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Highlights

- High efficient copper-based catalyst was prepared with ordered mesoporous silica as support precursor.
- 2. Appropriate pH value of the solution can ensure the high dispersion of copper species.
- 3. The presence of mesoporous structure enhanced the formation of copper phyllosilicate.
- 4. 20Cu/OMS presented excellent catalytic performance in dimethyl oxalate hydrogenation.

Structure evolution of mesoporous silica supported copper catalyst for dimethyl oxalate hydrogenation

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ABSTRACT:

A modified ammonia evaporation method with an ordered mesoporous silica as the precursor of the support was applied to prepare the well dispersed copper-based catalysts. Appropriate amount of ammonia was used during the aging stage to prevent the destruction of the ordered mesoporous structure, which can ensure the homogeneous pre-distribution of the copper precursor $([Cu(NH_3)_4]^{2+})$ in the mesopores. Then the formation of copper phyllosilicate or surface Cu-O-Si species can be prompted during the ammonia evaporation stage, resulting in large surface areas of both Cu⁰ and Cu⁺ species in the final catalysts. It was also revealed that the formation of copper phyllosilicate led to the destruction of mesoporous silica structure in the ammonia evaporation stage especially at the higher copper loading. The catalysts with various copper loading were systematically characterized and applied in the hydrogenation of dimethyl oxalate to ethylene glycol (EG). An excellent low-temperature catalytic performance and stability were achieved on 20Cu/OMS with EG selectivity of 98.2% at 453K, due to the superior surface areas of both Cu^0 and $Cu^{\scriptscriptstyle +}\!,$ as well as the highest ratio of $Cu^{\scriptscriptstyle +}\!/\,(Cu^0{+}Cu^{+}).$

Keywords: copper phyllosilicate, mesoporous silica, hydrogenation, copper catalyst

Introduction:

Ethylene Glycol (EG) is an important chemical product, which has been versatilely applied in the manufacturing of polyester, lubricant and antifreeze [1, 2]. Traditionally, EG is industrially produced by the direct hydration of ethylene oxide. Nevertheless, the shrinking of the fossil-fuel resource and the sustained increasing of demand of EG hinder its wide application. The indirect route for the production of EG from syngas via dimethyl oxalate (DMO) is one of the most attractive approach owing to its advantages in economy and environmental benign feature [3-6]. This route includes two main steps: the oxidative coupling of CO to DMO and then the hydrogenation of DMO to EG. Plentiful works have been involved in the homogeneous hydrogenation of oxalate upon ruthenium-based homogeneous catalysts [7, 8]. However, the lower selectivity and the difficulties in the products separation limited its practical applications.

Due to the excellent activity in the hydrogenation of C=O group and lower ability to dissociative adsorption of the C-C bonds, copper-based catalysts have been applied in the hydrogenation of DMO [9, 10]. Although CuCr catalysts show reasonable performance [11], the toxicity of the chromium restricts its application. Accordingly, increasing research focused on Cr-free Cu-based catalysts with various supports, such as SiO₂, Al₂O₃, ZnO, and La₂O₃ [12, 13]. Strong acid sites of the support would lead to the intramolecular dehydration of EG to ethanol, and strong basic sites would promote the formation of 1, 2-butanediol (1, 2-BDO) by Guerbet reaction between EG or DMO and ethanol [14, 15]. Up to now, the Cu/SiO₂ catalysts

showed the superior performances due to the neutral properties of SiO₂ and the suitable interaction between the copper species and silica. Various method, including impregnation [16], sol–gel [17], deposition precipitation [18], ion-exchange [19] and ammonia evaporation (AE) method [20] have been applied to prepare copper-based catalysts for the hydrogenation of DMO. Among these preparation methods, the AE method was found to be an efficient method and the as-prepared catalyst showed higher activity in the hydrogenation reactions.

