

Electronic Supplementary Information

Strategic use of CuAlO_2 as a sustained release catalyst for production of hydrogen from methanol steam reforming

1. Experimental methods

1.1 Catalyst preparation

CuAlO_2 were prepared by a simple solid-phase method. Copper (II) hydroxide and pseudo-boehmite powders, with a molar ratio of $\text{Cu/Al}=1$, were mixed well and ball milled. The ball milling cylinder was made from stainless steel, and the total volume was 2 L. The volume ratio of raw material/ball was 4 and the ball milling time was 6 h. After that, the obtained powder was calcined at different temperatures (1000-1200 °C) for 4 h in nitrogen. The samples were denoted as CA-1000, CA-1100 and CA-1200.

1.2 Catalyst regeneration

First, the used catalyst was calcined in Air at 500 °C, then in N_2 at the same temperature to that of fresh catalyst for 0 h. For instance, the regenerated process of CA-1100-t was that the used catalyst was calcined in Air at 500 °C, then in N_2 at 1100 °C for 0 h, and the obtained regenerated sample was denoted as CA-1100-t-R. If the catalyst was calcined at the final temperature for 4h, the obtained sample was denoted as CA-1100-t-R4.

1.3 Catalyst characterization

A nitrogen adsorption system (JW-BK122W) was used to determine the adsorption-desorption isotherm at liquid nitrogen temperature of -196 °C. The Brunauer-Emmett-Teller (BET) approach was employed to determine the specific surface area of the catalysts.

The X-ray diffraction patterns (XRD) were recorded on a Rigaku MiniFlex II desktop X-ray diffractometer operated at 30 kV and 15 mA with $\text{Cu K}\alpha$ radiation source. The measurements were made with a scanning angle (2θ) ranging from 10° to 80° at a scanning rate of 5°/min. The particle sizes of CuAlO_2 were calculated by using Scherrer equation.

Temperature Programmed Reduction (TPR) was carried out on a FINESORB-3010C multi-function adsorption instrument using 0.05 g sample for each run. The catalyst was loaded into a quartz tube and pretreated in Ar at 300 °C for 30 min, then cooled to room temperature (RT). After that H_2 -TPR was started from RT to 1000 °C at a heating rate of 10 °C/min in 15 ml/min of 10% H_2 /Ar. A thermal conductivity detector (TCD) was used to monitor the consumption of H_2 . The total consumption of H_2 was measured by $A_{\text{CuO}}+A_{\text{CuAl}_2\text{O}_4}+2\times A_{\text{CuAlO}_2}$ and marked as H^T .

The releasing of copper from CA-1100 was simulated by reducing a 50 mg sample in 10% H_2 /Ar at 550 °C. ①The catalyst was reduced in 10% H_2 /Ar (15 ml/min) with the temperature increasing from RT to 550 °C, then cooled to RT in 10% H_2 /Ar. ②The partial reduced catalyst was oxidized with 5% N_2O /Ar (15 ml/min) at 50 °C for 20 min. ③The oxidized catalyst was reduced in 10% H_2 /Ar (15 ml/min) with the temperature increasing from RT to 280 °C, and the consumption of H_2 was marked as H^a . ④The reduced catalyst in third step was oxidized with Air

at 300 °C for 30 min. ⑤The oxidized sample was reduced in 10% H₂/Ar (15 ml/min) with the temperature increasing from RT to 550 °C and kept 30 min. The consumption of H₂ below 300 °C was marked as H^b, which was corresponding to the amount of copper releasing in the first step. The step from ① to ⑤ was named as a cycle. The releasing of copper from catalyst was simulated by repeating this step. The degree of reduction and copper surface area were calculated by the following two equations:

$$RD = H^b / H^T * 100\%$$

$$S_{Cu} = 1353 * H^a / H^T (m^2/g-Cu) [1]$$

The high resolution transmission electron microscopy (HRTEM) images of catalysts were obtained by a JEM 2010 microscope operating at 200 kV. The samples were dispersed in ethanol by ultrasonic for 30 min. The obtained suspension liquid was deposited on copper grids coated with amorphous carbon films.

