Effects of pretreatments of Cu/ZnO-based catalysts on their activities for the water–gas shift reaction

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The effects of the pretreatments of Cu/ZnO-based catalysts prepared by a coprecipitation method on their activities for the water–gas shift reaction at 523 K were investigated. The activity of a $Cu/ZnO/ZrO_2/Al_2O_3$ catalyst for the water–gas shift reaction was less affected by calcination at temperatures ranging from 673–973 K and by H_2 treatment at 573 or 723 K than that of a $Cu/ZnO/Al_2O_3$ catalyst. The catalyst activity could be correlated mainly to the Cu surface area of the catalyst.

KEY WORDS: water–gas shift reaction; Cu/ZnO-based catalyst; calcination; treatment in H_2.

1. Introduction

H_2 production from hydrocarbons such as natural gas, LPG and oil has been of great importance for ammonia synthesis, refining heavy oil, and so on. Furthermore, H_2 production has recently received much attention for fuel cells, especially for PEFC. The water–gas shift reaction is one of the important reaction steps for H_2 production from hydrocarbons. High-performance catalysts for the water–gas shift reaction are highly required for reducing the size of a water–gas shift reactor in a H_2 production process. Cu/ZnO-based catalysts have been used for the water–gas shift reaction at low temperatures ranging from 473–573 K [1–7]. The authors have tried to improve the activity of Cu/ZnO-based catalysts for the water–gas shift reaction.

In the present study, the effects of pretreatment of Cu/ZnO-based catalysts such as calcination temperature and treatment in H_2 at high temperatures on their activities for the water–gas shift reaction were investigated in order to obtain some useful information for developing high-performance catalysts.

2. Experimental

A $Cu/ZnO/Al_2O_3$ catalyst and a $Cu/ZnO/ZrO_2/Al_2O_3$ catalyst used in the present study were prepared by a coprecipitation method using Na_2CO_3 as a precipitant, as described in detail elsewhere [8]. The precipitate obtained was dried overnight at 383 K, calcined at 623 K for 2 h and then the powder calcined was pelletized, crushed and screened to a size between 250 and 600 μm. The catalysts prepared were calcined again at different temperatures ranging from 673 K to 973 K. The composition of a $Cu/ZnO/Al_2O_3$ catalyst was 40 wt% of Cu, 55 wt% of ZnO and 5 wt% of Al_2O_3, and that of a $Cu/ZnO/ZrO_2/Al_2O_3$ catalyst was 40 wt% of Cu, 30 wt% of ZnO, 25 wt% of ZrO_2, and 5 wt% of Al_2O_3.

The catalysts calcined at different temperatures were characterized by X-ray diffraction (XRD) measurements, surface area measurements, bulk density measurements and temperature-programing reduction (TPR) measurements. XRD measurement was carried out to analyze the phases present in the catalyst. The bulk density of the catalyst was determined by dividing the weight of a certain amount of catalyst by its volume measured with a measuring cylinder. The total surface area of the catalyst in m^2/g was measured by a flow method of N_2 adsorption at 77 K using a gas mixture of N_2 (10%) and He (90%). The total surface area of the catalyst in m^2/mL was calculated by multiplying the total surface area of the catalyst in m^2/g by its bulk density in g/mL. TPR measurement for the catalyst was carried out in a stream of a gas mixture of H_2 (10%) and Ar (90%) in the temperature range from 323–700 K.

The activity of the catalyst calcined for the water–gas shift reaction was examined using a fixed-bed down-flow reactor. The catalyst loaded in the reactor was reduced and treated in a stream of a gas mixture of H_2 (10%) and He (90%) at 573 K or at 723 K for 2 h before starting the reaction. Then, the water–gas shift reaction was performed under the following reaction conditions: temperature = 523 K, total pressure = 0.15 MPa, feed gas composition = $CO(10\%)/CO_2(18\%)/H_2(72\%)$, H_2O/feed gas (H_2O/CO) = 0.27 (2.7) (mol/mol), space

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velocity of the feed except water = 36000 h^{-1}. The reactor effluents were analyzed by a TCD gas chromatograph directly connected to the reactor. The products in the water–gas shift reaction were H_2 and CO_2.

