ChemComm

COMMUNICATION

View Article Online
View Journal | View Issue

Cite this: *Chem. Commun.*, 2018, **54**, 12242

Received 13th August 2018,
Accepted 29th September 2018

DOI: 10.1039/c8cc06600k

rsc.li/chemcomm

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

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Using the new method of sustained release catalysis, $CuAlO_2$ demonstrates stable catalytic performance for methanol steam reforming (MSR). Importantly, the used catalyst can be completely restored to its original state by a simple calcination treatment, demonstrating the super regenerability of the catalytic system.

Copper based catalysts have been widely used in many important transformation processes.[1–4] However, they are liable to deactivation, ascribed to the sintering nature of copper,[5–7] and complete regeneration of the deactivated catalysts caused by copper sintering is very difficult. Due to this, the catalytic stability of copper catalysts is still a big challenge for their application and how to improve their stability is an important research direction at the present time. In aiming to improve the catalytic stability of copper based catalysts, much research has been done and the catalytic stability has been greatly enhanced. For example, when using boron oxide to modify the copper catalyst, the dispersion of copper was promoted and thus demonstrating good catalytic activity and stability.[8,9]

Previously, we have shown that the sintering of Cu can be partially avoided by using a copper containing spinel oxide as the catalyst without a pre-reduction treatment.[10,11] In so doing, active Cu metal can be released from the spinel structure under the reaction conditions, and the catalytic performance is obviously improved as compared to the pre-reduction technique. Typically, the conversion rate initially increases through a maximum and then decreases gradually as demonstrated by both methanol steam reforming (MSR)[10] and methanol decomposition.[11] We have also proved that the reaction is initiated by the reaction of methanol with the non-spinel CuO phase, followed by gradual release of Cu from the $CuAl_2O_4$ structure.[10] However, most of the copper in the spinel structure is released in a short time period, giving rise to a gradual decline after the maximum conversion. Therefore, in order to maintain a stable conversion rate, new catalytic materials with suitable reductive properties have been explored.

The crystal structure of delafossite-type $CuAlO_2$, which consists of a layered O–Cu–O dumbbell and a AlO_6 edge sharing layer, belongs to the space group $R\bar{3}m$ and the primitive unit cell is rhombohedral.[12,13] Surprisingly, the Cu(I) in $CuAlO_2$ is very stable and has a very high reduction temperature, starting at 650 °C.[14,15] Based on its reductive properties, the sustained catalytic performance of $CuAlO_2$ for MSR was studied in this research.

$CuAlO_2$ with $n(Cu)/n(Al) = 1$ was prepared by a simple solid-phase method using copper(II) hydroxide and pseudo-boehmite as the raw materials (details in ESI†). The fresh catalyst was named as CA-*T*, in which *T* indicates the calcination temperature. For the tested and regenerated catalyst, t and R were added to give CA-*T*-t and CA-*T*-t-R, respectively. CA-*T*-t-2R represents the second regeneration. The catalyst samples and their characterization results are listed in Table 1.

As shown in Fig. 1, MSR could be catalyzed by CA-*T* without pre-reduction. Both the initial methanol conversion after feeding for about 17 h and the increasing rate of activity were found to be vastly different depending on the catalysts used. With CA-1000, relatively stable methanol conversion was reached within a short time span, while a longer time was needed for CA-1100. With CA-1200 methanol conversion increased continuously within 557 h. When the weight hour space velocity (WHSV) doubled, the methanol conversion decreased accordingly. Among the three catalysts, CA-1100 demonstrated the best catalytic activity and stability.

