Preparation of CuO-CeO₂-Al₂O₃ catalyst with mesopore structure for water gas shift reaction

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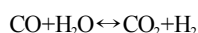**Department of Chemical Engineering, Kwangwoon University, Seoul 139-701, Korea*
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Abstract−The water gas shift (WGS) reaction has been investigated widely in fuel cell technologies due to the potential for high fuel efficiency and lower emissions during 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-Al₂O₃. 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-CeO₂-Al₂O₃ 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]:

$$CO + H_2O \leftrightarrow CO_2 + H_2$$

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 m²/g) and narrow pore size distribution (D_{FWHM}<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-CeO₂-Al₂O₃ 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-CeO₂-Al₂O₃ Catalyst

A one-pot synthesized catalyst was prepared by using Al(sec-OBu)₃ and Ce(NO₃)₂ as the aluminum precursor and cerium source,

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‡This article is dedicated to Professor Chang Kyun Choi for celebrating his retirement from the School of Chemical and Biological Engineering, Seoul National University.

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(NO$_3$)$_2$2.5H$_2$O 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 H$_2$O), 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 H$_2$O(l) (0.1 ml/min). For the model feed gases of CO(g) (12 ml/min), CO$_2$(g) (14 ml/min), H$_2$(g) (50 ml/min) and H$_2$O(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 N$_2$ 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 Cu/CeO$_2$ catalyst without a mesoporous structure generally showed a small surface area (100 m^2/g), pore volume (0.15 cm^3/g) and a broad pore size distribution (D$_{FWHM}$=5-10 nm) [1,2]. Therefore, from the standpoint of pore properties, the catalytic support prepared through the
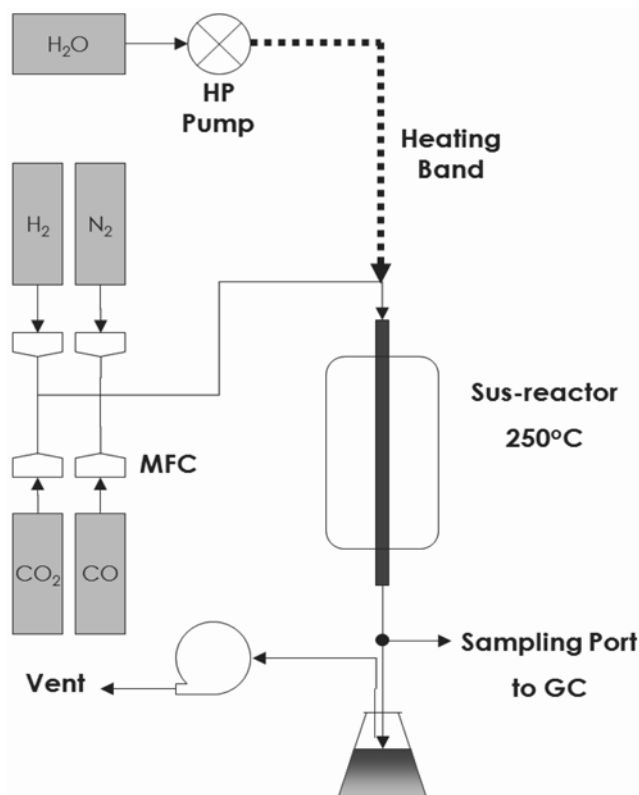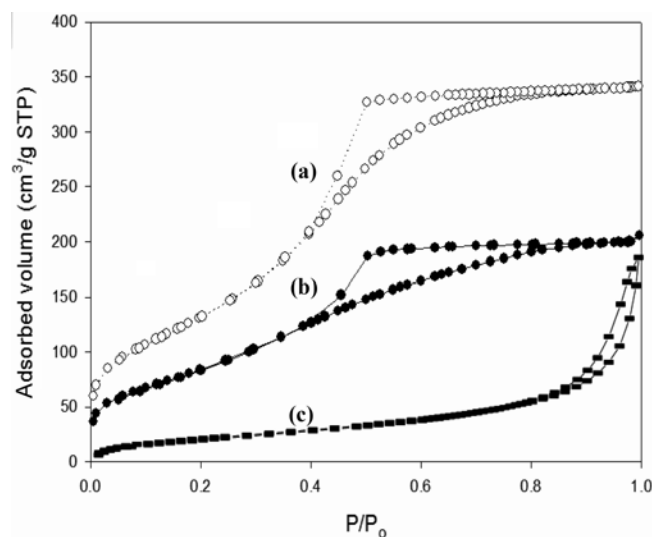

Fig. 2. N$_2$ adsorption/desorption isotherms of (a) pure MA, (b) Cu-1, and (c) Degussa alumina.

