doi:10.1246/cl.2012.900

Adsorption State of Carbon Monoxide on a Structured Copper-based Catalyst Prepared by Electroless Plating for Low-temperature Water–Gas Shift Reaction

Choji Fukuhara,* Tomohiro Yamada, Hiromichi Ohkura, and Ryo Watanabe
Department of Materials Science and Chemical Engineering, Faculty of Engineering, Shizuoka University,
3-5-1 Johoku, Naka-ku, Hamamatsu, Shizuoka 432-8561

(Received April 19, 2012; CL-120346; E-mail: tcfukuh@ipc.shizuoka.ac.jp)

In the low-temperature water–gas shift reaction, the effect of the catalyst pretreatment conditions on the adsorption state of CO was investigated on a structured copper-based catalyst, which was prepared by electroless plating. The amount of CO adsorbed on the catalyst was higher due to the oxidation pretreatment than that by the reduction treatment. The CO adsorbed on the oxidized catalyst formed many carbonate and carboxylate species, which have a slightly weak adsorption. Such an adsorption state would enhance shift performance.

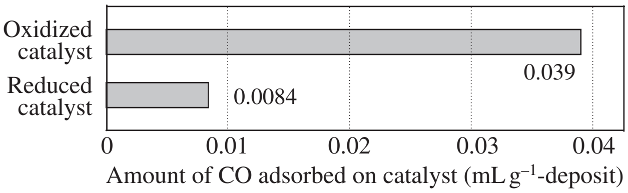

Figure 1. Amount of CO adsorbed on the structured copper-based catalysts with different pretreatment conditions.

When designing on-site or on-board type fuel cell power generation systems, requirements for the reformer and shift converter include a reaction with compact dimensions, an efficient exchange of thermal energy, and a quick response to load fluctuations. We previously prepared a structured copper-based catalyst (Cu–Fe/Zn) by an electroless plating on an aluminum plate and proved that the prepared catalyst provides a high performance for CO shift reaction.[1] Using the structured Cu–Fe/Zn catalyst, a CO shift converter could be equipped with the above-mentioned requirements. Furthermore, it was found that an oxidation pretreatment of the plated catalyst produced some positive progression of shift performance. Such property is very unique for a copper-based catalyst, suggesting no need for hydrogen reduction.

As one of the factors for the performance enhancement by oxidation, we pointed out that the oxidation pretreatment causes much of the zinc near the substrate to migrate to the surface and form a CuZn alloy-like compound.[1,2] Such a close presence of the copper and zinc components would be one of the active sites for the shift reaction. In this study, focusing on the relation between the pretreatment conditions and the adsorption state of the surface chemical species involved in the shift reaction, we investigated the effect of the oxidation on the adsorption state of carbon monoxide onto the structured catalyst by FT-IR and a kinetic study.

A structured copper-based (Cu–Fe/Zn) catalyst was prepared on an aluminum plate by electroless plating, which consisted of a displacement plating of zinc, an intermediate plating of iron, and a chemical plating of copper. The plating process was the same as that in the previous studies.[1,2] After being plated, the structured catalyst was conventionally dried in an air for about 12 h.

The states of carbon monoxide and the chemical species formed on the catalyst were investigated by infrared spectroscopy using the in situ DRIFTS method. The catalyst was first reduced by hydrogen (25 mL min^{-1}) at 300 °C for 1 h in a diffuse reflection cell and then supplied with carbon monoxide (25 mL min^{-1}) for 2 min at 180 °C. After lowering the cell temperature to 40 °C under helium evacuation (about 10 min), the IR measurement of the reduced catalyst was performed for 60 min. While held in the cell, the catalyst surface was oxidized by oxygen (25 mL min^{-1}) at 300 °C. The IR measurement of the oxidized catalyst was successively performed using the same procedure and conditions for the reduced catalyst. The amount of carbon monoxide adsorbed on the reduced and oxidized catalysts was estimated by CO pulse injection (5%CO/helium-balance, 0.192 mL/pulse, 10 shots with pulse duration of 5 min) at 35 °C. Furthermore, using the reduced and oxidized catalysts, the initial shift reaction rate was measured by changing the partial pressures of carbon monoxide and water at 140–200 °C, which produced a lower shift conversion (below 15%).