It is well known that the hydrogenation of DMO involved three main reactions: first the hydrogenation of DMO to methyl glycolate (MG), then the further hydrogenation of MG to EG, and the deep hydrogenation of EG to ethanol. (Equation 1-3)

$$CH_{3}OOCCOOCH_{3} + 2H_{2} \rightarrow CH_{3}OOCCH_{2}OH + CH_{3}OH$$
(1)

$$CH_{3}OOCCH_{2}OH + 2H_{2} \rightarrow HOCH_{2}CH_{2}OH + CH_{3}OH$$
(2)

$$HOCH_2CH_2OH + H_2 \rightarrow CH_3CH_2OH + H_2O$$
(3)

Raising temperature benefits the further hydrogenation of MG to EG, while the copper species would irreversibly deactivate due to the particle agglomeration under high temperature. Moreover, the Guerbet reaction can occur easily at high temperature with the formation of 1, 2-BDO byproduct, which is difficult to be separated from EG. As reported in the earlier literatures, temperature around 473K is favored for the hydrogenation of DMO to EG [5, 16, 19]. The preparation of catalyst with perfect hydrogenation performance at lower temperature is still a challenge.

Mesoporous materials have drawn much attention in many fields of chemistry

since the successful synthesis of the M41S materials [21]. The ordered mesoporous materials are used as the catalyst support, due to its high specific surface area and pore volume, regular structure, uniform pore size distribution, and excellent thermal stability [22]. Immobilization of copper species into ordered mesoporous materials would improve copper dispersion and promote the catalytic performance in DMO hydrogenation. Yin et al [16] reported HMS as support could promote the uniform dispersion of copper species. Guo et al [18] reported Cu/SBA-15 catalyst with ultra-high copper loading had high dispersion and small nanoparticle size. Ma et al [20] identified that copper could be well incorporated into MCM-41 through the AE method and Cu/MCM-41 showed high dispersion and excellent catalytic performance in DMO hydrogenation. However, although it is crucial important in designing more efficient catalyst, the structure effect of these mesoporous materials on the formation of the final catalyst has not yet revealed up to now.

In this work, series of ordered mesoporous silica (OMS) were synthesized and used for the preparation of Cu/OMS by a modified AE method under weaker alkaline environment. The structure evolution of the ordered mesoporous structure at different stage during the preparation process was systematically study. The structural affect on the dispersion and formation of copper species were explored. The catalytic performance of the Cu/OMS was examined in the low-temperature hydrogenation of DMO to EG, and the structure-activity relationship was revealed.

2. Experimental

2.1 Catalyst preparation

Ordered Mesoporous Silica (OMS): tetraethyl orthosilicate (TEOS), cetyltrimethylammonium bromide (CTAB), water and ammonia aqueous were mixed at room temperature in a ratio of 1:0.2:160:1.5 to obtain a homogeneous mixture. Then the mixture was stirred continuously until turning into a white gel. The white gel was loaded into a PTFE-lined stainless steel autoclave and heated at 373K for 48h. After cooling to room-temperature, the products were separated by filtering, washed with deionized water, and dried in air at 373K for 3h. The resulting solid was calcined in air by heating at a rate of 2K/min to 823K and then maintained at this temperature for 6 h.

Cu/OMS: Cu/OMS catalysts were prepared by the AE method described as follows: a certain amount of Cu(NO₃)₂·3H₂O was dissolved in deionized water, and then 25 wt% ammonia aqueous was added and stirred for 0.5 h at 303 K, followed by the addition of ordered mesoporous silica powder and stirring for 4 h with the initial pH value of 10. This process was named aging stage. The suspension was heated from 303 to 353 K to remove ammonia. The temperature was kept at 353 K about 2 h until the pH value of the suspension decreased to 6-7. This process is called evaporation stage. The filtrate was washed with deionized water and then dried at 373 K overnight. Finally, the resulting solid was calcined at 673 K in air for 4 h. The catalysts were denoted as xCu/OMS. The x represents the weight percentage of copper in the catalyst.

During the aging and evaporation process for the preparation of 20Cu/OMS catalyst, sampling of the mixture was conducted at different time for examination.

The samples were denoted as 20Cu-AGE-y and 20Cu-EVA-z. Both y and z mean treatment time (h).

20Cu/SiO₂: About 15.4 g Cu(NO₃)₂·3H₂O was dissolved in deionized water, and then 52 mL ammonia aqueous solution (25 wt%) was added and stirred for 0.5 h at room temperature. Then, 45 mL silica sol (30 wt%) was added and stirred for 4 h. The suspension was heated to 353 K to evaporate ammonia until the pH value of the suspension decreased to 6-7. The precipitate was filtrated and washed with deionized water and then dried at 373 K overnight. The resulting solid was finally calcined at 673 K for 4 h.

