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Optimization of preparation conditions and improvement of stability of Cu/ZnO-based multicomponent catalysts for methanol synthesis from CO_2 and H_2

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Abstract

The operation conditions for preparing a Cu/ZnO-based multicomponent catalyst by a coprecipitation method were optimized. The temperature during coprecipitation should be less than 313 K, and the removal of Na from the catalyst by washing the precipitates is most important. Furthermore, a small amount of silica added to the catalyst greatly improved its long-term stability in methanol synthesis from CO_2 and H_2.

Keywords: CO_2 hydrogenation into methanol; Cu/ZnO-based catalyst; Preparation conditions; Stability improvement

1. Introduction

Methanol synthesis from CO_2 and H_2 has been considered to play an important role in the conversion and the transportation of hydrogen energy produced from natural energy such as solar energy, hydropower and so on, as shown in Fig. 1 [1]. According to some estimations [2], an electric power of 300 MWh could be obtained from a methanol fired power plant in Japan, if methanol synthesized from CO_2 and H_2 produced by an electrolysis of water using an electric power of 1000 MWh is transported to through the system shown in Fig. 1.

A practical methanol synthesis process greatly requires a high performance catalyst, which must be highly active and selective for methanol synthesis and also stable for a long period in a continuous operation. The authors developed highly active Cu/ZnO-based multicomponent catalysts on the basis of the role of metal oxides contained in a Cu/ZnO-based catalysts [3]. In the present workshop, the effects of the conditions for preparing a Cu/ZnO-based multicomponent catalyst on its methanol synthesis activity and the drastic effect of silica on the stability of the catalyst in a long-term methanol synthesis operation will be reported

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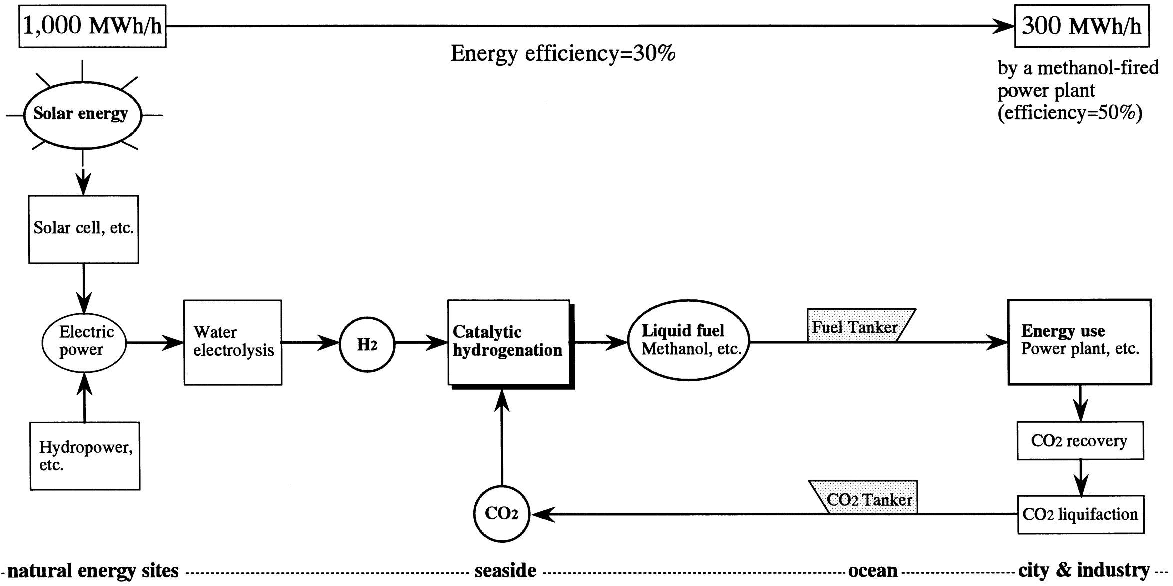

Fig. 1. Global energy network combined with catalytic hydrogenation of CO_2.

