Preparation of CuO-CeO$_2$-Al$_2$O$_3$ catalyst with mesopore structure for water gas shift reaction


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Abstract—The water gas shift (WGS) reaction has been investigated widely in fuel cell technologies due to the potential for high fuel efficiency and lower emissions during the production of pure hydrogen. Industrially, the WGS reaction occurs in one of the following two ways: (a) high-temperature in the range of 310-450°C with Fe-Cr catalyst, (b) low-temperature in the range of 210-250°C with Cu-ZnO-Al$_2$O$_3$. In this study, a mesoporous catalyst was prepared, with a large surface area and uniformity in both pore size and distribution, by using a one-pot synthesis method. The prepared CuO-CeO$_2$-Al$_2$O$_3$ brought high CO conversion (82%), and was suitable for WGS reaction at low temperature (250°C).

Key words: Ceria, CO Oxidation, Hydrogen Production, Mesoporous Alumina, Water Gas Shift (WGS)

INTRODUCTION

Waste as a resource might appear to be a paradoxical concept. This perception could soon change, however, as the result of the ‘zero waste, and extended producer responsibility’ initiatives currently being implemented in many countries like USA, Canada, Sweden, Japan, and Korea. In addition, interest in alternative energy has been increased due to serious environmental pollution and the exhaustion of fossil fuels. Therefore, there are many studies about hydrogen energy in progress, because hydrogen energy is unlimited and nonpolluting. The water gas shift (WGS) reaction is crucial in producing pure hydrogen. This is a reversible chemical reaction, usually assisted by a catalyst [1]:

\[\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2\]

Ceria is known to promote the WGS reaction and to affect the dispersion of supported metals. Noble or transition metal’s promotion enhances the reduction of the ceria and facilitates the generation of very active centers at the interface between metal and support. Therefore, ceria-based WGS reaction catalysts have been studied as an alternative to the commercially available transition metal catalysts. Tabakova et al. have described a low-temperature (LT)-WGS catalysis prepared by the urea-nitrate combustion method that showed better performance when the Sm and Zn was doped on the catalyst [2]. Interestingly, a recent review showed that gold nanoparticles supported by oxides demonstrate high reactivity for a WGS reaction. However, much debate has occurred in the literature with respect to the activity and stability of supported gold catalysts [3]. A common feature among the gold catalysts with high levels of activity is the presence of nanosized gold, primarily in a zerovalent, metallic state. Gorte and Zhao have reviewed methods for enhancing catalytic activity using additives [4].

Mesoporous materials have a more uniform pore structure and a larger surface area than typical industrial catalyst supports do. Controlling their mesoporosity may reduce the extent of deactivation due to coke formation and the plugging phenomenon that occurs in the micropores, which hinders the diffusion of reactants and products [5]. Therefore, mesoporous materials have the potential for use as high performance catalyst supports. Mesoporous alumina (MA), prepared by the post-hydrolysis method, shows a large surface area (300-500 m$^2$/g) and narrow pore size distribution (D$_{\text{mean}}$<1 nm) [6]. This structural effect (i.e., the nanopore effect) on the catalytic activity in a WGS reaction was confirmed by the Nb/MCM-41 case [7], which found that Nb in a Nb/MCM-41 matrix enhances the oxidative properties of the catalyst.

WGS catalysts are usually prepared by conventional methods such as precipitation, impregnation and vapor phase grafting. However, these methods have some disadvantages, such as a large metal size in support with poor dispersion of metal and the complicated process of the grafting method. One possible way to solve this problem is to co-condensate an aluminum precursor with the metal source in the presence of template molecules, where the interaction between metal ions and the template enhances the formation of highly dispersed metal particles [8].

In this study, this preparation of the CuO-CeO$_2$-Al$_2$O$_3$ catalyst and its catalytic test for LT-WGS reaction is described. The prepared ceria-alumina supported Cu catalyst was applied to the LT-WGS reaction in model mixture gas.