The Cu surface area of the post-reaction catalyst was measured with N_2O/He (2.4% N_2O) gas by reactive frontal chromatography after re-reducing the post-reaction catalyst with H_2 at 523 K [9,10]. The post-reaction catalyst was transferred from the reaction tube to a small glass bottle at room temperature in air, and then the sample in the bottle was placed in a sample tube for the Cu surface area measurement. Since a part of the surface of Cu in the post-reaction catalyst was oxidized with air while it was moved from the reaction tube to the sample tube, the post-reaction catalyst in the sample tube was re-reduced with H_2 at 523 K before measuring its Cu surface area. The present procedure gave a reproducible Cu surface area of the catalyst sample.

3. Results and discussion

Figure 1 shows the XRD profiles of the catalysts calcined at different temperatures, indicating that the crystallization of the constituents of the catalysts progressed with increasing calcination temperature. Figure 2 shows the surface areas and the bulk densities of the catalysts as a function of temperature in calcining the catalysts. The surface area of the catalyst decreased with increasing calcination temperature in contrast to the bulk density increasing with an increase in calcination temperature. These findings suggest that the decrease in the surface area of the catalysts should be due to the crystallization of the catalysts with an increase in calcination temperature.

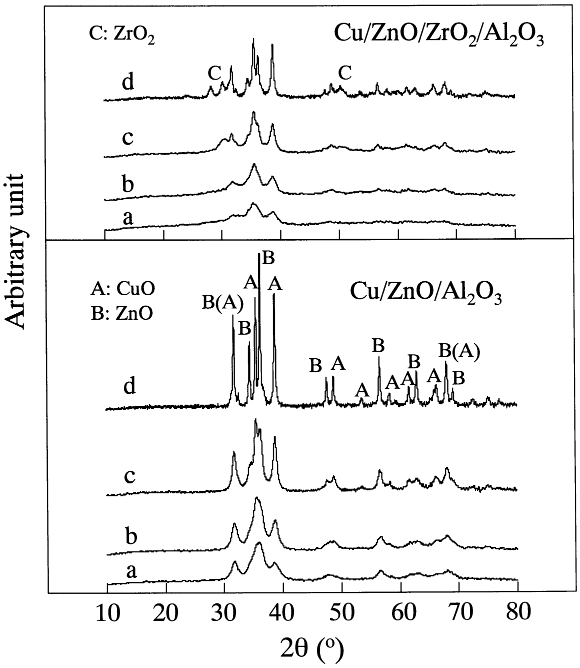

Figure 1. XRD profiles for a $Cu/ZnO/Al_2O_3$ catalyst and a $Cu/ZnO/ZrO_2/Al_2O_3$ catalyst calcined at (a) 673 K, (b) 773 K, (c) 873 K and (d) 973 K.

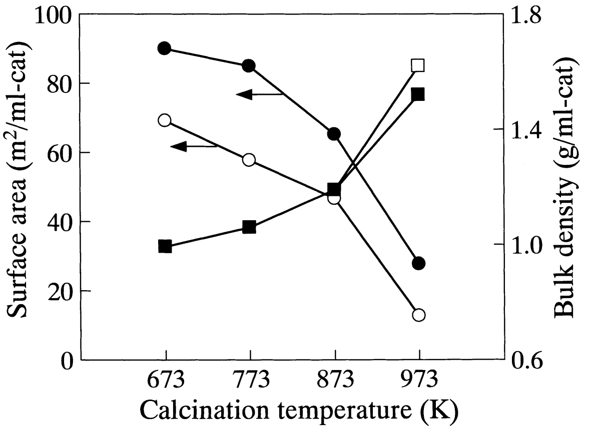

Figure 2. Surface areas (○, ●) and bulk densities (□, ■) of a $Cu/ZnO/Al_2O_3$ catalyst (○, □) and a $Cu/ZnO/ZrO_2/Al_2O_3$ catalyst (●, ■) as a function of temperature in calcining the catalysts.