2. Experimental

Cu/ZnO-based multicomponent catalysts (Cu/ZnO/ZrO_2/Al_2O_3/Ga_2O_3 and Cu/ZnO/ZrO_2/Al_2O_3) were prepared by a coprecipitation method using Na_2CO_3 as a precipitant, as described in detail elsewhere [1]. The conditions of preparing the catalyst such as the temperature during coprecipitation, the time of aging precipitates, the extent of washing precipitates and so on were varied. A small amount of silica was added to the catalysts by using a colloidal silica supplied by Nissan Chemical. Two ways of adding silica to the catalyst were employed. In one way, colloidal silica was added to a mixed aqueous solution of metal nitrates for the coprecipitation. In the other way, the precipitates prepared were washed with distilled water containing colloidal silica. Both ways gave almost quantitative content of silica in the catalyst, suggesting that silica was incorporated into the catalyst by the adsorption of colloidal silica on the precipitates. A conventional fixed bed flow reactor was used both for short-term methanol synthesis tests and for long-term tests. The surface areas of the catalysts were measured by a flow method employing N_2 adsorption at 77 K. The Cu surface areas of the catalysts were measured in the same way as described elsewhere [1]. X-ray diffraction measurements were performed for analysing the structure of the catalysts.

3. Results and discussion

3.1. *Optimization of operation conditions for preparing the catalyst*

The various operation conditions for preparing the precipitate except the temperature during the coprecipitation had no significant effect on the activity of a Cu/ZnO-based multicomponent catalyst for methanol synthesis from CO_2 and H_2. This finding is very favorable for preparing a practical catalyst.

No significant difference among the activities of the catalysts from the precipitates prepared at temperatures between 273 and 313 K has been observed, whereas the activity of the catalyst prepared at 333 K was slightly (only 7%) lower, as shown in Fig. 2. XRD measurements showed that the crystallite size of the precipitate prepared at 333 K was slightly larger than those of the precipitates prepared at temperatures ranging from 273 to 313 K. These findings suggest that the temperature during coprecipitation should be less than 313 K for preparing active catalysts.

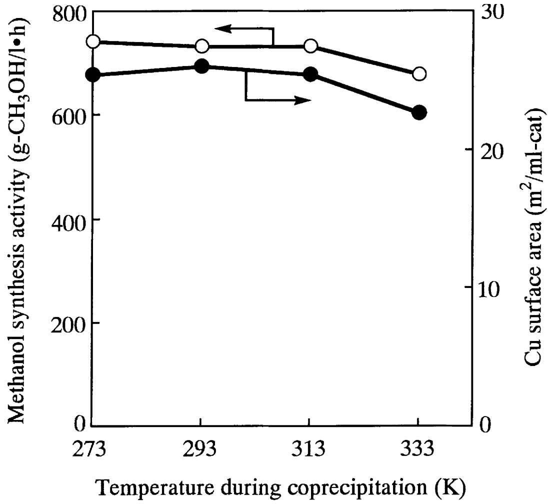

Fig. 2. The activity (○) and Cu surface area (●) of a Cu/ZnO/ $ZrO_2/Al_2O_3/Ga_2O_3$ catalyst as a function of the temperature of coprecipitation. Reaction conditions: 523 K, 5 MPa, SV= 18 000 h^{-1}, feed gas composition=CO_2(75)/H_2(25).

The Na remaining in the catalyst after washing the precipitate with distilled water greatly reduced the catalyst activity, as shown in Fig. 3. The precipitates after being washed different times and then dried overnight at 383 K gave almost the same XRD patterns, whereas the XRD patterns for the catalysts calcined at 623 K, which is shown in Fig. 4, became sharper with the increase in the amount of Na in the catalyst. These findings clearly indicate that the Na remaining in the catalyst causes the crystallization of the components of the catalyst during calcination, and thus reduces the surface area, the Cu surface area and the activity of the catalyst. Consequently, washing the precipitates to remove Na from the precipitates is the most important step for preparing highly active catalysts.