2.2 Catalyst Characterization

Textural properties were measured by the method of nitrogen adsorption at 77 K using a Micromeritics Tristar II 3000 analyzer instrument. The sample was deaerated at 573 K for 3 h in vacuum before analysis. Mesoporous surface areas were calculated from desorption isotherms through the method of Brunauer–Emmett–Teller (BET). And pore size distribution was calculated by the method of Barrett–Joyner–Halenda (BJH) from desorption branches of the adsorption isotherms.

The actual copper loading in the catalysts was determined by the inductively coupled plasma optical emission spectrometry (ICP-OES). The sample was dissolved in the HF solution, neutralized with HBO₃, and diluted with water before analysis.

Transmission electron microscopy (TEM) images were obtained with a Philips TECNAI G2 F20 system electron microscope equipped with a field emission gun. The samples powders were scattered in ethanol solution by ultrasonic. The resultant

was dropped and dried on copper grid-supported transparent carbon foil. The particle size distributions of copper were obtained by counting more than 80 nanoparticles for all the catalysts.

X-ray powder diffraction (XRD) measurement was carried out by Rigaku C/max-2500 diffraction meter using the graphite filtered Cu K α radiation ($\lambda = 1.5406$ Å) at room temperature. Data were collected by scanning from $2\theta = 10^{\circ}$ to $2\theta = 90^{\circ}$ at a rate of 8°/min. To avoid the phase transformation for the reduced samples, catalysts were carefully collected under hydrogen atmosphere and sealed before XRD analysis. The Scherrer equation was used to calculate the particle size of the copper species.

Fourier Transform infrared spectra (FT-IR) were carried out on a Nicolet 6700 spectrometer. The catalysts were disked with KBr and placed into sample holder. The spectra region was recorded from 4000 to 400 cm⁻¹ by averaging 32 scans with resolution ratio of 4 cm⁻¹.

Temperature-programmed reduction (TPR) was carried out on a Micromeritics Autochem II 2920 equipped with a thermal conductivity detector (TCD). The samples of about 50mg were placed into quartz tubes and dried in Ar atmosphere at 393K for 1h. The samples were then heated in 10%H₂/Ar to 1073K by the heating rate of 10K/min. The TCD was employed to quantify the amount of hydrogen consumption during this process.

The specific surface area of metallic copper was measured by N_2O using the pulse titration method [23]. 50 mg of sample was reduced in 10% H₂/Ar at 573 K for 2 h and then cooled to 363 K. The consumed H₂ was calculated and denoted as A1.

Then 15% N₂O/He was introduced at a rate of 30 mL/min for 1h. During this process, surface metallic Cu atoms were completely oxidized to Cu₂O. Then the surface Cu₂O was reduced by hydrogen pulse to metallic Cu. The consumed H₂ in this step was denoted as A2. The consumed amount of hydrogen was obtained by Micromeritics Autochem II 2920 apparatus with a TCD. Then the surface metallic Cu areas of sample were calculated with 1.46×10^{19} Cu atoms per square meter [24]. All the reactions in these processes were described by following equations:

$$CuO + H_2 \rightarrow Cu + H_2O; \quad 2CuO + H_2 \rightarrow Cu_2O + H_2O$$
(1)

$$2Cu + N_2O \rightarrow Cu_2O + N_2 \tag{2}$$

$$Cu_2O + H_2 \rightarrow 2Cu + H_2O \tag{3}$$

The dispersion of metallic copper was calculated by follow equation:

$$D = 2A_2 / A_1 \times 100\%$$
 (4)

X-ray photoelectron spectra (XPS) and Auger electron spectroscopy (XAES) were carried out to analyze copper species on a PHI 1600 ESCA instrument (PE Company) equipped with an Al K α X-ray source (hv = 1486.6 eV). Before testing, the samples were reduced at 573 K under a flow of H₂ for 4 h, and cooled to room temperature. At last, the samples were transferred into glass bottle without air.