Figure 3 shows TPR profiles for the catalysts calcined at 673 K and at 973 K, indicating that CuO in the pre-reduction catalysts could be reduced in a temperature range from 423–493 K, not depending on the calcination temperature.

Figure 4 shows the activity (CO conversion) of the catalysts treated in H_2 at 573 K or at 723 K for the water–gas shift reaction as a function of calcination temperature. From practical points of view, the activity of the same volume of catalyst was measured. The catalyst activities hardly changed from 1–4 h after staring the reaction; the data taken at 4 h are shown in figure 4. The activity of the $Cu/ZnO/Al_2O_3$ catalyst treated in H_2 at 573 K or at 723 K decreased with an increase in the calcination temperature. On the other

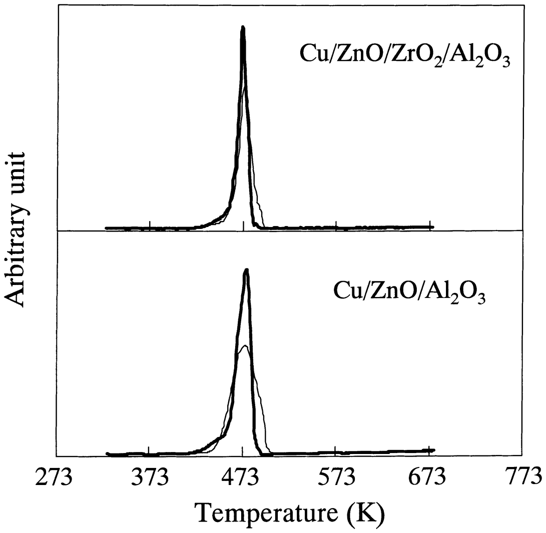

Figure 3. TPR profiles for a $Cu/ZnO/Al_2O_3$ catalyst and a $Cu/ZnO/ZrO_2/Al_2O_3$ catalyst calcined at 673 K (—) and at 973 K (—). Operating conditions for TPR measurement: 10 K/min, 0.1 MPa, $H_2/Ar = 1/9$(mol/mol), flow rate of $H_2/Ar = 20$ mL min^{-1}.

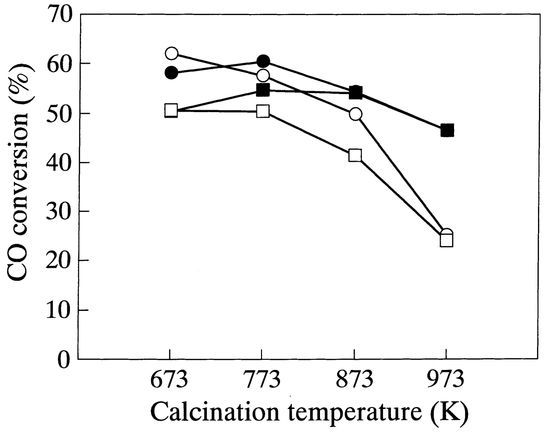

Figure 4. Activities of a $Cu/ZnO/Al_2O_3$ catalyst (○, □) and a $Cu/ZnO/ZrO_2/Al_2O_3$ catalyst (●, ■) treated in H_2 at 573 K (○, ●) or at 723 K (□, ■) for the water–gas shift reaction as a function of temperature in calcining the catalysts. Reaction conditions: 523 K, 0.15 MPa, feed gas = $CO(10\%)/CO_2(18\%)/H_2(72\%)$, $H_2O/CO = 2.7$, SV(exceptH_2O) = 36000 h^{-1}.