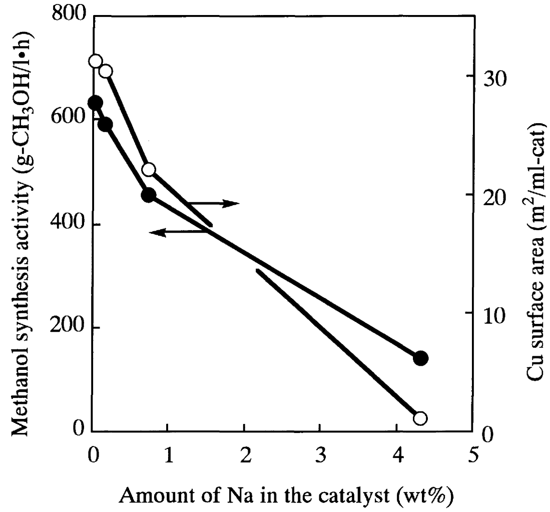

Fig. 3. The activity (○) and Cu surface area (●) of a Cu/ZnO/ $ZrO_2/Al_2O_3/Ga_2O_3$ catalyst as a function of the amount of Na in the catalyst. Reaction conditions were the same as shown in Fig. 2.

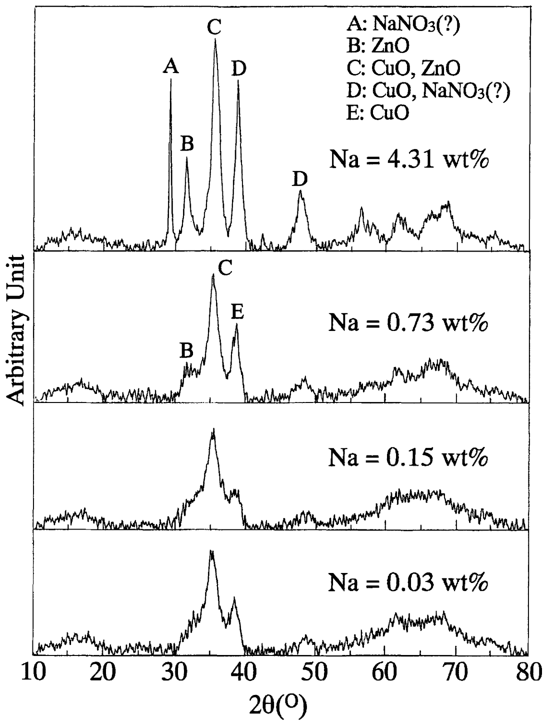

Fig. 4. XRD patterns for a $Cu/ZnO/ZrO_2/Al_2O_3/Ga_2O_3$ catalyst calcined at 623 K as a function of Na content in the catalyst.

3.2. *Improvement of a long-term stability of the catalyst*

The addition of a small amount of silica to Cu/ZnO-based catalysts was found to greatly improve their long-term stabilities in methanol synthesis. Calcining the catalyst at high temperatures of around 873 K is also important for stabilizing the catalyst activity. The activity of a $Cu/ZnO/ZrO_2/Al_2O_3$ catalyst containing