After testing for 1047 h, CA-1100-t was regenerated. Then the obtained sample (CA-1100-t-R) was tested under the same conditions. As shown in Fig. 1 (hollow circles), the variation in catalytic activity of CA-1100-t-R was similar to that of fresh

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c8cc06600k

Table 1 Characteristics of fresh $CuAlO_2$ and regenerated samples

	CA-1000	CA-1000-t-R	CA-1100	CA-1100-t-R	CA-1100-t-2R[i]	CA-1200	CA-1200-t-R
S [m^2 g^{-1}]	21.3	20.5	14.3	13.9	14.1	12.1	11.7
wt (Cu)[a] [%]	51.38	51.48	51.59	51.62	51.68	51.73	51.76
X_{CuAlO_2}[b] [%]	86.3	89.3	92.7	93.5	95.5	96.7	97.6
d_{CuAlO_2}[c] [nm]	25.4	23.6	27.6	26.3	27.5	28.5	29.8
a[d] [Å]	2.8530	2.8559	2.8565	2.8506	2.8578	2.8546	2.8577
c[d] [Å]	16.959	16.973	16.955	16.900	16.979	16.960	16.969
TOS[e] [h]	1039	—	1047	334	—	1045	—
d_{Cu}[f] [nm]	24.1	—	20.4	17.2	—	27.9	—
SR[g] [%]	84.8	—	62.9	29.1	—	28.5	—
R[h] [% h^{-1}]	0.082	—	0.060	0.087	—	0.027	—

[a] The content of copper was calculated according to the composition of the catalyst. [b] The molar ratio of the $CuAlO_2$ phase to total Cu is equal to the H_2-consumption ratio of 2 × $CuAlO_2$/(CuO + $CuAl_2O_4$ + 2 × $CuAlO_2$) in the TPR pattern (Fig. 2b). [c] The crystallite sizes were calculated by the Scherrer equation from the XRD patterns (Fig. 2a and 4b). [d] Cell parameter of $CuAlO_2$. [e] Reaction times. [f] Copper crystallite sizes in tested catalysts were calculated by the Scherrer equation from the XRD patterns (Fig. S4, ESI). [g] Sustained release ratio of $CuAlO_2$, which was calculated with the H_2-consumption from the TPR of tested catalysts (Fig. S3, ESI). [h] Average sustained release rate of $CuAlO_2$ is equal to the SR/TOS. [i] Regeneration of tested CA-1100-t-R after testing for 334 h.

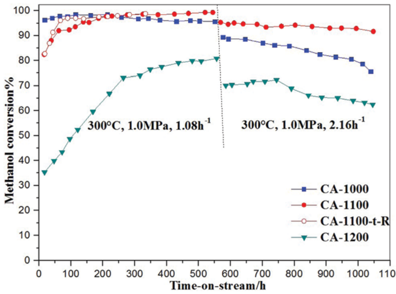

Fig. 1 CH_3OH conversion in MSR on CA-*T* and CA-1100-t-R at 300 °C, 1.0 MPa.

CA-1100, indicating that the tested catalyst could be almost completely regenerated.

It should be mentioned that the production of the main by-product, CO, varied similarly with catalytic activity (Fig. S1, ESI†) within 557 h. When the WHSV was increased, the production rate of CO increased. The production rates of CO were all below 0.075 mmol s^{-1} kg-cat^{-1} within the tested time on the three catalysts and the regenerated sample.

All samples were characterized by XRD, H_2-TPR and BET analysis, and the results are shown in Table 1 and Fig. 2–4. As shown in Fig. 2a, the main phase composition of CA-1000, CA-1100 and CA-1200 was $CuAlO_2$ (PDF 75-2356).[14–17] Based on the XRD data, the cell parameter of $CuAlO_2$ was calculated, listed in Table 1. The calculated data was consistent with the standard values, which were a = 2.8584 Å and c = 16.958 Å.[12,17,18] The phase composition was further affirmed by the HRTEM results (Fig. S2, ESI†). In the HRTEM image of CA-1100, (0 0 3) planes with a d-spacing of 0.564 nm were identified.[17]

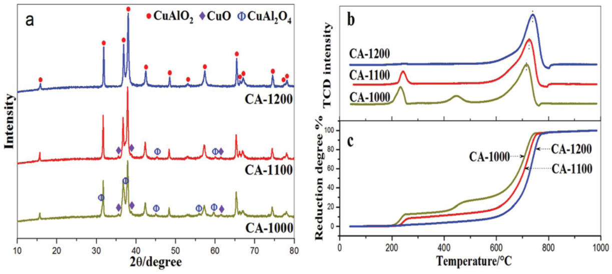

Fig. 2 XRD patterns (a), TPR profiles (b) and reduction degree (c) of fresh CA-*T* catalysts.