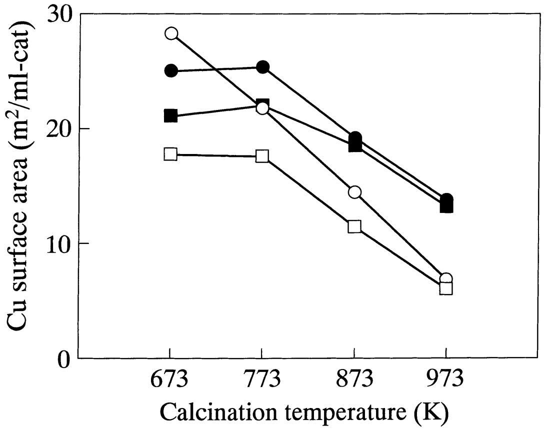

Figure 5. Cu surface areas of the post-reaction catalysts used for the water–gas shift reaction (figure 4) as a function of temperature in calcining the catalysts. The symbols are the same as shown in figure 4.

hand, in the case of the $Cu/ZnO/ZrO_2/Al_2O_3$ catalyst, the activity of the catalyst calcined at 773 K and reduced at 573 K was the highest, as shown in figure 4. Figure 4 also indicates that the difference between the highest activity and the lowest activity of the $Cu/ZnO/ZrO_2/Al_2O_3$ catalyst was smaller than that of the $Cu/ZnO/Al_2O_3$ catalyst. This finding suggests that the $Cu/ZnO/ZrO_2/Al_2O_3$ catalyst would be less affected by the pretreatments such as calcination and treatment in H_2 at high temperatures than the $Cu/ZnO/Al_2O_3$ catalyst, and that the $Cu/ZnO/ZrO_2/Al_2O_3$ catalyst should be more practical than the $Cu/ZnO/Al_2O_3$ catalyst. Figure 5 shows the Cu surface areas of the post-reaction catalysts as a function of the calcination temperature. The change in the Cu surface area of the catalyst with calcination temperature was similar to the change in the catalyst activity with calcination temperature, suggesting that the catalyst activity could be correlated mainly to the Cu surface area of the catalyst, as suggested in our previous paper [10].

4. Conclusions

(1) The crystallization of the constituents of Cu/ZnO-based catalysts progressed with an increase in calcination temperature leading to a decrease in the surface area of the catalyst and to an increase in the bulk density.

(2) The activity of the $Cu/ZnO/ZrO_2/Al_2O_3$ catalyst for the water–gas shift reaction was less affected by the pretreatments such as calcination and treatment in H_2 at high temperatures than that of the $Cu/ZnO/Al_2O_3$ catalyst. Accordingly, the $Cu/ZnO/ZrO_2/Al_2O_3$ catalyst is considered to be more suitable for practical use for the water–gas shift reaction.

(3) The catalyst activity could be correlated mainly to the Cu surface area of the catalyst.

Acknowledgments

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References

[1] D.S. Newsome, Catal. Rev. Sci. Eng. 21 (1980) 275.
[2] C. Rhodes, G.J. Hutchings and A.M. Ward, Catal. Today 23 (1995) 43.
[3] M.J. Gines, N. Amadeo, M. Laborde and C.R. Apesteguia, Appl. Catal. A 131 (1995) 283.
[4] A.A.G. Lima, M. Nele, E.L. Moreno and H.M.C. Andrade, Appl. Catal., A 171 (1998) 31.
[5] J.R. Mellor, N.J. Coville, S.H. Durbach and R.G. Copperthwaite, Appl. Catal., A 171 (1998) 273.
[6] O. Hinrichsen, T. Genter and M. Muhler, in *Studies in Surface Science and Catalysis*, A. Corma, F.V. Melo, S. Mendioroz and J.L.G. Fierro (eds), Vol. 130D (Elsevier Science B.V., 2000) pp. 3825–3830.
[7] J. Wu and M. Saito, J. Catal. 195 (2000) 420.
[8] M. Saito, T. Fujitani, M. Takeuchi and T. Watanabe, Appl. Catal. A 138 (1996) 311.
[9] G.C. Chinchen, C.M. Hay, H.D. Vandervell and K.C. Waugh, J. Catal. 103 (1987) 79.
[10] M. Saito, J. Wu, K. Tomoda, I. Takahara and K. Murata, Catal. Lett. 83 (2002) 1.