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Copper-Alumina Spinel Catalysts for Steam Reforming of Methanol

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A high activity and stability for steam reforming of methanol were attained with a copper-alumina catalysts prepared by the coprecipitation method, particularly with those composed of a copper-alumina spinel ($CuAl_2O_4$) formed by calcination at relatively high temperatures (773 - 973 K).

Recently, increasing attention has been paid to steam reforming of methanol in relation to the production of highly pure hydrogen for semiconductor and metallurgical industries. Although copper is an excellent catalyst component as to catalytic activity and selectivity,[1,2] this metal has been shown to be of insufficient stability.[3] We wish to report in the present communication that the highly active and thermally stable copper catalyst can be obtained by reduction of $CuAl_2O_4$.

Copper catalysts were prepared by a coprecipitation method using alumina, zinc oxide, and chromia as supports. A copper-containing hydroxide gel was precipitated from a mixed aqueous solution of copper and support-constituent nitrates. Sodium carbonate and ammonia aqueous solutions were used as precipitating agents for alumina or zinc oxide and for chromia, respectively. The resulting precipitate was dried at 383 K and calcined in air at 773 K for 3 h. Steam reforming of methanol was carried out in a continuous flow system with a fixed bed of catalyst at atmospheric pressure. The catalyst was generally reduced in a hydrogen stream at 573 K for 2 h. The CH_3OH/H_2O molar ratio in the feedstock was unity. Product gas compositions were determined by means of a gas chromatography after the volumetric flow rates were measured. Catalytic activity was evaluated as percent conversion of methanol to hydrogen (X_H).

As shown in Fig. 1, copper-alumina possessed a higher activity for hydrogen production than copper-chromia and copper-zinc oxide. A copper-silica catalyst containing 10 wt% of copper was prepared by the kneading method according to Kobayashi et al.[2)] and it showed X_H=12% under the same conditions as shown in Fig. 1. The activity of the copper catalyst prepared by the kneading method was not prominently increased by the increase of copper content. The activity of catalyst prepared by the coprecipitation method showed a maximum at approximately 30 wt% of copper content regardless of the type of supports. The color of copper-chromia and copper-zinc oxide after calcination was dark-brown, while that of copper-alumina below 30 wt% loading of copper was green indicating a formation of $CuAl_2O_4$. On the other hand, copper-alumina above 30 wt% loading showed brown color indicating the presence of CuO. By means of X-ray powder diffraction (XRD), copper-zinc oxide with 30 wt% loading gave sharp reflections of CuO and ZnO, while a broadened reflection of $CuAl_2O_4$ was solely detected in copper-alumina. Therefore, we can suppose that the high activity of copper-alumina is attributable to the highly dispersed copper resulting from reduction of $CuAl_2O_4$. To ascertain that $CuAl_2O_4$ is responsible for the appearance of the high catalytic activity, CuO on the catalyst surface was selectively extracted in ammonia solution. The resulting catalyst regarded as having only $CuAl_2O_4$ possessed high activity, for example X_H as high as 47% over the catalyst having 20 wt% copper under the same condition as those in Fig. 1. Therefore, we conclude that reduction of the spinel

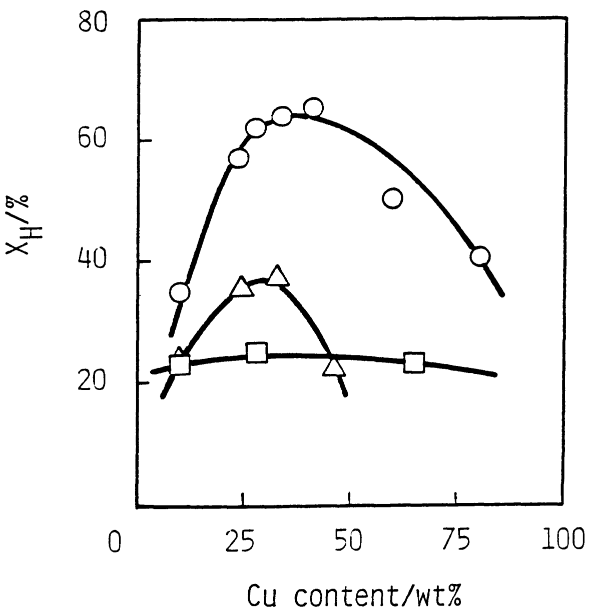

Fig. 1. Effect of Cu content on the activities of various copper catalysts prepared by co-precipitation method. Catalyst: ○,copper-alumina; △,copper-zinc oxide; □,copper-chromia. Reaction temperature, 523 K. W/F, 120 g-cat min mol-CH_3OH^{-1}.