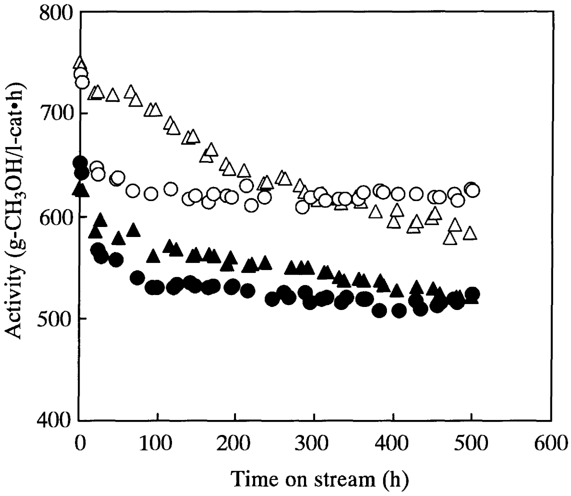

Fig. 5. The effect of a small amount of silica added to a Cu/ZnO/ZrO_2/Al_2O_3 catalyst on its long-term stability in methanol synthesis. (△) Without SiO_2, calcined at 873 K, (▲) without SiO_2, calcined at 623 K, (○) with 0.6 wt% SiO_2, calcined at 873 K and (●) with 0.6 wt% SiO_2, calcined at 623 K. Reaction conditions: 523 K, 5 MPa, SV=10 000 h^{-1}, $CO_2/CO/H_2$=22/3/75.

0.6 wt% of silica and calcined at 873 K decreased by 10% of its initial activity in 40 h of methanol synthesis, but after that time no significant decrease in the activity was observed until 500 h, as shown in Fig. 5. On the other hand, the activity of the catalyst without silica decreased monotonously and did not become stable until 500 h.

Table 1 shows both the surface area and Cu surface area of the catalysts without and with silica as a function of time on stream in methanol synthesis. Both the surface area and the Cu surface area changed in the same manner as the methanol synthesis activity of the catalyst did.

Figs. 6 and 7 show the XRD patterns for the catalysts with and without silica as a function of time on stream in methanol synthesis, respectively. The XRD peaks corresponding to ZnO in the catalyst without silica greatly increased with an increase in time on stream, whereas those peaks in the catalyst containing 0.6 wt% of silica hardly increased. Furthermore, the effect of silica on the stability of a $Cu/ZnO/Al_2O_3$ catalyst was similar to that for a $Cu/ZnO/ZrO_2/Al_2O_3$ catalyst, although the activity of a $Cu/ZnO/Al_2O_3$ catalyst was around 20% lower than that of a Cu/$ZnO/ZrO_2/Al_2O_3$ catalyst. These findings strongly suggest that the catalyst deactivation in methanol synthesis should be caused by the crystallization of the metal oxides in the catalyst, especially ZnO, which leads to the reduction of the surface area and the Cu surface area, and that the silica added could suppress the crystallization of the metal oxides in the catalyst and thus lead to the improvement of the stability of the catalyst. Although the mechanism of

Table 1
Changes in the surface area and Cu surface area of $Cu/ZnO/ZrO_2/Al_2O_3$ catalysts without and with silica during methanol synthesis from CO_2 and H_2

Catalyst[a]	Time on stream (h)	Surface area[b] (m^2/ml)	Cu surface area[b] (m^2/ml)	Activity[c] (g-CH_3OH ml h)
$Cu/ZnO/ZrO_2/Al_2O_3$ without SiO_2	1	82.9	24.9	750
	141	75.2	23.6	679
	500	62.7	19.3	583
$Cu/ZnO/ZrO_2/Al_2O_3$ with 0.6 wt% SiO_2	1	85.3	27.9	721
	20	78.8	23.2	632
	90	76.9	22.1	607
	500	76.8	22.6	609
$Cu/ZnO/ZrO_2/Al_2O_3$ with 2.2 wt% SiO_2	1	73.3	20.0	636
	163	73.5	13.8	395

[a] Calcined at 873 K.
[b] Determined after the methanol synthesis reaction.
[c] Reaction conditions: 523 K, 5 MPa, SV=10 000, $CO_2/CO/H_2$=22/3/75.