2.3 Catalyst activity tests

The gas-phase hydrogenation of DMO to EG was performed in a stainless steel fixed-bed tubular reactor with an internal diameter of 8 mm. The catalyst sample of 0.4 g (40-60 mesh) was placed in the middle of the reactor tube with a height of about 35 mm. The catalyst was reduced in hydrogen atmosphere at 573 K for 4 h under 2.5 MPa, and then cooled to the desired reaction temperature (453K). Then the reactant

(10 wt % DMO (99.9% purity) in methanol (AR purity) solution) was injected continuously through a high-pressure pump (Lab Alliance Series II Pump). The reactions were performed at 453K and system pressure of 2.5MPa. The molar ratio of H_2 /DMO was 80/1 and the weight hourly space velocity (WHSV) of DMO was changed from 0.2 to 2.0 h⁻¹.

The reaction products were analyzed by a gas chromatograph (Agilent Micro GC 6820). This gas chromatograph has an HP-INNOWAX capillary column (Hewlett–Packard Company, 30 m \times 0.32 mm \times 0.50 µm) equipped with a flame ionization detector (FID). The main by-products included MG, ethanol and 1, 2-BDO. Four to six separate samples under the same experiment conditions were taken and analyzed by GC to ensure repeatability. The results were obtained by averaging the experimental data for each point, and the uncertainties were within 3%.

3. Results

3.1 Textural Properties of Cu/OMS

The physicochemical properties of the ordered mesoporous silica and Cu/OMS catalysts with different copper loading are listed in Table 1. The ordered mesoporous silica has a BET surface area of 1019 m²/g and pore volume of 1.10 cm³/g ,which are much higher than those of HMS and MCM-41 reported in previous literatures [16, 20], implying the presence of more abundant pore structure in the as-prepared OMS. All of the actual copper contents in different samples are close to their desired value, indicating the complete precipitation of copper species. While the uploading of copper species cause tremendous changes to the physical properties of OMS. The specific

surface area of the catalyst shows a big decrease compared to that of OMS, probably due to the blockage and destruction of the ordered mesoporous structure during the preparation process. Interestingly, the specific surface area of the catalyst rise up from 394 to 574 m²/g with the increase of copper loading. Meanwhile, the pore volume and diameter gradually increase as well. These changes could be assigned to the generation of more copper phyllosilicate in the catalyst with the increasing copper loading [25, 26].

The N_2 adsorption-desorption isotherms are illustrated in Fig. 1(A). The adsorption curve of the support is very similar to its desorption curve, suggesting the narrow and uniform pore distribution in the support [20]. The five copper containing catalysts present Langmuir type IV isotherms with a H1-type hysteresis loop [27], showing the typical mesoporous structure with 2-dimensional cylindrical channels of the catalysts. As shown in Fig. 1(B), copper loading has a great impact on the pore-size distribution. The average pore diameter rises with the increase of copper loading, indicating the expansion of some mesopores or the destruction of some mesopores followed by the formation of accumulated pores [17]. During the preparation, the copper precursor (copper tetraammine complex, $[Cu(NH_3)_4]^{2+}$) could react with ordered mesoporous silica to form copper phyllosilicate which has a lamellar structure [10, 28]. When copper was loaded on the support, pore-size distributions changed from monomodal to bimodal with two ranges of pores, one estimated at 2.4 nm and the other at around 3.8 nm. Further increasing the copper loading resulted in the emergence of another pores at around 6.1nm. The 10Cu/OMS

shows highest peak intensity at about 2.4nm, however, this peak disappears with the increase of copper loading. This structure change might be attributed to the blockage of initial ordered mesopores by copper species, and the ordered mesopores were gradually consumed and eventually disappeared with the increment of copper loading. The pores around 3.8 nm and 6.1 nm should belong to the accumulated pores resulted from the destruction of the ordered structure in the alkaline environment. The formation of more tube and lamellar structure of copper phyllosilicate lead to the augment of the accumulated pores, which could be further proved in the following TEM results.

Copper dispersion and surface area of the various catalysts were measured by N_2O titration. As showed in Table 1, the Cu dispersion declines with the increase of copper loading, while the metallic copper surface area gives a volcano variation trend and maximizes at the copper loading of 20%. This could be attributed to the agglomeration of the metallic copper when the copper exceeds the optimum amount that the ordered mesoporous silica could burden.

