Heterogeneous Catalysis

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Cu–Al Spinel Oxide as an Efficient Catalyst for Methanol Steam Reforming**

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Abstract: *Cu–Al spinel oxide, which contains a small portion of the CuO phase, has been successfully used in methanol steam reforming (MSR) without prereduction. The omission of prereduction not only avoids the copper sintering prior to the catalytic reaction, but also slows down the copper-sintering rate in MSR. During this process, the CuO phase can initiate MSR at a lower temperature, and $CuAl_2O_4$ releases active copper gradually. The catalyst CA2.5-900, calcined at 900°C with $n(Al)/n(Cu) = 2.5$, has a higher $CuAl_2O_4$ content, higher BET surface area, and smaller $CuAl_2O_4$ crystal size. Its activity first increases and then decreases during MSR. Furthermore, both fresh and regenerated CA2.5-900 showed better catalytic performance than the commercial Cu–Zn–Al catalyst.*

Copper-based catalysts have been widely used in many fields owing to their low cost and high activity. However, the activity of most copper catalysts gradually declines with time on stream, and one of the main reasons is the thermal sintering of copper particles.[1] Many methods have been applied to delay copper sintering, such as the addition of a second component, the use of an appropriate support, and the improvement of copper dispersion.[2]

Copper-based spinel oxide, in which Cu^{II} is atomically dispersed by other metal oxides, has been used in many reactions, including the water–gas shift, the hydrogenolysis of glycerol, and the steam reforming of dimethyl ether and methanol.[3] Usually, spinel oxides are activated by reduction to form the active copper-metal particles prior to catalytic reactions. With $CuFe_2O_4$ spinel supported on SiO_2, when the reduction temperature was increased from 360 to 600°C, the observed copper-particle size increased from 7.9 to 18.5 nm, which is still smaller than the particle size of the non-spinel catalyst Cu/SiO_2.[4] Cu–Mn spinel oxide prereduced by hydrogen at 250°C generated copper particles of 11 nm and showed higher activity in methanol steam reforming (MSR).[5] $CuFe_2O_4$ spinel, prepared by a space-confined synthesis method, produced nanosized copper (ca. 3.6 nm crystal size) after reduction in H_2 at 300°C and demonstrated enhanced activity.[6] However, theoretical calculations revealed that the 3.6 nm copper crystal contains about 4000 copper atoms,[7] which means that a mass of copper atoms aggregated during the prereduction step. Thus, the agglomeration of copper not only took place during the reaction, but also during the prereduction process. It has been reported that supported CuO catalysts can be used in MSR without prereduction.[8] Similarly, copper-based spinel catalysts ($CuAl_2O_4$, $CuFe_2O_4$, and $CuCr_2O_4$) prepared by the citrate process were applied in MSR without prereduction in our previous study.[9] Cu–Al spinel showed better catalytic performance than the other two catalysts. With the Cu–Al spinel catalyst, the activity first increased and then gradually decreased. This behavior can be explained by a mechanism of gradual release of active copper from spinel oxide during MSR. Furthermore, the release of copper from Cu–Al spinel was also observed in methanol decomposition.[10] However, the catalytic performance of Cu–Al spinel oxide could not meet the commercial requirements, probably owing to its low surface area ($2.2\ m^2 g^{-1}$).[11]

Herein, the Cu–Al spinel catalyst was prepared by a green and simple solid-phase method by the use of copper(II) hydroxide and high-surface-area pseudoboehmite (ca. $349\ m^2 g^{-1}$) as raw materials. An excess amount of pseudoboehmite was added during the preparation to disperse the spinel phase. Hence, Cu–Al spinel oxides with higher surface areas were obtained and applied in MSR, which is an attractive process for hydrogen production.[12] Without prereduction, variation of the Cu–Al spinel catalyst during the catalytic reaction was investigated. Furthermore, the catalytic performance and the regenerability of the Cu–Al spinel catalyst were compared with those of a commercial Cu–Zn–Al catalyst (CZA).