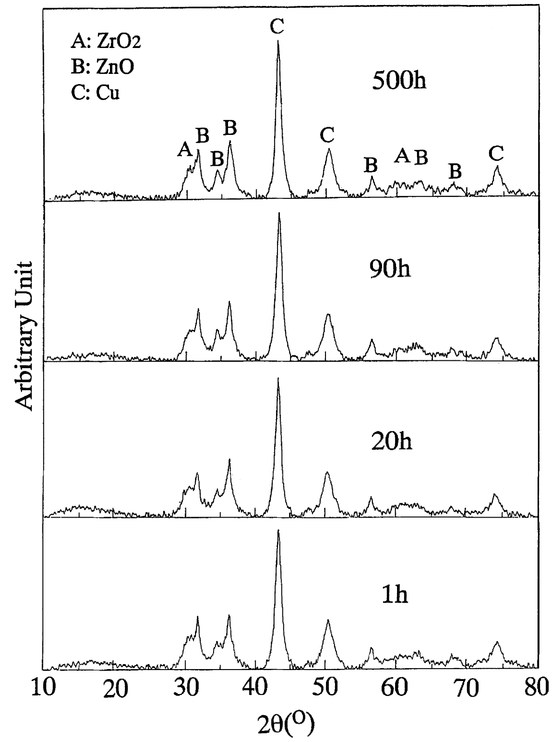

Fig. 6. XRD patterns for a $Cu/ZnO/ZrO_2/Al_2O_3$ catalyst containing 0.6 wt% of silica and calcined at 873 K as a function of time on stream in methanol synthesis.

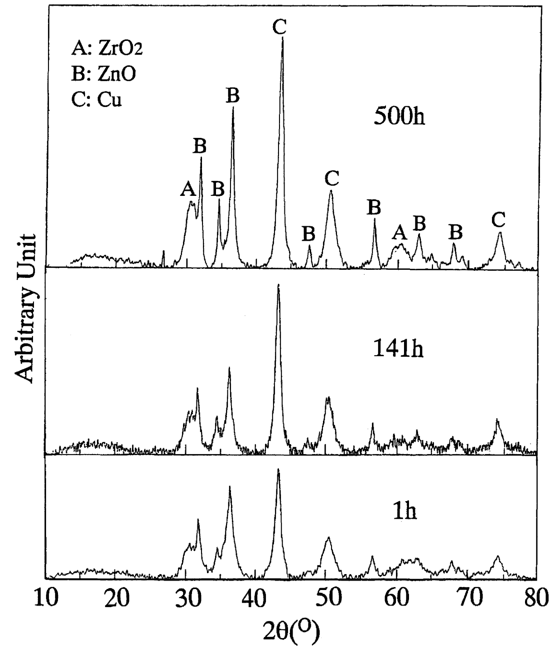

Fig. 7. XRD patterns for a $Cu/ZnO/ZrO_2/Al_2O_3$ catalyst without silica and calcined at 873 K as a function of time on stream in methanol synthesis.

the effect of silica for suppressing the crystallization of metal oxides in the catalyst is not clear in the present study, there might be some strong interaction between silica particle and the particles of metal oxides.

On the other hand, when a larger amount of silica (1.1 or 2.2 wt%) was added to a $Cu/ZnO/ZrO_2/Al_2O_3$ catalyst, the initial decrease of its activity was much larger than that for the catalyst containing 0.6 wt% of SiO_2, as shown in Fig. 8. In addition, as shown in Table 1, the surface area of the catalyst with 2.2 wt% of SiO_2 did not change during the methanol synthesis for 160 h, whereas the Cu surface area and the activity of the catalyst decreased by 31% and by 38%, respectively. These findings suggest that some of silica might move to and block the active sites, and thus lead to an initial decrease in the activity of the catalyst. This could also explain the decrease in the activity of the catalyst containing 0.6 wt% of silica during 40 h from