3.2 TEM images

Fig. 2 shows the TEM images of calcined catalysts and the support. The support exhibits a long-range ordered mesoporous structure with uniform pore diameter due to the self-assembly of TEOS in the synthesis process. All the catalysts have lamellar structure, but the ordered mesoporous structure disappears gradually when copper loading is increased. During the catalyst synthesizing process, the copper precursor $([Cu(NH_3)_4]^{2+})$ accessed into the pores of the support, and reacted with surface silica to form copper phyllosilicate or surface Cu-O-Si structure, leading to the destruction

of some ordered mesopores. Because of the lower copper loading, many ordered structure were maintained in 10Cu/OMS and 15Cu/OMS. A few ordered mesoporous channels could be also observed in 20Cu/OMS, but they completely disappeared and more lamellar or tubular structure were formed in those catalysts with more copper loading. These results are in good accordance with the physical properties described by the BET characterization.

Fig. 3 shows TEM images of reduced catalysts. It is observed that copper species are uniformly distributed on the support and copper phyllosilicate with lamellar or tubular structure vanished after reduction. The ordered mesopores can be still found clearly on the catalysts with lower copper content. As listed in Table 1, when the copper loading increases from 10% to 30%, the mean particle size of copper grows from 2.08 to 3.16 nm. The ordered mesoporous structure was believed to contribute to the high copper dispersion. When the copper loading reached certain degree, the surface of the OMS has no enough capability to well disperse all of these copper species. So the inevitable aggregation of copper species led to the increment of the copper nanoparticle size.

3.3 XRD profiles

The XRD patterns of all the calcined samples are shown in Fig. 4(A). The broad and diffuse diffraction peak at 22° belongs to the feature peak of amorphous SiO₂. No characteristic peaks of any crystalline phase for copper species are observed on these catalysts, even with 30% copper loading, indicating the high dispersion of copper species.

Fig. 4(B) shows the XRD patterns of the reduced xCu/OMS catalysts. Except for the characteristic peak of SiO₂, no diffraction peak is observed when the copper loading is lower than 20%. However, with the continuous increment in copper loading, the diffraction peak at $2\theta = 36.4^{\circ}$ arises gradually, which could be ascribed to the characteristic peak of Cu₂O (JCPDS05-0667). It suggested the existence of Cu⁺ in the reduced catalysts. When copper loading arrives at 30%, the characteristic peak of Cu₂O becomes intensive, and a weak diffraction peak at $2\theta = 43.3^{\circ}$ assigned to Cu⁰ (JCPDS04-0836) can be also observed.

Generally, when the crystalline particles exist below 3 nm in size, their characteristic peaks cannot be detected by the XRD [16]. The particle size of all the reduced catalysts are too small to be detected by XRD method, which is consistent to the results of TEM images. Therefore, it could be deduced that the structure of ordered mesoporous silica promoted the dispersion of the copper precursor and the formation of more copper phyllosilicate during AE process, which in turn restrained the growth of copper nanoparticle during the reduction process. The presence of Cu_2O species might be attributed to the strong interaction between copper species and the silica support, which inhibited the completely reduction of these copper species to metallic copper.

3.4 FT-IR spectra

The FT-IR spectroscopy was applied to determine the existence of the copper hydroxide and copper phyllosilicate species and evaluate the amount of copper phyllosilicate in the catalysts [29, 30]. As shown in Fig. 5(A), all the samples have the adsorption band of symmetric stretching vibrations of Si-O-Si at 800 cm⁻¹ and the

band of asymmetric stretching vibrations of Si-O-Si bond at 1110 cm⁻¹ in amorphous SiO₂. Interestingly, a shoulder peak at 970cm⁻¹ which assigned to stretching vibrations of surface Cu-O-Si bond can be observed at lower copper loading [16]. When the copper content exceeded 20%, this peak becomes less obvious. The formation of copper phyllosilicate can be further verified by the existence of the adsorption band at 670 cm⁻¹, which can be assigned to the δ_{OH} bands in copper phyllosilicate. Besides, the red shift of Si-O-Si bond vibrations frequency from 1110 cm⁻¹ to 1040 cm⁻¹ could also certified the presence of more copper phyllosilicate [28].