A series of Cu–Al oxide catalysts were prepared and named as follows: The fresh catalyst was named "CA*x*-*T*", in which *x* and *T* indicate the Al/Cu atomic ratio and the calcination temperature, respectively. The sample denoted "CA*x*-*T*-H" indicates the prereduction of CA*x*-*T* with H_2. For the tested catalyst, "*t*" was added to "CA*x*-*T*" to give "CA*x*-*T*-*t*". CA2.5-900 and CZA after MSR were regenerated by calcination in air at 900 and 500°C, respectively. "R" is then used to indicate the regenerated catalyst, for example, "CA2.5-900-R". The catalyst samples and their characterization results are listed in Table 1.

Both the Cu–Al oxides and CZA, without prereduction, could catalyze MSR, as shown in Figure 1. The activity of CA2.0-900 first increased and then decreased with time on stream, whereas the activity of CA2.0-900-H, which was obtained by prereducing CA2.0-900 in H_2 at 300°C, gradually decreased. With CA2.0-500, a similar trend to that of CA2.0-900-H was observed (Figure 1A). Hence, we can conclude that the catalytic performance of CA2.0-900 is far better than

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Table 1: Characteristics of Cu–Al oxides and commercial CZA.

	CA2.0		CA2.5	CA4.0	CA6.0	CZA
T_{cal} [°C]	500	900	900	900	900	500
w(Cu) [%]	35.01	35.01	30.70	22.42	16.49	37.20
$X(CuAl_2O_4)$ [%][a]	0	93.0	91.8	87.0	84.8	0
w(CuO) [%][b]	43.82	3.09	3.17	3.68	3.15	46.56
d_{CuO} [nm][c]	10.2	/	/	/	/	8.1
$d_{CuAl_2O_4}$ [nm][c]	/	30.5	24.2	27.9	27.9	/
$d_{\alpha\text{-}Al_2O_3}$ [nm][c]	/	/	/	34.7	46.6	/
d_{Cu} [nm][d]	21.4	15.7	8.5	14.9	18.3	20.6
S [$m^2 g^{-1}$]	75.0	16.6	33.1	19.1	16.6	34.7

[a] The molar ratio of the $CuAl_2O_4$ phase to total Cu is equal to the H_2-consumption ratio of $CuAl_2O_4/(CuO+CuAl_2O_4)$ in the TPR pattern (see Figure S3). [b] The content of the CuO phase in the catalyst was obtained by the equation $w(CuO) = 79.6/63.6 \times w(Cu) \times (1\text{-}X(CuAl_2O_4))$. [c] The crystallite sizes were calculated by the Scherrer equation from the XRD patterns (see Figure S2). [d] Copper crystallite size in tested catalysts.

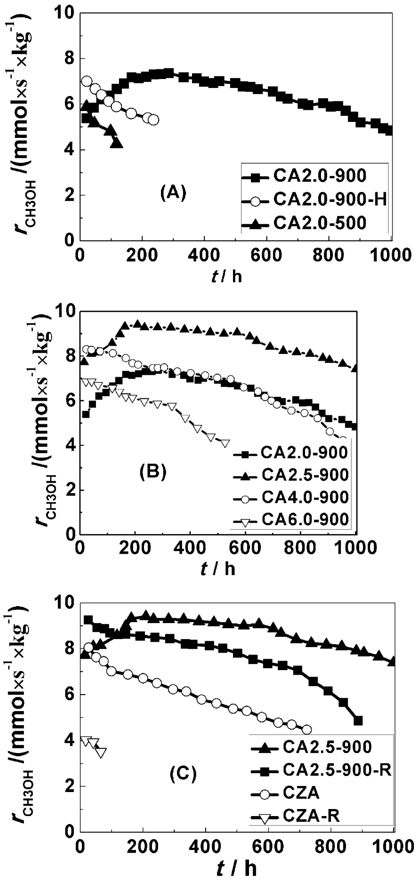

Figure 1. CH_3OH conversion rate in MSR on Cu–Al oxides and CZA.

that of both CA2.0-900-H and CA2.0-500, although the initial activity of CA2.0-900 is lower.