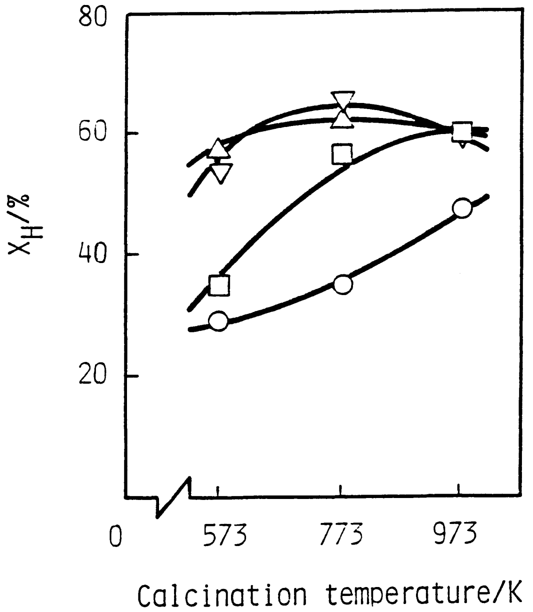

Fig. 2. Effect of calcination temperature on the activities of copper-alumina catalysts. Cu content: ○,9.0 wt%; □,18 wt%; ▽,31 wt%; △,39 wt%. Reaction temperature, 523 K. W/F, 120 g-cat min mol-CH_3OH^{-1}.

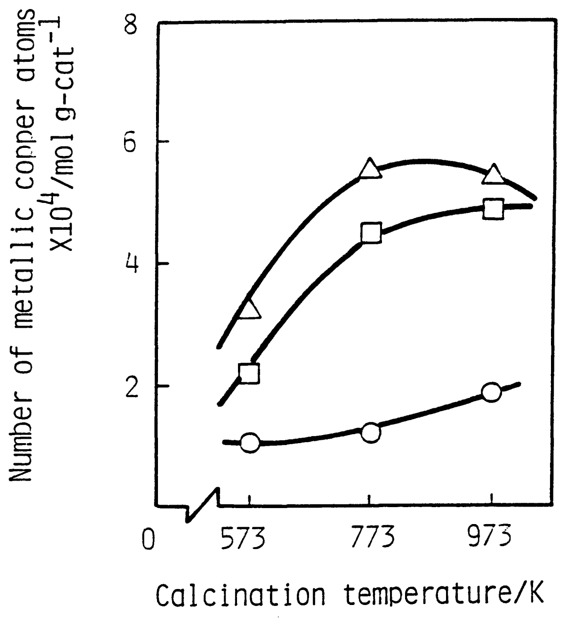

Fig. 3. Effect of calcination temperature on the number of metallic copper atoms on copper-alumina catalysts. Cu content: ○,9.0 wt%; □,18 wt%; △,31 wt%.

effectively gives the active site.

As the spinel structure is generally formed at high temperatures, it is expected that the catalytic activity will depend on the calcination temperaturte. Figure 2 shows the effect of calcination temperature on the activity of copper-alumina. The activity of the catalyst having less than 30 wt% of copper increased with increasing calcination temperature. When the copper content was higher than 30 wt%, however, a maximum catalytic activity was attained by calcination at 773 K. These results are accountable by assuming that the formation of the spinel structure is promoted at higher calcination temperatures leading to high activity, whereas, when copper exsists in excess, CuO covers the surface of the spinel and reduces the activity.

Figure 3 shows the relationship between calcination temperature and the number of metallic copper atoms on the surface, i.e. the active sites,[3-5] determined by a N_2O pulse method.[6,7] The number of copper atoms behaved similarly to the activity shown in Fig. 2. That is to say, the number of copper atoms on the catalyst having less than 30 wt% of copper increased with calcination temperature up to at least 973 K, while the activity of the catalytst having copper in excess gave a maximum at 773 K. These results supports our proposal that formation of the spinel results in the increase of the active site. Furthermore, we confirmed that the life of the $CuAl_2O_4$ catalyst obtained by a high temperature calcination is superior to that of the catalyst composed of CuO: for instance, the catalyst having 9 wt% copper calcined at 973 K showed the initial and steady state activity of X_H=80% at least up to 10 h, whereas the catalyst having 31 wt% copper calcined at 773 K showed the initial activity of X_H=80% which decreased to 70% after 10 h of run.

A small amount of dimethyl ether (DME) was formed as a by-product in a selectivity of less than 0.1% at X_H=80% on these copper-alumina catalysts. The selectivity to DME increased with increasing X_H, although we ascertained that the catalytic activity and the catalyst life were not reduced if DME was intentionally added to this reaction system.

In conclusion, copper-alumina catalysts prepared by the coprecipitation method showed a high activity for steam reforming of methanol probably due to the formation of highly dispersed copper by reduction of $CuAl_2O_4$. The activity of the catalyst containing 9 wt% of copper obtained by calcination at relatively high temperatures was not deteriorated at least in 10 h.

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