The two catalysts synthesized at 1000 °C and 1100 °C also revealed characteristic diffraction peaks of CuO and $CuAl_2O_4$ phases,[19,20] while CA-1200 showed a pure $CuAlO_2$ phase. With increasing calcination temperature, the diffraction peak intensity of $CuAlO_2$ increased, which might result from aggregation of $CuAlO_2$ at high temperature, thus leading to a larger crystal size and small specific surface area (Table 1).

The H_2-TPR profiles in Fig. 2b present three reduction peaks, ascribed to reduction of CuO (180–300 °C), $CuAl_2O_4$ (300–520 °C)[20] and $CuAlO_2$ (520–800 °C), respectively. The onset reduction temperature of $CuAlO_2$ was obviously lower than that reported in the literature, starting at 650 °C.[14,15] This difference may be ascribed to different synthetic raw materials, methods and conditions, leading to different reduction performances.

As expected, the reduction peak areas of CuO and $CuAl_2O_4$ decreased with increasing calcination temperature, while that of $CuAlO_2$ increased (Table 1, X_{CuAlO_2}). It should be noted that the reduction peak of $CuAlO_2$ shifted to high temperatures with increasing calcination temperature, probably due to larger crystal sizes. The reducibility of the three fresh samples is further shown in Fig. 2c, which shows the reduction degree *versus* temperature by integration of H_2-TPR (Fig. 2b). It could be obviously found that the reduction of CA-*T* increased in difficulty in the order CA-1000 < CA-1100 < CA-1200. At 300 °C the reduction degree of CA-1000, CA-1100 and CA-1200 was 12.6%, 9.1% and 1.4%, respectively. This order was consistent with that of the initial activity of CA-*T* (Fig. 1), which supports our view point that copper metal is the active site [details in ESI†].

It was expected that the characteristics of the reduction behaviour could be used to estimate the degree of release of Cu during MSR. As such, it was speculated the release rate decreased in the order CA-1000 > CA-1100 > CA-1200. This was proved by the H_2-TPR characterization data of the tested catalysts (Fig. S3, ESI†), which gave rise to a sustained release

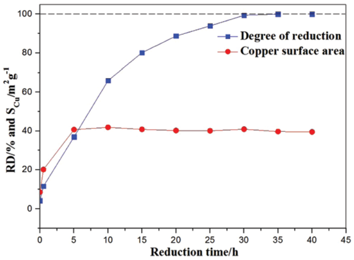

Fig. 3 Degree of reduction and copper surface area of CA-1100 at 550 °C.

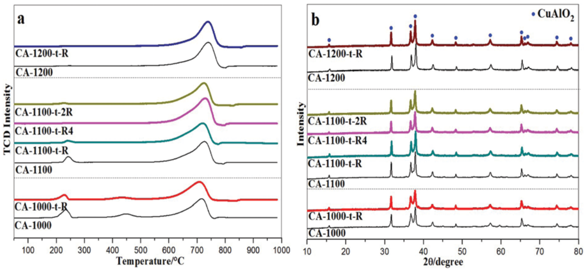

Fig. 4 TPR profiles (a) and XRD patterns (b) of fresh and regenerated catalysts.

ratio of $CuAlO_2$ of 84.8% (1039 h) for CA-1000, 62.9% (1047 h) for CA-1100 and 28.5% (1045 h) for CA-1200 (Table 1). Compared with the above results, the release ratio of $CuAl_2O_4$ reached 88% after testing for 300 h at 255 °C.[20] Hence, it could be said that the release rate of Cu from $CuAlO_2$ was drastically lower than that from $CuAl_2O_4$.