When the Al/Cu atomic ratio was increased from 2.0 to 6.0, the initial CH_3OH conversion rate showed a maximum with $n(Al)/n(Cu) = 4.0$. During MSR, the activity of CA2.5-900 first increased and then decreased, whereas the activities of CA4.0-900 and CA6.0-900 decreased all the time (Figure 1 B).

Of these catalysts, CA2.5-900 showed the best catalytic performance. We therefore compared its activity and regenerability with those of the CZA catalyst. Both fresh and regenerated CA2.5-900 showed better catalytic performance than fresh CZA (Figure 1 C), and the latter could not be renewed after MSR. In summary, the catalytic performance and regenerability of CA2.5-900 is superior to those of CZA, even though the former has a lower total copper content than the latter.

The production rate of the main by-product, CO, showed a similar trend to that for catalytic activity (see Figure S1 in the Supporting Information). The CO production rate on CA2.0-500, CA2.0-900-H, CA6.0-900, and CZA decreased, whereas on CA2.0-900, CA2.5-900, and CA4.0-900, a maximum was reached during MSR.

All samples were characterized by XRD, temperature-programmed reduction with H_2 (H_2-TPR), and BET analysis (Table 1). When the calcination temperature was increased from 500 to 900 °C, most CuO reacted with pseudoboehmite to form high-density $CuAl_2O_4$, thus causing a sharp decrease in the BET surface area. At a fixed calcination temperature of 900 °C, an increase in the Al/Cu atomic ratio from 2.0 to 6.0 resulted in a decrease in the molar content of the $CuAl_2O_4$ phase $X(CuAl_2O_4)$ from 93.0 to 84.8 %, and high-density α-Al_2O_3 formed with higher $n(Al)/n(Cu)$ ratios of 4.0 and 6.0. Thus, a maximum in the surface area and a minimum in the $CuAl_2O_4$ crystallite size at $n(Al)/n(Cu) = 2.5$ were observed. An appropriate excess of high-surface-area pseudoboehmite appears to be beneficial for dispersion of the $CuAl_2O_4$ crystals to provide a high surface area.

After MSR, both CuO and $CuAl_2O_4$ in the catalysts were reduced to Cu metal.[13] The copper crystallite size decreased in order CA2.0-500-t > CZA-R-t > CA6.0-900-t > CA2.0-900-t > CA4.0-900-t > CA2.5-900-R-t (Table 1). In summary, copper sintering was delayed when copper species existed mainly in the form of $CuAl_2O_4$, and the formed catalyst has a higher BET surface area as well as a smaller $CuAl_2O_4$ crystallite size.

As confirmed by XRD data, all catalysts containing the $CuAl_2O_4$ phase also produced σ-Al_2O_3 crystals during MSR. Both $CuAl_2O_4$ and σ-Al_2O_3 had a cubic crystal structure.[14] In the former, Cu atoms occupied the tetrahedral sites and Al atoms were in octahedral sites, whereas in the latter, both sites were occupied by Al atoms. Thus, it was concluded that during MSR copper atoms were released and aggregated, whereas some of the Al atoms transferred from the octahedral site to the tetrahedral site to form σ-Al_2O_3.