Table 1. Pore properties of prepared materials

Samples	Pore size (nm)	Surface area (m^2/g)	Pore volume (cm^3/g)
MA	3.5[a]	410	0.69
Cu-1	3.5[a]	399	0.64
Degussa	9.6[b]	206	0.45

[a]Pore size at maximum of dV/dD, [b]Average pore size.

Fig. 1. Schematic diagram of the WGS reaction system.
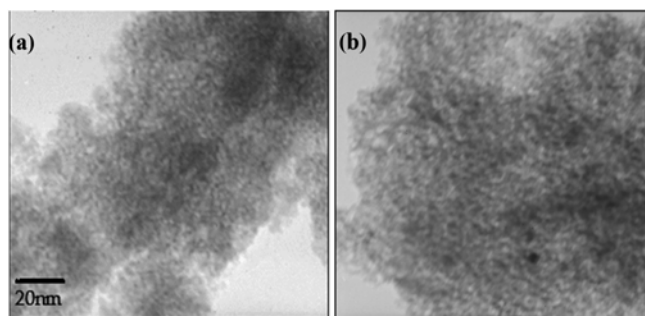
Fig. 3. TEM images of (a) pure MA and (b) Cu-1.

one-pot templating method is good material for use in a WGS reaction.

In XRD analysis of Cu-1 [5,6,8], no detectable diffractions of copper oxide crystallites could be distinguished, suggesting that copper oxide is highly dispersed. This feature is generally found in transition metal catalysts supported in mesoporous materials, a result which was confirmed through TEM images of Cu-1. The pore morphology was analyzed with TEM, as shown in Fig. 3. Cu-1, as well as MA, have a sponge-like appearance, which confirms the advantage of having a highly interconnected pore system. This result showed that the pore morphology of catalytic support was less affected by the preparation process.

2. WGS Reaction

A series of experiments were conducted, with the activity of the catalysts at fixed temperature as the primary test. The aim of these tests was to study the influence of the metal contents, preparation method and feed gas mixture on the activity of the catalysts.

For the Cu-1 catalyst, the molar ratio of alumina to ceria was fixed at 4. When the ceria ratio in the alumina-ceria support was increased, the mesoporous structure of the support could not be formed due to the non-matching of the ionic valance (Al^{3+} and Ce^{2+}). This phenomenon is readily found in the case of bi-metal oxide structures, such as aluminosilicate [9]. When pure MA was used as a catalytic

support, instead of alumina-ceria, catalytic activity decreased lower than with the Cu-1 (alumina-ceria support) catalyst. It should be noted that ceria acted as a promoter to enhance the CO mobility in the catalyst, and alumina also contributed to the elevation of thermal stability.

In the case of the influence of the copper contents on catalytic activity (Fig. 4), the metal contents were adjusted from 1 to 10 wt% of Cu on the alumina-ceria prepared with the one-pot method. It was observed that the CO conversion increased with the increase in metal content up to 10 wt% of Cu. CO conversion of 1 wt% Cu-1 is about 40% at the initial value, while with 10 wt% Cu-1, the conversion increases up to 2 times. As the metal content increased, the metal size also increased, and thus catalytic activity decreased. This decrease is probably related to the loss of the specific surface area and the plugging of the pores of the catalysts due to the increase in the copper content. The deactivation of the catalyst with time occurs with all Cu-1 catalysts. After 6 hr, CO conversion decreased to 30%. However, the prepared Cu-1 catalyst is highly active in the initial reaction range as compared to the reported data; the CO conversion of the 10 wt% $Cu-CeO_2$ catalyst at 250 °C was about 25% [1].