The relative amount of copper phyllosilicate could be estimated qualitatively by considering the integrated intensity of the bands at 670 cm⁻¹ normalized to the integrated intensity of the bands at 800 cm⁻¹, which was defined as I_{670}/I_{800} [31, 32]. Fig. 5(B) clearly shows that the ratio of I_{670}/I_{800} rises with the increment of copper loading, indicating much more copper phyllosilicate was formed. Obviously, the FT-IR spectra results strongly proved the coexistence of Cu-O-Si structure and copper phyllosilicate on the calcined Cu/OMS, which has never been reported before for copper-based catalysts. The mesoporous structure of OMS should play an important role on their formation, which will be further confirmed in the discussion section.

3.5 TPR results

TPR measurements were implemented to investigate the reducibility of the catalysts. As presented in Fig. 6, the reduction curves of all the samples have a main and almost symmetrical reduction peak at around 473K, indicating a narrow particle size distribution. This has also been revealed by the TEM images and the XRD

patterns. Chen et al. [28] reported that the reduction of well dispersed CuO to Cu^0 occurred at about 515K. Van Der Grift et al. [23] reported that the reduction peak at about 510 K belonged to the reduction of copper phyllosilicate to Cu^+ . And further reduction of these Cu^+ species having strong interaction with silica requires a temperature above 873 K.[5, 33] Therefore, the main reduction peak at about 473 K for Cu/OMS catalysts could be assigned to the overlapped of the reduction peak of well dispersed CuO to Cu^0 and copper phyllosilicate or Cu-O-Si species to Cu^+ .

Notably, a shoulder peak at about 553K is observed, and gradually vanished with the increase of copper loading. And this variation trend happened to be similar with that of Cu-O-Si species revealed by FT-IR spectra (the peak at 970 cm⁻¹). Meanwhile, no bulk CuO was found in the calcined catalysts according to the TEM and XRD results. Therefore, the peak at about 553K might belong to the reduction of a fraction of Cu⁺, likely the Cu⁺ formed from the reduction of Cu-O-Si species. While the further reduction of those Cu⁺ derived from copper phyllosilicate commonly requires a temperature about 873 K.

3.6 XPS

The chemical composition and valence state of the reduced catalysts were determined by XPS and XAES. The Cu 2p XPS spectra are illustrated in Fig. 7(A). It shows only two peaks at around 932.5eV and 952.3eV, which belong to Cu $2p_{3/2}$ and Cu $2p_{1/2}$, respectively [34]. The peak at 942-944eV which is assigned to Cu 2p satellite peak can not be found in all the samples [35]. This indicated that all Cu²⁺ species had been completely reduced to a low valence state of Cu⁺ or Cu⁰ [28].

Nevertheless, it is difficult to distinguish between Cu^+ and Cu^0 by XPS spectra due to the almost identical BE between these two species.

The Cu LMM X-ray induced Auger spectra (XAES) was used to distinguish the chemical states by their difference in the peak position. As shown in Fig. 7(B), all the samples present an asymmetric and broad peak, suggesting a stable coexistence of Cu^+ and Cu^0 on the catalyst surface [17, 20]. The two overlapping peaks at 916.7 eV and 913.6 eV are assigned to kinetic energy of Cu⁰ and Cu⁺, respectively. From the deconvolution results, the ratios of the surface $Cu^+/(Cu^+ + Cu^0)$, which is denoted as X_{Cu}^+ , are listed in Table 2. The ratios of $Cu^+/(Cu^++Cu^0)$ presents a volcanic curve with the increasing copper loading due to the hindered reduction effect. Assuming that the Cu⁺ ions and the Cu⁰ atoms occupy the same areas and have identical atomic sensitivity factors, the surface area of Cu⁺ can be calculated based on surface area of Cu^0 and the ratio of $Cu^+/(Cu^++Cu^0)$ [28, 35]. The surface area of Cu^+ first rises and then declines with the increasing copper loading, and the maximum value reaches 41.6 m^2/g at 20% copper loading. The amount of both Cu^0 and Cu^+ on various catalysts obey the rules: 20Cu/OMS > 25Cu/OMS > 30Cu/OMS > 15Cu/OMS > 10Cu/OMS. However, the sequence for the amount of Cu⁺ is not consistent with the amount of copper phyllosilicate in the calcined catalysts, which was generally believed to be the origin of Cu⁺. This might be an important clue to further demonstrate that the Cu⁺ specie was derived from not only the reduction of copper phyllosilicate but also the reduction of surface Cu-O-Si species, both of which were also found by the FT-IR characterization.