To understand the details of the variation of the catalyst during the reaction, we investigated the copper surface area and CO_2 adsorption of catalysts with different degrees of reduction (X_R). The release of copper from the Cu–Al oxide during MSR was simulated by reducing a 30 mg sample in 10 % H_2/Ar at 280 °C, which is lower than the reduction temperature of $CuAl_2O_4$ (300-520 °C) in TPR. When the temperature reached 280 °C, CA2.0-500 had been reduced to a degree of 93.1 %, whereas only 7.8 % of CA2.0-900 was reduced (Figure 2 A). When the temperature was maintained at 280 °C, CA2.0-500 had been completely reduced after 3 h, and the copper surface area decreased sharply. However,

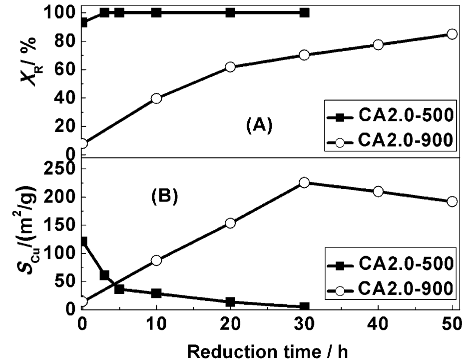

Figure 2. Degree of reduction (A) and copper surface area (B) of Cu–Al oxide catalysts during reduction.

CA2.0-900 was reduced by 84.9% over 50 h, and its copper surface area reached a maximum at 30 h. The above results are in good agreement with the catalytic behavior. Thus, the readily reduced CuO phase provided high activity in the initial period, but the formed active copper was not stable and aggregated readily. Under the same conditions, the gradual release of active copper from the $CuAl_2O_4$ phase resulted in a low copper-sintering rate. Hence, copper release combined with its low sintering led to maximum activity in MSR. Some spinel catalysts, such as CA4.0-900 and CA6.0-900, did not show maximum activities, which may be ascribed to the fact that at the first sampling time the copper-release rate was lower than the sintering rate in these catalysts.

It was hypothesized that the CuO phase in Cu–Al spinel was first reduced during MSR, and that its content, w(CuO), was related to the initial activity. As shown in Table 1 and Figure 1, both w(CuO) and the initial activity showed a maximum at n(Al)/n(Cu) = 4.0.

To investigate the role of the CuO phase in the Cu–Al spinel catalyst during MSR, we treated CA2.5-900 with dilute nitric acid and then characterized it by H_2-TPR (see Figure S2). After acid treatment, the low-temperature reduction peak (186–247 °C) assigned to the CuO phase disappeared. Methanol decomposition was then carried out on an automatic temperature-programmed chemisorption analyzer equipped with a mass spectrometer. As shown in Figure 3, methanol decomposition on CA2.5-900 was initiated at 225 °C, whereas on the acid-treated sample, the initiation temperature was increased to 293 °C. Furthermore, when the reaction temperature was maintained at 240 °C for 3 h, methanol decomposition did not start on acid-treated CA2.5-900 (see Figure S4). Therefore, the presence of a small amount of the CuO phase in Cu–Al spinel catalysts as an initiator can cause MSR to start at a lower temperature.

It is believed that the by-product CO results from the reverse water–gas shift reaction ($CO_2 + H_2 \rightarrow CO + H_2O$).[15] Thus, CO_2 adsorption on samples with different degrees of reduction was measured (Figure 4). Fresh CA2.0-500 showed two peaks of CO_2 desorption, at 65–234 (peak I) and 234–574 °C (peak II). Upon reduction of the catalyst, both peaks showed small changes, which indicated that the CO_2 adsorption was less affected by the release of active copper. On fresh CA2.0-900, CO_2 adsorption was so low that it can be ignored.

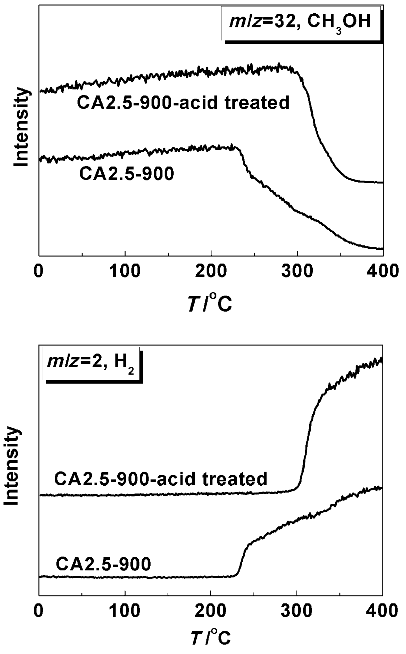

Figure 3. Methanol decomposition on CA2.5-900 and acid-treated CA2.5-900.