The average release rate of Cu was calculated to be 0.082, 0.060 and 0.027% h^{-1} for CA-1000, CA-1100 and CA-1200, respectively (Table 1). These data demonstrate that the release rate was seriously affected by the synthetic temperature.

The average release rate for the regenerated CA-1100-t-R catalyst after testing in MSR for 334 h was 0.087% h^{-1}, which was obviously higher than that of CA-1100 tested for 1047 h. This result showed that the release rate would become slower with time-on-stream. In order to prove this conclusion, the release of copper from CA-1100 was simulated by reducing a 50 mg sample in 10% H_2/Ar at a constant temperature of 550 °C. As can be deduced from Fig. 3, with increasing reduction time, the rate of copper release from CA-1100 was fast within 10 h, and then became slower and slower. Nonetheless, the measured copper surface area remained almost unchanged after 5 h, which was in good agreement with the relatively stable activity shown in Fig. 1. These results strongly suggest copper sintering and the coalescence of Cu might become slower with time-on-stream since less Cu is released. Interestingly, when Cu was completely reduced in CA-1100 at 30 h, and even sintered for a prolonged time, the observed copper surface area almost remained unchanged, indicating further sintering of copper could be ignored even at 550 °C.

Generally, the sintering likelihood can be indicated by the Tamman temperature of a metal.[21] Copper metal has a pretty low Tamman temperature of 174.6 °C,[22,23] so copper based catalysts have to be used at relatively low temperatures, usually no higher than 300 °C as suggested by previous reseachers.[5,6] The stable Cu surface area observed from 30–40 h indicated no further sintering of Cu after complete release from $CuAlO_2$. Thus, we think that the resulting structure, which was produced by the release of copper from $CuAlO_2$, had a good effect in stabilizing the copper nanoparticles.

Using the as-synthesized $CuAlO_2$ as the catalyst, Cu metal could be generated *in situ* by gradual release from the $CuAlO_2$ lattice, and the released Cu might coalesce into large particles (Table 1). When the release rate was greater than the sintering rate, the catalytic activity presented an increasing trend. When the activation and deactivation reached a state of balance, the catalytic activity became relatively stable. As shown above, CA-1100 demonstrated the best catalytic stability for MSR, indicating that the release rate and deactivation rate matched well under the reaction conditions. Based on this, it was suggested that the catalytic stability of CA-1000 and CA-1200 could also be enhanced by adopting suitable reaction parameters.

In order to obtain more information on restoring of the tested catalysts, all tested samples were re-calcined and characterized by TPR and XRD. The CA-1100-t sample, tested for 1047 h in MSR, was treated at 1100 °C for 0 and 4 h, giving CA-1100-t-R and CA-1100-t-R4. The TPR profiles of the two regenerated samples were similar to that of fresh CA-1100 (Fig. 4a). The molar ratios of $CuAlO_2$ were 93.5% (CA-1100-t-R) and 96.6% (CA-1100-t-R4), which were higher than that of fresh CA-1100 (92.7%). These data indicate that the $CuAlO_2$ phase formed more easily with the tested catalyst. The TPR profile of CA-1100-t-2R, which is the regenerated sample of the tested CA-1100-t-R after 334 h, was similar to that of fresh CA-1100 catalyst (Fig. 4a), indicating that the twice used catalyst could also be regenerated. Similar results were obtained by regenerating CA-1000-t and CA-1200-t (Table 1 and Fig. 4a). The regenerability of all the test samples was further confirmed by XRD characterization, which showed identical diffraction patterns to that of the fresh catalysts (Fig. 4b). Since the release degree after testing in MSR varied from 28.5% to 84.8% for different catalysts, it could be inferred that within the sustained release degree of 84.8%, the used catalysts can be completely regenerated.