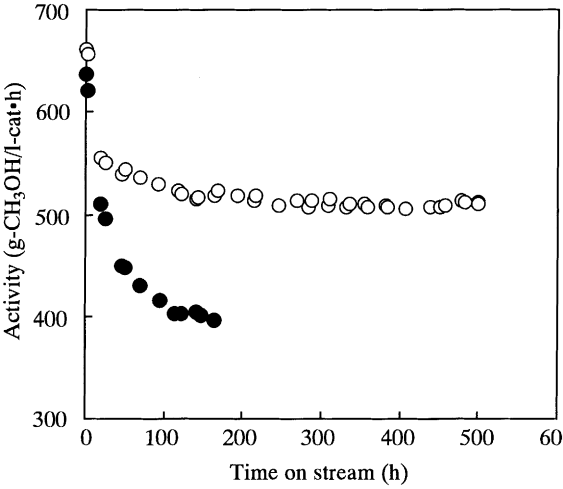

Fig. 8. The effect of a larger amount of silica added to a Cu/ZnO/ZrO_2/Al_2O_3 catalyst on the change in its activity for methanol synthesis. (○) With 1.1 wt% SiO_2, calcined at 873 K and (●) with 2.2 wt% SiO_2, calcined at 873 K. Reaction conditions were the same as shown in Fig. 5.

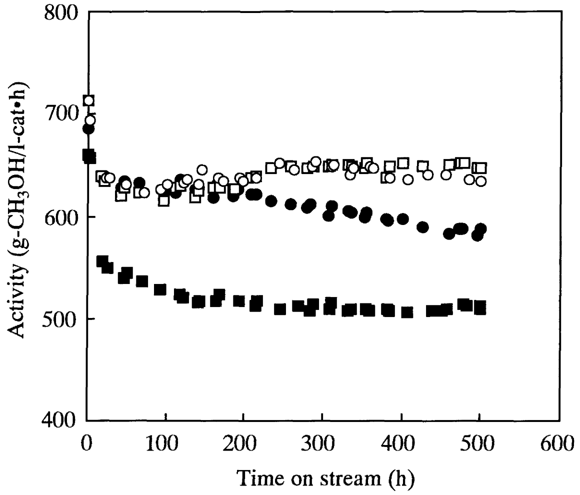

Fig. 9. The effect of the amount of silica added to a Cu/ZnO/ZrO_2/Al_2O_3 catalyst on its activity and long-term stability in methanol synthesis. (○) With 0.36 wt% SiO_2, (●) with 0.53 wt% SiO_2, (□) with 0.71 wt% SiO_2 and (■) with 1.1 wt% SiO_2. The catalysts were calcined at 873 K. Reaction conditions were the same as shown in Fig. 5.

the beginning of methanol synthesis, as shown in Fig. 5.

Fig. 9 shows the effect of the amount of silica added to a Cu/ZnO/ZrO_2/Al_2O_3 catalyst on its activity and its long-term stability in methanol synthesis. The initial activity of the catalyst containing 0.36 wt% of silica was almost the same as those of the catalysts containing 0.53 and 0.71 wt%, but the stability of the former catalyst was a little less than those of the latter catalysts. On the other hand, the initial activity of the catalyst containing 1.1 wt% of silica was lower than those of the catalysts containing 0.53 and 0.71 wt%, and the initial decrease in the activity of the catalyst containing 1.1 wt% of silica was much larger than those of the catalysts containing 0.53 and 0.71 wt%. Accordingly, the optimum amount of silica added to a Cu/ZnO/ZrO_2/Al_2O_3 catalyst should be 0.5–0.7 wt%.

4. Conclusions

The present study is summarized as follows:

1. The operation conditions for preparing a Cu/ZnO-based multicomponent catalyst for methanol synthesis from CO_2 and H_2 was optimized. The various operation conditions for preparing the precipitate except the temperature during the coprecipitation had no significant effect on the catalyst activity. The temperature during coprecipitation should be less than 313 K. Washing the precipitates to remove Na coming from Na_2CO_3 used as a precipitant is the most important step for preparing highly active catalysts.
2. A small amount of silica added to Cu/ZnO-based multicomponent catalysts greatly improved their long-term stabilities in methanol synthesis by suppressing the crystallization of the metal oxides in the catalysts. However, a larger amount of silica added to the catalyst caused a large decrease in the catalyst activity during a short time from the beginning of methanol synthesis. Accordingly, the optimum amount of silica added to the catalyst should be determined.

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