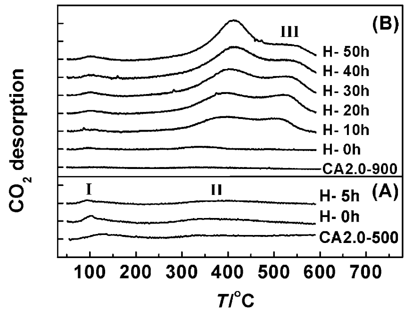

Figure 4. CO_2-TPD profile (temperature-programmed desorption of CO_2) for A) CA2.0-500 and B) CA2.0-900 with different degrees of reduction.

When the degree of reduction was increased, an additional shoulder peak III (483–600 °C) appeared, and the CO_2 adsorption increased significantly. By comparing the above results, we hypothesized that the higher CO_2 adsorption on reduced CA2.0-900 was mainly due to porous Al_2O_3 after the release of Cu from $CuAl_2O_4$. CO selectivity on the Cu–Al spinel catalyst in MSR varied accordingly.

In conclusion, Cu–Al spinel oxide, which contained a small portion of the CuO phase, was successfully used in MSR without prereduction. In this process, the CuO phase initiated methanol transformation at a low temperature, and $CuAl_2O_4$ gradually released active Cu. The omission of prereduction not only avoided copper sintering prior to the catalytic reaction, but also slowed down the copper-sintering rate during the reaction. Moreover, the catalytic performance of the Cu–Al spinel catalyst could be further improved by adding an appropriate excess of Al_2O_3, which was beneficial in increasing the surface area and dispersing $CuAl_2O_4$ crystals.

The catalyst CA2.5-900, which was calcined at 900 °C with $n(\mathrm{Al})/n(\mathrm{Cu}) = 2.5$, had a higher $CuAl_2O_4$ content, higher BET surface area, and smaller $CuAl_2O_4$ crystal size. It showed excellent catalytic performance in MSR without prereduction, and the tested catalyst could be regenerated almost completely by calcination at 900 °C in air. Both the catalytic performance and regenerability of this catalyst were better than that of CZA. This improvement in catalytic performance by the omission of prereduction may be applied in other reactions with copper-based spinel catalysts.

Experimental Section

Cu–Al oxides were prepared by a solid-phase method. Copper hydroxide and pseudoboehmite powders were mixed well and ball milled for 6 h, and then calcined at different temperatures for 3 h in air. The calcined Cu–Al oxides were mixed with graphite (3 wt %) and then tableted, crushed, and sieved (8–14 mesh). The catalyst (ca. 3.0 g) was then loaded into a fixed-bed reactor. Most catalysts were tested without prereduction. When needed, prereduction was carried out by increasing the temperature from 20 to 300 °C at 10 °C min^{-1} and maintaining this temperature for 0.5 h with a H_2 flow of 30 $\mathrm{mL\,min}^{-1}$, followed by cooling to 240 °C. All MSR reactions were performed under the following conditions: 240 °C, 1.0 MPa, $n(\mathrm{CH_3OH})/n(\mathrm{H_2O}) = 1.0$, weight hourly space velocity (WHSV) = 1.75 h^{-1}. The techniques XRD, TPR, BET, N_2O adsorption and CO_2-TPD were used to characterize the catalysts.

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[13] A small amount of the CuO phase in tested catalysts probably resulted from the oxidation of copper metal when the catalysts were exposed to air after MSR.

[14] $CuAl_2O_4$ in the fresh catalyst and σ-Al_2O_3 in the tested catalyst were assigned to $CuAl_2O_4$ (ICSD #24491) and σ-Al_2O_3 (ICSD #69213), respectively.

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