Figure 1 shows the amount of carbon monoxide adsorbed on the surface of the reduced and oxidized catalysts. As shown in the figure, the oxidized catalyst adsorbed about four times the amount of carbon monoxide than that of the reduced catalyst. In general, the shift reaction on the copper-based catalyst would proceed by the Langmuir–Hinshelwood (L–H) mechanism, forming a formate group on the catalyst surface.[3] Thus, the change in the adsorption amount of carbon monoxide could have some effect on the shift performance of the plated catalyst.

Figure 2 shows the IR spectrum changes with time after adsorbing carbon monoxide on the reduced and oxidized catalysts and following evacuation by flowing helium. The bands due to the CO stretching vibration were observed at 2104 cm^{-1} on both catalysts, which was assigned to a linear CO adsorbed on the copper.[4] In general, π-back donation between the copper and CO chemical bond decreases by the electron-withdrawing ability of O_2 when the copper component is oxidized. Therefore, the stretching vibration peak of CO adsorbed on the oxidized copper surface shifted to higher wavenumber.[4] However, there is no difference in the frequency of the stretching vibration for the oxidized and reduced catalysts. The following factor was considered to be the reason. In this structured copper-based catalyst, zinc near the substrate migrated to the surface by the oxidation treatment, forming a close proximity with the copper at the surface.[1,2] Such a close presence of these elements facilitates the electron donation from zinc to copper.[4] Thus, the wavenumber of the CO stretching vibration did not shift due to such a donation. As for the peak intensity, the vibration on the

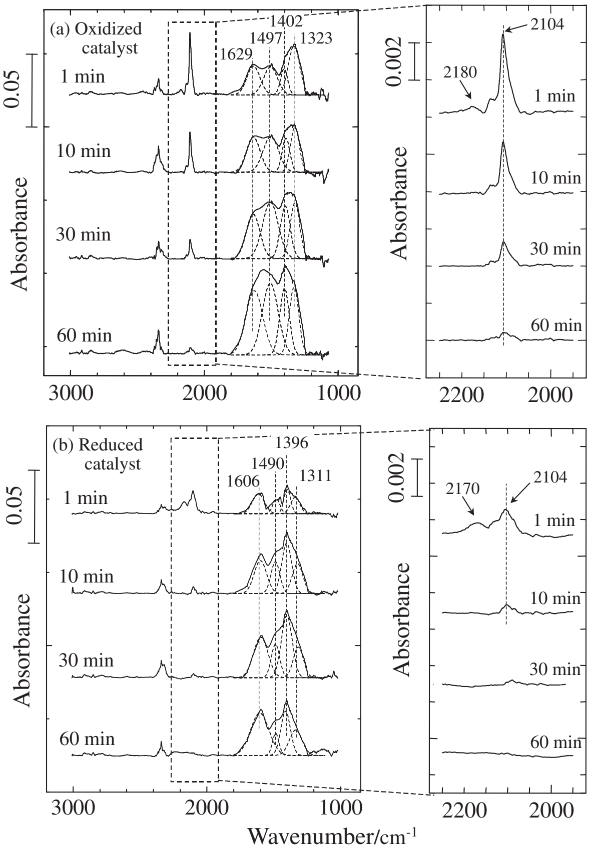

Figure 2. IR spectrum change after adsorbing CO on (a) oxidized and (b) reduced catalysts and following evacuation.

oxidized catalyst was greater than that on the reduced catalyst, suggesting a large amount of adsorbed CO. The CO peak adsorbed on Zn^{2+} was observed at 2170 and 2180 cm^{-1} respectively on both catalysts after a 1 min evacuation.[5]

The bands between 1200 and 1800 cm^{-1} originated from the carbonate and carboxylate species. From the decomposed IR profiles, the 1606 and 1629 cm^{-1} peaks were assigned to the asymmetric vibration of the carbonate species, and the 1396 and 1402 cm^{-1} to the symmetric one. The 1490 and 1497 cm^{-1} peaks were assigned to the asymmetric vibration of the carboxylate species, and the 1311 and 1323 cm^{-1} to the symmetric one.[4] Comparing these peaks, the peak on the oxidized catalyst shifted from that on the reduced catalyst to the higher wavenumber. The adsorption of these species on the oxidized surface was thought to be weaker than that on the reduced one. Although the peak grew with time, an increase in the peak intensity on the oxidized catalyst was greater than that on the reduced one. The chemical species forming on the oxidized surface was thought to be a higher reactivity.