1.4 Catalysts test

Methanol steam reforming was carried out in a 10 mL fixed-bed down-flow reactor. The powder samples mixed with 3 wt% graphite were tableted, crushed and sieved (8-14 mesh). The catalyst (5 g/4 mL) was loaded into the constant temperature section of the reactor. Then the reaction system was purged with N₂, and increased from RT to 300 °C. After that, methanol steam reforming was performed under the following conditions: the feed was 44 wt%CH₃OH+56 wt%H₂O (n_{H₂O}/n_{CH₃OH}=2.26), and the reaction temperature, pressure, weight hourly space velocity (WHSV) were 300 °C, 1.0 MPa, 1.08 h⁻¹ and 2.16 h⁻¹, respectively.

Reaction products were cooled using a condenser with cooling water (16-17 °C). Both liquid and gas products were analyzed with two gas chromatograph (Porapak T column, TCD, H₂ carrier and carbon molecular sieve column, TCD, Ar carrier). Combined with the analytic results, the methanol conversion and CO production rate were calculated.

$$X_{CH_3OH} = (w_1 - w_2) / w_1 * 100\%$$

$$r_{CO} = F_{CH_3OH} * X_{CH_3OH} * S_{CO} / W_{cat}$$

X_{CH₃OH} was the CH₃OH conversion.

w₁ and w₂ were the amounts of feed and residual CH₃OH after MSR.

r_{CO} was the CO production rate in MSR on per kg catalyst.

F_{CH₃OH} was the feed rate of methanol in mmol/s.

S_{CO} was the CO selectivity.

W_{cat} is the weight of catalyst in Kg.

2. Discussion of the active site for MSR

The as synthesized catalyst contains mainly CuAlO₂ with a few amount of CuO and CuAl₂O₄. The valence state of Cu is +1 in CuAlO₂ and it is +2 in both CuO and CuAl₂O₄. With CA-1200, which has the highest Cu⁺, demonstrated low catalytic activity for MSR reaction, indicating Cu⁺ in the CuAlO₂ structure is not active, probably due to the inaccessibility of the lattice Cu⁺ by methanol or water vapor. However, these bonded Cu can be freed by interaction with H₂, generating metal Cu served as the active valence state. Consequently, the activity increased with time on stream because more active Cu metal was released from CuAlO₂. As have pointed out in

our previous papers on CuAl_2O_4 catalyst, the liberated Cu may coalesce into large entities while take the catalytic action [2,3]. The sintering of Cu leads to a decrease of activity, and the gradual release of Cu results in an activity increase. When they reach a point of balance, the activity should not change as show in Fig.1.

As copper metal is the active site, one may expect that the activity should have a close relationship with surface area of the formed copper metal. However, the characterization data did not support the conclusion. The area of Cu in CA-1000-t, CA-1100-t and CA-1200-t, which was characterized by N_2O titration, was 58.8, 34.9 and 31.7 $\text{m}^2/\text{g-Cu}$, respectively. Apparently, the variation of the area of Cu could not well correlated with that of the catalytic activity. The catalytic activity of CA-1100 was highest, but the area of released Cu was not the highest. This phenomenon had also found in the traditional pre-reduced Cu-based catalyst. Therefore, further investigations are needed in order to better elucidate the real nature the active site as well as the reaction mechanism.

Furthermore, it is still not clear whether the newly generated Cu atoms have higher intrinsic activity than those of the agglomerated clusters and nano particles. This is a big challenge for the investigation of the sustained release catalysis.