3.7 Catalytic performance in the hydrogenation of DMO

The low-temperature gas-phase hydrogenation of DMO was carried out in a fixed-bed reactor at 453K to discuss the catalytic performance of the xCu/OMS catalysts. As shown in Fig. 8(A-C), the activity of the catalysts can be sequenced as: 20Cu/OMS > 25Cu/OMS > 30Cu/OMS > 15Cu/OMS > 10Cu/OMS. Under a low WHSV, the conversion of DMO on all catalysts reached 100%, and it decreased with the increasing of WHSV. The superior catalytic performance can be achieved on 20Cu/OMS catalysts, whose DMO conversion was much higher than other catalysts at the WHSV above 1.0 h^{-1} . As shown in Fig. 8(B) and (C), the selectivity to EG show volcanic curves except 10Cu/OMS, and the selectivity to MG rise gradually for all the catalysts with the increasing WHSV. The resident time should be not long enough for the further hydrogenation of MG to EG at the relatively higher WHSV. While the lower selectivity to EG under low WHSV is attributed to the deep hydrogenation of EG to ethanol. The 20Cu/OMS catalyst shows the highest EG selectivity of 98.2% and 100% DMO conversion at the WHSV of 1.0 h⁻¹ under 453 K. Furthermore, as shown in Fig. 8(D), 20Cu/OMS catalyst exhibits an excellent stability in the chemoselective hydrogenation of DMO to EG, owing to the advantage in low-temperature reaction, and thus displays a feasible prospect in the industrial application.

4. Discussion

4.1 Correlation between copper species and catalytic performances

As proved by the characterization results, the catalyst with higher copper dispersion and larger copper surface areas can be achieved by the use of ordered mesoporous silica as the support and the modified AE method. It was believed that the ordered mesoporous structure of OMS should play important role in the formation of

active species. The optimal 20Cu/OMS catalyst had the highest surface areas for Cu⁰ and Cu⁺ species, which were $36.9m^2/g$ and $41.6m^2/g$ respectively. These characters led to the remarkable catalytic performance in the hydrogenation of DMO to EG. For low copper loading catalysts, the amount of active species was not enough for the activation of DMO and H₂ at higher WHSV. When copper loading exceeded 20%, the inner surface area of ordered mesoporous silica was not enough to well disperse these copper species, thus the aggregation of copper nanoparticles happened. The larger copper nanoparticle and lower copper surface area led to a worse activity.

Many work reported the viewpoint that the synergic effect of Cu^0 and Cu^+ might be the reason for the excellent performance in hydrogenation of DMO [16, 28]. Our previous work indicated the balanced of the copper species contributed to the catalytic activity in ester hydrogenation [10, 35]. The synergy mechanism of Cu^0 and Cu^+ was further proved by a kinetics study for DMO hydrogenation [36]. In this work, the change of the catalytic performance showed the same trend as that of the surface area of both Cu^0 and Cu^+ , indicating that the apparent catalytic activity was strongly dependent on the amount of Cu^0 or Cu^+ . This result is consistent with the previous findings: Cu^+ and Cu^0 are the active sites for the ester hydrogenation. The space time yield of EG (STY_{EG}) also presented a positive correlation with the surface areas, especially Cu^0 species (Fig. 9). Therefore, Cu^0 species might be the determining factors for the DMO hydrogenation on these catalysts.

4.2 Comparison between Cu/OMS and Cu/SiO₂

For a comparison, the $20Cu/SiO_2$ catalyst was prepared by the same method as 20Cu/OMS except silica sol instead of OMS as support. Obviously, 20Cu/OMS catalyst had the higher surface areas of Cu^0 and Cu^+ than $20Cu/SiO_2$. (Table 2) The

copper species could be highly dispersed in the ordered mesoporous silica during the preparation process due to its abundant pore structure. On the contrary, the silica sol could not provide enough surfaces to fully contact with copper precursor $[Cu(NH_3)_4]^{2+}$, leading to the formation of less copper phyllosilicate (Fig. S2a) and larger particle size of copper species after reduced (Fig. S2b). Therefore, 20Cu/OMS possessed the higher ratios of surface Cu⁺/ (Cu⁺ + Cu⁰) and surface areas of both copper species than 20Cu/SiO₂. As a result, the 20Cu/OMS showed a remarkable higher catalytic performance than 20Cu/SiO₂ (Fig. S1).