Figure 3 shows plots of the initial reaction rate (r_0) of the shift reaction for the oxidized and reduced catalysts versus the partial pressures of carbon monoxide (p_{CO}) and water (p_{H_2O}), by obtaining from a kinetic measurement.[6] The initial reaction rate, of which the slope was calculated from the on-drawing differentiation of the correlation line at the origin, was obtained by correlating the conversions and contact times (S/F, S: apparent surface area, F: feed rate) by the second-order least-squares method. Based on the slope of a linear line in Figure 3, an exponent-type rate equation for the initial reaction rate was estimated as follows.

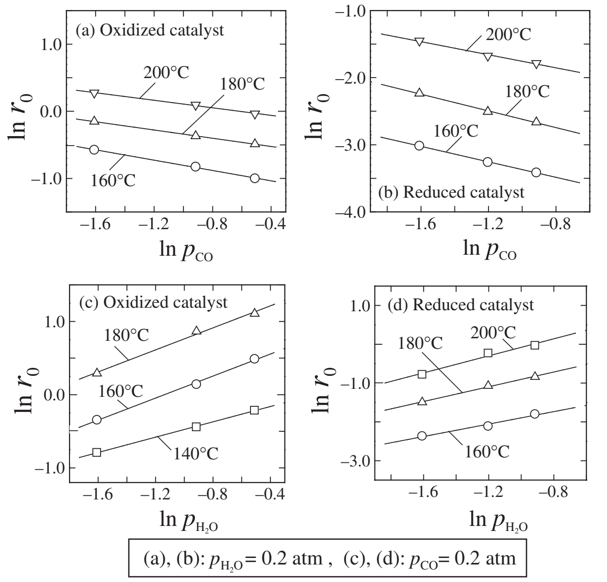

Figure 3. Relationship between partial pressure changes in (a), (b) carbon monoxide and (c), (d) water and the initial reaction rate over the oxidized and reduced catalysts.

$$\text{Oxidized catalyst:}\quad r_0 = kp_{CO}^{-0.33}p_{H_2O}^{0.67}\quad (\mathrm{mol\,m^{-2}\,h^{-1}})$$

$$\text{Reduced catalyst:}\quad r_0 = kp_{CO}^{-0.56}p_{H_2O}^{0.95}\quad (\mathrm{mol\,m^{-2}\,h^{-1}})$$

The estimated equations indicated that, although the catalyst adsorbed carbon monoxide more strongly than water, the oxidized surface adsorbed carbon monoxide with a slightly weak adsorption compared to the reduced surface. The difference in the estimated power number of CO would reflect the different forming rate of an intermediate species, like as the formate group for the shift reaction. In fact, the CO adsorbed on the oxidized catalyst formed the chemical species having a higher reactivity, as shown in Figure 2. Such an adsorption state would be one of the factors of enhancing the shift performance. From an evaluation of the rate constant (k) by the Arrhenius plot, the activation energy was estimated to be 39.5 kJ mol^{-1} for the oxidized catalyst and 66.1 kJ mol^{-1} for the reduced catalyst.

In conclusion, the amount of CO species adsorbed on the copper-based (Cu–Fe/Zn) structured catalyst, prepared by electroless plating on an aluminum plate, was increased by the oxidation treatment of the catalyst. The adsorptive condition of the carbonate and carboxylate species on the oxidized catalyst was weaker than that on the reduced catalyst, suggesting the easy formation of the intermediate species of the shift reaction.

References

1 C. Fukuhara, H. Ohkura, K. Gonohe, A. Igarashi, *Appl. Catal., A* **2005**, *279*, 195.
2 C. Fukuhara, H. Ohkura, *Appl. Catal., A* **2008**, *344*, 158.
3 C. T. Campbell, K. A. Daube, *J. Catal.* **1987**, *104*, 109.
4 L. H. Little, *Infrared Spectra of Adsorbed Species*, Kagaku Dojin, **1971**.
5 D. Scarano, S. Bertarione, G. Spoto, A. Zecchina, C. O. Areán, *Thin Solid Films* **2001**, *400*, 50.
6 C. Fukuhara, A. Igarashi, *J. Chem. Eng. Jpn.* **2002**, *35*, 1322.