As is well known in the discipline of catalysis, the deactivation of catalysts due to reasons such as coking, poisoning and sintering of the active metal cannot be avoided, thus leading to limited catalyst life. Consequently, the topic of regeneration of a used catalyst is essentially important. Depending on the type of metal, some spent catalysts can be partially or fully regenerated for secondary use.[7,24] However, for Cu-based catalysts, the effective regeneration of used catalyst has seemed too difficult to tackle. If the deactivation of a copper based catalyst was only caused by coking, the deactivated catalyst could be regenerated. Wu-Hsun Cheng observed slow deactivation of a Cu/Cr catalyst in methanol decomposition, and the deactivated catalyst could be completely restored by treatment in an O_2 containing atmosphere followed by reduction in H_2. They also found the crystallite size of active metallic Cu remained unchanged during deactivation and after regeneration, thus they concluded that the deactivation was caused by carbonaceous deposits.[25] Similarly, Yang *et al.* also found that the activity of a 7Cu@mSiO_2 core–shell catalyst for the dehydrogenation of methanol into methyl formate could be nearly recovered after regeneration in air. They suggested that the deactivation is probably caused by deposition of carbonaceous material on the surface, not agglomeration/growth of Cu NPs. The latter view was supported by almost the same size of Cu NPs in fresh, spent and regenerated samples.[26] However, a close check of the above two reports revealed the regenerated catalyst varied somewhat, as could be derived from the testing and characterization data. For example, the selectivity to methyl formate decreased with the regenerated 7Cu@mSiO_2 catalyst, suggesting the core–shell catalyst could not be fully regenerated even after testing for about 140 h.

When the sintering of copper contributed to deactivation, the regeneration of sintered copper became very difficult. Twigg *et al.*[6] pointed out that any regeneration of the catalyst following deactivation mainly caused by the sintering would require the formation of small copper crystallites, at least approximately the same size as those in freshly reduced catalysts. According to Twigg's report, the complete regeneration of a sintered copper catalyst was achieved by Lee *et al.* on a laboratory scale, but details were not given.

For the sintered copper catalyst, recovery of the copper and re-preparation is one method for regeneration. Yin *et al.*[27] reported that the activity of a deactivated catalyst increased to some extent by washing with H_2O, CO, CO_2, H_2, NH_3 and H_2O_2, or with CO_2 and ethyl ether in super-critical fluid conditions. Only by dissolving the deactivated catalyst with HNO_3 followed by a re-preparation method could the activity approach that of fresh catalyst.

As reported in our previous study,[10] the initial activity of used Cu–Al spinel oxide catalyst could be recovered by regeneration in air at 900 °C, but the variation trend of activity became worse as compared to that of fresh catalyst, indicating the tested Cu–Al spinel oxide catalyst could not be completely regenerated.

In this study, the results showed that although copper was sintered to large particles in the used $CuAlO_2$ catalyst (Table 1), it could be completely regenerated by calcining the used catalyst in air at 500 °C, then in N_2 at the same temperature as that of fresh catalyst. The reduction performance, phase composition and catalytic performance were nearly identical with that of fresh catalyst. Obviously, the regeneration process is somewhat like the above mentioned re-preparation method, but no additional chemical reagents were required.

In conclusion, delafossite-type $CuAlO_2$ was synthesized by a simple solid-phase method and could serve as an efficient sustained release catalyst in MSR without pre-reduction treatment. Under the tested reaction conditions, the best catalytic performance was obtained with the CA-1100 catalyst, showing stable catalytic activity after the initial increase. After testing for about 1047 h, the used catalyst with 62.9% of Cu released from the crystal lattice could be fully regenerated in milder conditions than those for the synthesis of fresh catalyst, revealing nearly identical catalytic behaviour. The findings of this contribution provide a new approach to deal with the copper sintering problem, and might be useful for the development of a catalyst system with super regeneration abilities.

This work is supported by the National Natural Science Foundation of China (21503254, 21673270, and 21763018).

Conflicts of interest

There are no conflicts to declare.

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