and BET surface area, pore volume and pore size distribution, low temperature oxygen chemisorption analysis using Micromeritics adsorption equipment (Model ASAP2000 manufactured by Micromeritics Instruments Inc., Norcross, GA, USA).

2.4. Experimental set-up and procedure

The experiments on water-gas shift reaction were carried out in a fixed-bed reactor set-up. A schematic diagram of the set-up is shown in figure 1. The reactor consisted of a stainless steel tube (10 mm id, 460 mm length) with a SS mesh placed at the center of the reactor to support the catalyst bed. The reactor was placed in an electrically heated furnace, the temperature of which was controlled by a Series SR22 microprocessor based auto tuning PID temperature controller (Shimaden Co. Ltd., Tokyo, Japan).

The feed gas used for the experiments had a molar composition of 2% CO, 15% CO₂, 45% H₂ and 38% N₂ (obtained from Praxair, Mississauga, ON, Canada). A