As for the influence of the preparation method on catalytic activity (Fig. 5), initial CO conversion of both Cu-1 and Cu-imp in the model mixture gas was almost identical at 80%. However, the deactivation rate of Cu-imp was faster than that of Cu-1. This tendency appeared in simple feed. Cu-imp, prepared by metal impregnation, generally showed a larger metal size than the catalysts prepared by grafting [10] or by the one-step method using metal ion in the pore [8]. A higher activity of Cu-1, compared to Cu-imp, appeared when the feed gas was changed to a simpler gas (only CO and H_2O), as shown in Fig. 6. The initial CO conversion of Cu-x in the simple feed gas was 60% and smaller than that in the model mixture gas. The stable CO conversion in the simple feed was about 25% after 3 hr reaction time for both Cu-x catalysts, while that of the model mixture gas was reached at 5 hr. Both catalysts are more active when used with the model mixture gas. The hydrogen yield
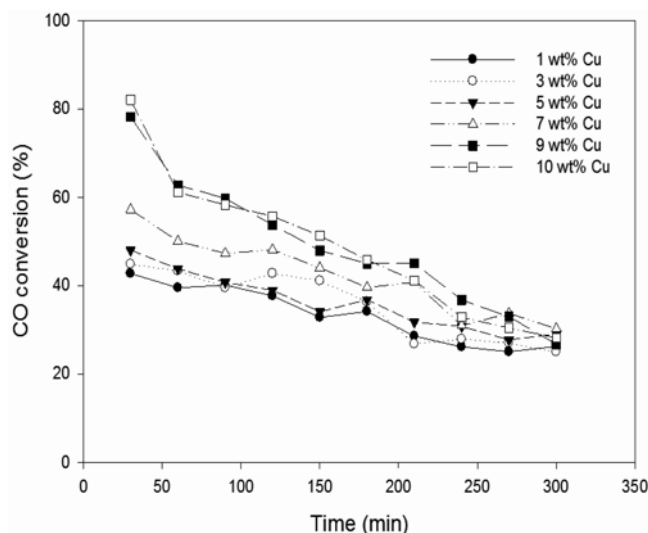

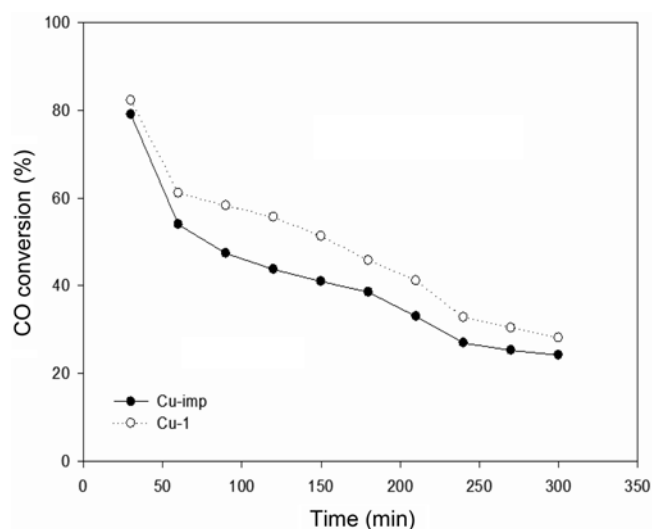**Fig. 4. Dependence of CO conversion on Cu contents for model mixture gas (CO, CO_2, H_2 and H_2O) at 250 °C.**

Fig. 5. Dependence of CO conversion for model mixture gas (CO, CO_2, H_2 and H_2O) at 250 °C with 10 wt% Cu content.
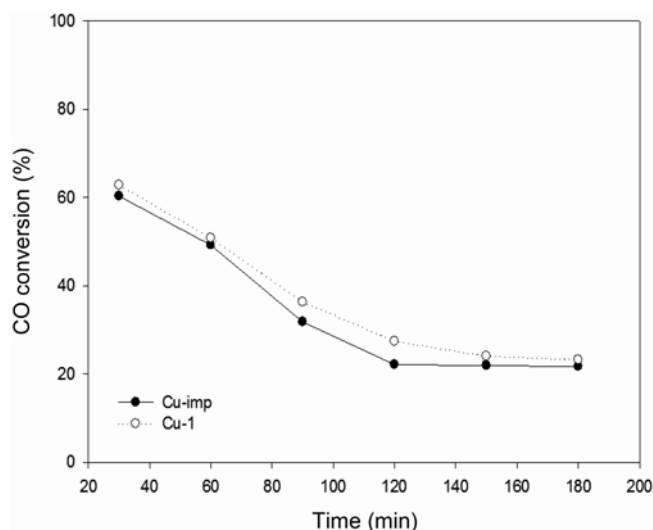
Fig. 6. Dependence of CO conversion for simple feed (CO and H$_2$O) at 250 °C with 10 wt% Cu.

of Cu-1 with the simple feed and the model mixture was about 71% and 80%, respectively.

CONCLUSIONS

In this study, the CuO-CeO$_2$-Al$_2$O$_3$ catalyst for LT-WGS reaction was prepared by using the one-pot templating method. Cu content in support was adjusted from 1 to 10 wt%, and catalytic activity increased with metal content. Cu-imp prepared by metal impregnation demonstrated less activity than Cu-1 prepared with the one-pot method. The initial CO conversion of 10 wt% for the Cu-1 catalyst in the model mixture gas was about 80%, but reached 30% conversion after 5 hr. To solve this deactivation problem, research on the prevention of water condensation in the reactor column is required.

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