

RESEARCH NOTE

Improvement of Stability of a Cu/ZnO/Al₂O₃ Catalyst for the CO Shift ReactionJingang Wu* and Masahiro Saito†¹

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The stability of a Cu/ZnO/Al₂O₃ catalyst in the CO shift reaction was improved by the addition of a small amount of silica into the catalyst, probably due to the suppression of the crystallization of the metal oxides contained in the catalyst, especially ZnO, which could be caused by the steam in the feed during the reaction. © 2000 Academic Press

INTRODUCTION

Currently, the most widely employed way to produce hydrogen is steam reforming of hydrocarbons. CO is a coproduct of the reforming reaction. Unless the mixture of H₂/CO is needed, most of the CO produced is converted to hydrogen by the CO shift reaction (1–6). Recently, interest in this reaction has been renewed because of increasing attention to H₂ production for use in fuel cells. The CO shift reaction is performed industrially in two steps, a high-temperature shift and a low-temperature shift, for which Fe/Cr-based catalysts and Cu/Zn-based catalysts are used, respectively. From a practical viewpoint, the catalysts for the CO shift reaction should be not only active for the reaction, but also stable for a long period in continuous operation. In previous studies, the authors found that the addition of a small amount of colloidal silica into a Cu/ZnO-based catalyst improved the long-term stability of the catalyst for methanol synthesis from CO₂ hydrogenation by suppressing the crystallization of the metal oxides contained in the catalyst, especially ZnO (7, 8). It was suggested that the crystallization of the metal oxides should be caused mainly by the action of the steam produced during methanol synthesis from CO₂ and H₂. In the present study, the authors have applied the novel technology to a Cu/ZnO-based catalyst for

the CO shift reaction, and proved that the new technology also very effectively improved the long-term stability of the catalyst.

EXPERIMENTAL

A Cu(40)/ZnO(50)/Al₂O₃(10) catalyst was prepared by a coprecipitation method using Na₂CO₃ as a precipitant, as described in detail elsewhere (9). Silica was introduced into the catalyst by adding colloidal silica into an aqueous solution of metal nitrates. The colloidal silica was supplied by Nissan Chemical Co. The precipitates obtained by coprecipitation were thoroughly washed with distilled water, dried overnight at 393 K, and calcined at 673 K for 2 h. The calcined catalyst was then pelletized, crushed, and screened to a size between 250 and 600 μm. The catalyst was tested for its effectiveness in the CO shift reaction using a fixed-bed reactor. A 0.5-ml amount of the catalyst was loaded into the reactor. The following reaction conditions were employed in the present study: total pressure = 1.1 MPa; temperature = 478 K; feed gas composition = 3% CO/22% CO₂/75% H₂, steam/feed gas = 1.5; space velocity of the feed except water = 11,250 h⁻¹. Before being used for the reaction, the catalyst was reduced in a flow of H₂ (10%)/He (90%) at 573 K under a pressure of 1.1 MPa for 2 h after the temperature was gradually increased to 573 K to avoid a sudden increase in catalyst temperature. The reactor effluent was analyzed by an on-line gas chromatograph equipped with a Porapak Q column and a TCD detector. The total surface area of the postreaction catalyst was measured by a flow method of N₂ adsorption at 77 K. The Cu surface area of the postreaction catalyst was determined by the technique of N₂O reactive frontal chromatography (RFC) (10) after re-reducing the postreaction catalyst with H₂ at 523 K. X-ray diffraction (XRD) measurement was carried out to analyze the phases present in the catalyst. All the XRD measurements were conducted under the same operating conditions.

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RESULTS AND DISCUSSION

Figure 1 displays the changes in the activities of Cu/ZnO/Al₂O₃ catalysts without SiO₂ and with 0.8 wt% SiO₂ during the long-term CO shift reaction. The activity, expressed in CO conversion (%) of the catalyst without SiO₂, decreased monotonously and was not stabilized until 500 h. On the other hand, the activity of the catalyst containing 0.8 wt% of SiO₂ was almost unchanged during 500 h of CO shift reaction. These findings clearly indicate that the addition of a small amount of colloidal silica into a Cu/ZnO/Al₂O₃ catalyst greatly improves the stability of the catalyst during the long-term CO shift reaction.

Table 1 shows the surface areas, Cu surface areas, and activities of the Cu/ZnO/Al₂O₃ catalysts used for 500 h in the CO shift reaction. The surface area and Cu surface area of the catalyst containing 0.8 wt% of SiO₂ were around 30% higher than those of the catalyst without SiO₂.

Figure 2 shows XRD patterns for the postreaction catalysts with 0.8 wt% of SiO₂ and without SiO₂ after both 1 h and 500 h in CO shift reaction. The peaks assigned to ZnO and Cu became much sharper for the catalyst without SiO₂ during the reaction, whereas those for the catalyst with SiO₂ hardly changed during the reaction. These findings clearly indicate that ZnO and Cu in the catalyst without SiO₂ were more greatly crystallized than those in the catalyst with SiO₂.