3. Supporting figures

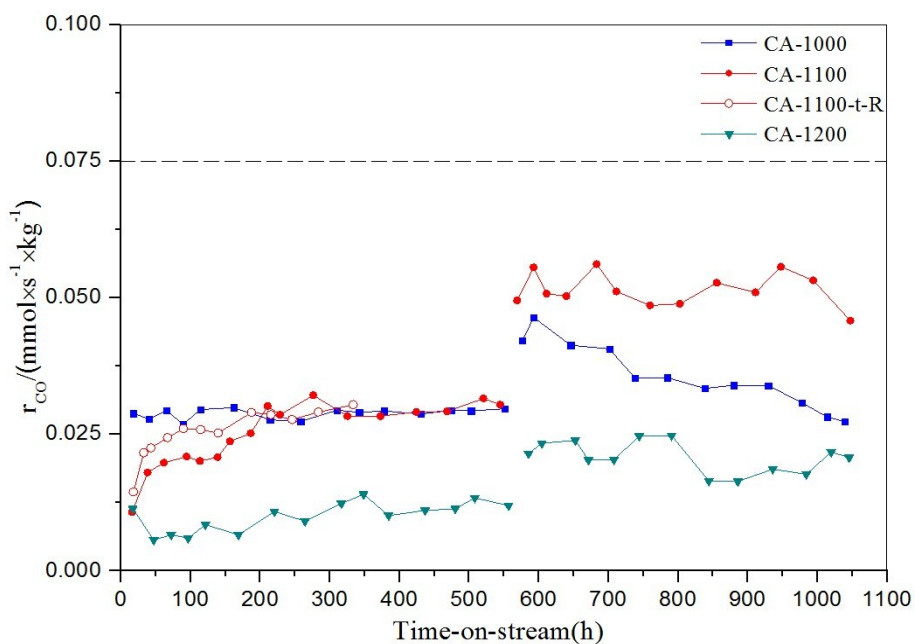


Fig. S1 CO production rate in MSR on CA-T and CA-1100-t-R

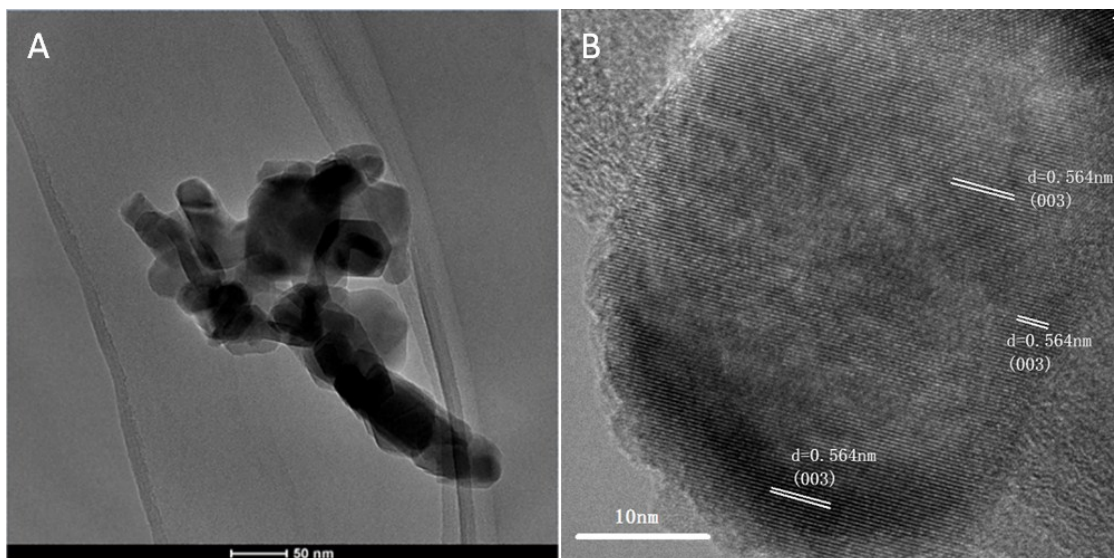


Fig. S2 TEM and HRTEM of CA-1100

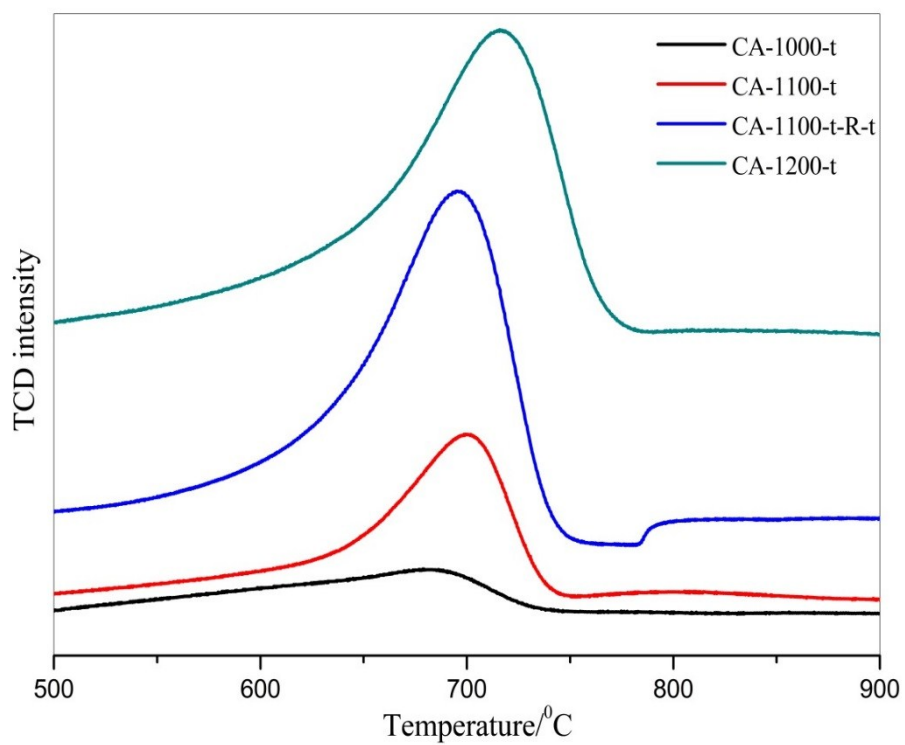


Fig. S3 TPR profiles of tested catalysts

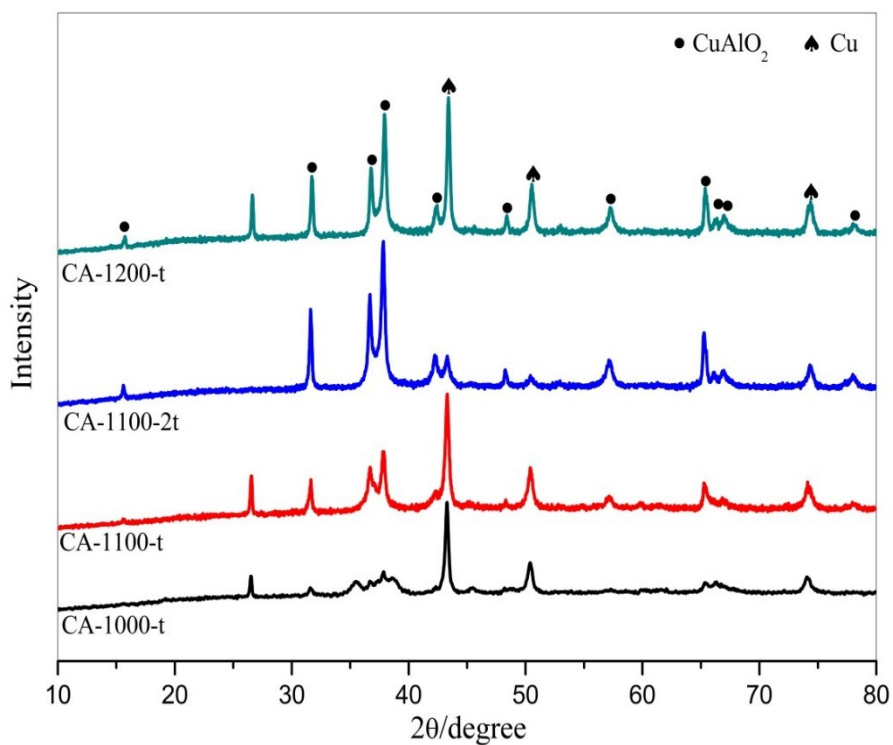


Fig. S4 XRD patterns of tested catalysts

Reference

- [1] Z. L. Yuan, L. N. Wang, J. H. Wang, S. X. Xia, P. Chen, Z. Y. Hou, X. M. Zheng, *Appl. Catal. B: Environ.*, 2011, 101, 431-440.
- [2] Y. J. Liu, S. J. Qing, X. N. Hou, F. J. Qin, X. Wang, Z. X. Gao and H. W. Xiang, *Catal. Sci. Technol.*, 2017, 7, 5069-5078.
- [3] H. J. Xi, X. N. Hou, Y. J. Liu, S. J. Qing and Z. X. Gao, *Angew. Chem. Int. Edit.*, 2014, 53, 11886-11889.