**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 CuAlO₄ releases active copper gradually. The catalyst CA₂5-900, calcined at 900°C with n(Al)/n(Cu) = 2.5, has a higher CuAlO₄ content, higher BET surface area, and smaller CuAlO₄ crystal size. Its activity first increases and then decreases during MSR. Furthermore, both fresh and regenerated CA₂5-900 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 dimethylether and methanol.[3] Usually, spinel oxides are activated by reduction to form the active copper-metal particles prior to catalytic reactions. With CuFe₂O₄ spinel supported on SiO₂, 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 CuO.[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] CuFe₂O₄ spinel, prepared by a space-confined synthesis method, produced nanosized copper (ca. 3.6 nm crystal size) after reduction in H₂ 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 (CuAlO₄, CuFe₂O₄, and CuCr₂O₄) 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 m² 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 m² g⁻¹) as raw materials. An excess amount of pseudo-boehmite 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 “CAₓ-T”, in which x and T indicate the Al/Cu atomic ratio and the calcination temperature, respectively. The sample denoted “CAₓ-T/H” indicates the prereduction of CAₓ-T with H₂. For the tested catalyst, “R” was added to “CAₓ-T” to give “CAₓ-T-R”. CA₂5-900 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, “CA₂5-900-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 CA₂0-900 first increased and then decreased with time on stream, whereas the activity of CA₂0-900-H, which was obtained by prereducing CA₂0-900 in H₂ at 300°C, gradually decreased. With CA₂0-900, a similar trend to that of CA₂0-900-H was observed (Figure 1A). Hence, we can conclude that the catalytic performance of CA₂0-900 is far better than
Table 1: Characteristics of Cu–Al oxides and commercial CZA.

<table>
<thead>
<tr>
<th></th>
<th>CA2.0</th>
<th>CA2.5</th>
<th>CA4.0</th>
<th>CA6.0</th>
<th>CZA</th>
</tr>
</thead>
<tbody>
<tr>
<td>(T_{\text{pr}}, \degree \text{C})</td>
<td>500</td>
<td>900</td>
<td>900</td>
<td>900</td>
<td>900</td>
</tr>
<tr>
<td>(\omega(\text{Cu})) [%]</td>
<td>35.01</td>
<td>35.01</td>
<td>30.70</td>
<td>22.42</td>
<td>16.49</td>
</tr>
<tr>
<td>(X(\text{CuAl}_2\text{O}_4)) [%]</td>
<td>0</td>
<td>93.0</td>
<td>91.8</td>
<td>87.0</td>
<td>84.8</td>
</tr>
<tr>
<td>(\omega(\text{CuO})) [%]</td>
<td>43.82</td>
<td>3.09</td>
<td>3.17</td>
<td>3.68</td>
<td>3.15</td>
</tr>
<tr>
<td>(d_{\text{CuO}}) [nm]</td>
<td>10.2</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>(d_{\text{CuAl}_2\text{O}_4}) [nm]</td>
<td>/</td>
<td>30.5</td>
<td>24.2</td>
<td>27.9</td>
<td>27.9</td>
</tr>
<tr>
<td>(d_{\text{CuAl}_2\text{O}_4}) [nm]</td>
<td>/</td>
<td>/</td>
<td>34.7</td>
<td>46.6</td>
<td>/</td>
</tr>
<tr>
<td>(S) [m² g⁻¹]</td>
<td>75.0</td>
<td>16.6</td>
<td>33.1</td>
<td>19.1</td>
<td>16.6</td>
</tr>
</tbody>
</table>

[a] The molar ratio of the CuAl₂O₄ phase to total Cu is equal to the H₂-consumption ratio of CuAl₂O₄/(CuO+CuAl₂O₄) in the TPR pattern (see Figure S3). [b] The content of the CuO phase in the catalyst was obtained by the equation \(\omega(\text{CuO}) = 79.6/63.6 \times \omega(\text{Cu}) \times (1-X(\text{CuAl}_2\text{O}_4))\). [c] The crystallite sizes were calculated by the Scherrer equation from the XRD patterns (see Figure S2). [d] Copper crystallite size in tested catalysts.

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 1C), 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 H₂ (H₂-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 CuAl₂O₄, 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 CuAl₂O₄ phase \(X(\text{CuAl}_2\text{O}_4)\) from 93.0 to 84.8 %, and high-density α-Al₂O₃ formed with higher \(n(\text{Al})/n(\text{Cu})\) ratios of 4.0 and 6.0. Thus, a maximum in the surface area and a minimum in the CuAl₂O₄ crystallite size at \(n(\text{Al})/n(\text{Cu}) = 2.5\) were observed. An appropriate excess of high-surface-area pseudoboehmite appears to be beneficial for dispersion of the CuAl₂O₄ crystals to provide a high surface area.

After MSR, both CuO and CuAl₂O₄ in the catalysts were reduced to Cu metal. 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 CuAl₂O₄, and the formed catalyst has a higher BET surface area as well as a smaller CuAl₂O₄ crystallite size.

As confirmed by XRD data, all catalysts containing the CuAl₂O₄ phase also produced α-Al₂O₃ crystals during MSR. Both CuAl₂O₄ and α-Al₂O₃ had a cubic crystal structure. 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 sites to the tetrahedral site to form α-Al₂O₃.

To understand the details of the variation of the catalyst during the reaction, we investigated the copper surface area and CO₂ adsorption of catalysts with different degrees of reduction (\(X_{\text{r}}\). The release of copper from the Cu–Al oxide during MSR was simulated by reducing a 30 mg sample in 10% H₂/Ar at 280°C, which is lower than the reduction temperature of CuAl₂O₄ (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 2A). 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,

![Image](Figure 1. CH₃OH conversion rate in MSR on Cu–Al oxides and CZA.)
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 CuAl2O4 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 \( \text{H}_2\text{-TPR} \) (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 (\( \text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O} \)). 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.

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\(_2\)O\(_3\) after the release of Cu from CuAl2O4. 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 CuAl2O4 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\(_2\)O\(_3\), which was beneficial in increasing the surface area and dispersing CuAl2O4 crystals.
The catalyst CA2.5-900, which was calcined at 900°C with $n$(Al)/$n$(Cu) = 2.5, had a higher CuAl2O4 content, higher BET surface area, and smaller CuAl2O4 crystal size. It showed excellent catalytic performance in MSR without pre-reduction, 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 pre-reduction 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. 0.361 nm, $a_0$ = 0.361, $b_0$ = 0.361, $c_0$ = 0.361, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$).

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[7] The number of copper atoms in the copper crystal was calculated according to its unit-cell parameters: $a = 0.361$, $b = 0.361$, $c = 0.361$ nm, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$.


[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] CuAl2O4 in the fresh catalyst and α-Al2O3 in the tested catalyst were assigned to CuAl2O4 (ICSD #24491) and α-Al2O3 (ICSD #69213), respectively.

Communications

Heterogeneous Catalysis

H. Xi,* X. Hou, Y. Liu, S. Qing, Z. Gao* —

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

Reforming reforming: Methanol steam reforming (MSR) was catalyzed by Cu–Al spinel oxide without prereduction. The catalysis is effectively initiated by the CuO phase present in CuAl2O4, which gradually releases active copper. Even the regenerated catalyst (CA2.5-900-R) was more active than the commercial Cu–Zn–Al (CZA) catalyst (see graph).