The findings obtained in the present study are very similar to those obtained in the previous study on methanol synthesis from CO₂ and H₂. Accordingly, the present findings can be also explained in the same manner as the deactivation

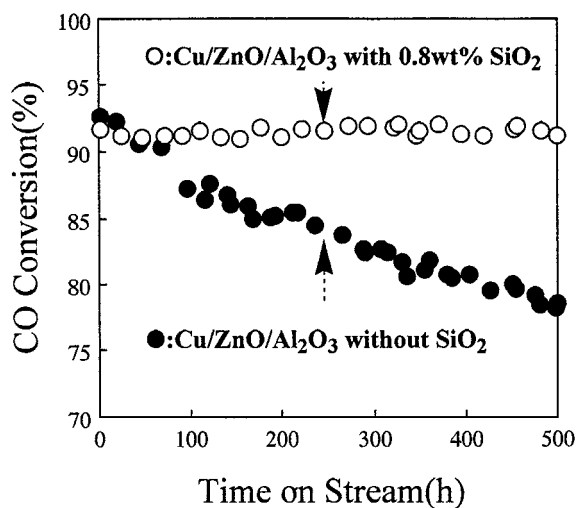


FIG. 1. Effect of addition of colloidal silica into Cu/ZnO/Al₂O₃ catalyst on the catalyst's long-term stability in the CO shift reaction. Reaction conditions: 1.1 MPa, 478 K, SV(dry) = 11,250 h⁻¹, steam/gas = 1.5, and CO/CO₂/H₂ = 3/22/75. ○, Cu/ZnO/Al₂O₃ catalyst with 0.8 wt% silica; ●, Cu/ZnO/Al₂O₃ catalyst without silica.

TABLE 1

Surface Areas and Activities of Cu/ZnO/Al₂O₃ Catalysts without SiO₂ and with 0.8 wt% SiO₂ Calcined at 673 K after 500 h on Stream of the CO Shift Reaction

Catalyst	CO conversion (%)	Surface area (m ² /ml-cat.)	Cu surface area (m ² /ml-cat.)
Cu/ZnO/Al ₂ O ₃ catalyst with 0.8 wt% SiO ₂	91.3	28.8	14.2
Cu/ZnO/Al ₂ O ₃ catalyst without SiO ₂	78.6	22.1	11.3

Note. Reaction conditions: 1.1 MPa, 478 K, SV(dry) = 11,250 h⁻¹, steam/gas = 1.5, and CO/CO₂/H₂ = 3/22/75.

process and the improvement of the catalyst stability by the addition of a small amount of SiO₂ during methanol synthesis, which is described in the Introduction section of the present paper.

In summary, it is strongly suggested that the deactivation of a Cu/ZnO-based catalyst during the CO shift reaction should occur through the following steps: (1) the

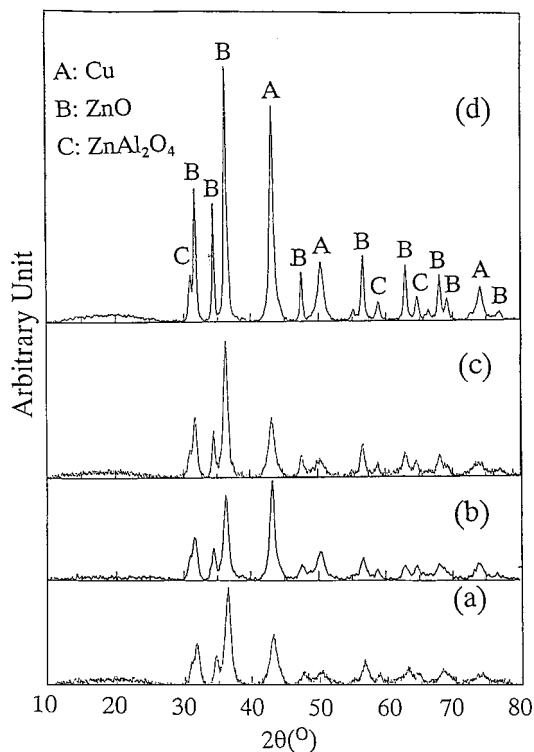


FIG. 2. X-ray diffraction patterns of Cu/ZnO/Al₂O₃ catalysts with 0.8 wt% silica after 1 h (a) and 500 h (b) in the CO shift reaction and of Cu/ZnO/Al₂O₃ catalysts without silica after 1 h (c) and 500 h (d) in the CO shift reaction.

crystallization of the metal oxides contained in the catalyst, especially that of ZnO which could be accelerated by the presence of steam in the feed; (2) the decrease in the surface area of the catalyst; and (3) the decrease in the Cu surface area of the catalyst. It is also indicated that the addition of a small amount of silica to the catalyst could improve the stability of the catalyst during the long-term CO shift reaction by suppressing the crystallization of the metal oxides contained in the catalyst, especially ZnO.

CONCLUSIONS

The deactivation of the Cu/ZnO/Al₂O₃ catalyst was caused mainly by the crystallization of ZnO contained in the catalyst. The addition of a small amount of silica into the catalyst was found to greatly improve the stability of the catalyst by suppressing the crystallization of ZnO contained in the catalyst.

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