EXPERIMENTAL PROCEDURES

1. Synthesis of the Mesoporous CuO-CeO$_2$-Al$_2$O$_3$ Catalyst

A one-pot synthesized catalyst was prepared by using Al(sec-OBu)$_3$ and Ce(NO$_3$)$_3$ as the aluminum precursor and cerium source,
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respectively, and using an assembly of stearic acid and copper ions as a template with a metal source. The typical procedure is as follows. Known amounts of aluminum/cerium precursor and stearic acid mixed with Cu(NO3)2·2.5H2O were dissolved separately in sec-butyl alcohol and the two solutions were then mixed. Small amounts of de-ionized water were dropped into the mixture. The resulting material was further stirred for 24 hr, followed by air drying. The as-made catalyst was calcined at 550 °C for 4 hr. To investigate the optimum metal contents in the catalysts, the copper concentration was adjusted from 1 to 10 wt% in the alumina-ceria. Conventional Cu catalysts were also prepared by impregnation. In this study, the one-pot synthesized and impregnated catalysts are referred to as Cu-1 and Cu-imp, respectively.

2. Characterization

The pore properties of the final products were analyzed with an ASAP-2010 (Micromeritics) apparatus, and pore morphologies were characterized by transmission electron microscopy (TEM, JEM-2000EXII). X-ray diffraction (XRD, M18XHF-SRA, MAC/Science) measurements were performed in order to investigate the phase transformation of the supports.

3. WGS Reaction

The WGS reaction was carried out in a continuous flow reactor at atmospheric pressure, which is schematically shown in Fig. 1. For the simple feed gas (CO and H2O), 0.3 g of Cu-x was charged into a tubular quartz reactor (L250×Φ15 mm) and heated at 250 °C in a reaction mixture consisting of CO(g) (20 ml/min) and H2O(l) (0.1 ml/min). For the model feed gases of CO(g) (12 ml/min), CO2(g) (14 ml/min), H2(g) (50 ml/min) and H2O(l) (0.02 ml/min), 0.6 g of catalysts was tested. The gas lines were heated and insulated with a heating band before and after the reaction. The products were periodically sampled and analyzed with a gas chromatograph (HP5890II, FID).

RESULTS AND DISCUSSION

1. Catalyst Characterization

As shown in Fig. 2, the pore properties of the prepared materials were analyzed with an N2 adsorption/desorption test. The one-pot synthesized catalyst showed a similar hysteresis loop in the isotherm to that of pure MA. This suggests that the mesoporous structure of Cu-1 was maintained even when it was passed through the one-pot process. In addition, the Cu-1 and MA had a well-developed framework of mesoporosity compared with the commercial support, Degussa (Fig. 2c), which only has textural porosity induced by the void fraction of interparticles. This feature of Cu-1 improved the accessibility of the target materials into the inner pore and enlarged the internal surface area. Table 1 summarizes the pore properties of the prepared materials. The main pore of Cu-1 has the typical size of a pure MA prepared by using stearic acid as a template [5,6,8]. Its surface area and pore volume were slightly smaller than those of MA, but larger than that of the commercial support. The CuCeO2 catalyst without a mesoporous structure generally showed a small surface area (100 m²/g), pore volume (0.15 cm³/g) and a broad pore size distribution (DFWHM=5-10 nm) [1,2]. Therefore, from the standpoint of pore properties, the catalytic support prepared through the

![Fig. 1. Schematic diagram of the WGS reaction system.](image)

![Fig. 2. N2 adsorption/desorption isotherms of (a) pure MA, (b) Cu-1, and (c) Degussa alumina.](image)

<table>
<thead>
<tr>
<th>Samples</th>
<th>Pore size (nm)</th>
<th>Surface area (m²/g)</th>
<th>Pore volume (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MA</td>
<td>3.5</td>
<td>410</td>
<td>0.69</td>
</tr>
<tr>
<td>Cu-1</td>
<td>3.5</td>
<td>399</td>
<td>0.64</td>
</tr>
<tr>
<td>Degussa</td>
<td>9.6</td>
<td>206</td>
<td>0.45</td>
</tr>
</tbody>
</table>

*Pore size at maximum of dV/dD, †Average pore size.