4.3 Structure evolution during the preparation process

In order to further reveal the function of the ordered mesoporous silica, real time sampling technique was employed to investigate the structure evolution of catalyst during the prepared process. The samples were taken at different time during the aging and evaporation process.

The physicochemical properties of these samples for 20Cu/OMS catalyst were listed in Table S1. The actual copper loading in different samples during the AE process were close to the designed value, implying copper species were well uploaded on the support in all the stages. For the samples obtained from the evaporation stage, the BET surface area showed a slight decline compared to aging samples, and the pore volume and pore diameter gradually ascent. The mesoporous structure of OMS can be maintained in the aging stage, but destroyed in the evaporation stage (Fig. 10). These can be further evidenced by TEM images (Fig. 11a-d), the mesoporous structure of the support was clearly found in the aging samples (Fig. 11a and b) and

gradually disappeared with time in the evaporation stage (Fig. 11c and d). The presence of ordered mesoporous structure ensured the uniform distribution of the copper precursor in their regular channels. Thus, the reaction between copper precursor ($[Cu(NH_3)_4]^{2+}$) and silica can be enhanced during the evaporation stage, leading to the structural destruction of the mesoporous silica and the formation of more copper phyllosilicate. The morphology of tubular and lamellar structure in the final catalyst (Fig. 11d) should be attributed to the character of copper phyllosilicate [28]. This might be one of the important reasons for the excellent dispersion of copper species in the final catalyst.

On basis of above results, the structure evolution of the Cu/OMS catalysts during the preparation process could be easily understood. The copper precursor $([Cu(NH_3)_4]^{2+})$ highly dispersed in the mesopores of OMS during the aging stage and reacted with support during the evaporation stage, which enhanced the formation of copper phyllosilicate in the catalyst. Thus, the presence of the mesoporous structure of OMS in the aging stage should be the key factor in improving the dispersion and copper surface areas.

4.4 Effect of pH on the structure evolution of Cu/OMS

It has been reported that the morphology and structure of Cu/SiO_2 catalysts can be greatly affected by the evaporation temperature [28]. While rare reports focused on the effect of the pH value on the structure evolution of Cu/OMS. In this study, one catalyst was prepared by the same method as above mentioned except the initial pH value was changed to 12 instead of 10. This catalyst was denoted as 20Cu/OMS(12)and the sample 20Cu-AGE-4(12) was also obtained by sampling after aging for 4 h

during the catalyst preparation process.

The ordered mesoporous silica was almost destroyed after aging stage under higher pH value (Fig. 11e, Fig. S3). After ammonia evaporation process, the obtained 20Cu/OMS(12) catalyst presented less amount of copper phyllosilicate (Fig. 11f) than 20Cu/OMS (Fig. 11d), as well as the specific surface area and pore volume (Table S1). Moreover, according to the lower actual copper loading in 20Cu-AGE-4(12) (Table S1), the copper precursor could not be well immobilized on the support in the aging stage when the pH of the mixture was 12.

Obviously, the ammonia containing mixture with higher pH destroyed the OMS structure during the aging stage, so that the copper species could not be well pre-distributed in the support. Thus, less copper phyllosilicate can be formed during the ammonia evaporation stage, because of the less contact between the copper precursor with silica surface. Therefore, the final catalyst gave the lower specific surface area and pore volume, as well as the worse catalytic performance compared to the 20Cu/OMS catalyst (Fig. S4).

5. Conclusion

A high efficient copper-based catalyst for the hydrogenation of DMO to EG has been successfully prepared by a modified ammonia evaporation method using ordered mesoporous silica as the support. The optimized copper loading would benefit the formation of more copper species including both Cu^0 and Cu^+ . While, excessive copper loading would result in the aggregation of copper species due to the total destruction of OMS. Moreover, for the first time it was found that Cu^+ specie was derived from not only the reduction of copper phyllosilicate but also the reduction of surface Cu-O-Si species. Given appropriate alkaline environment, the copper

precursor ([Cu(NH₃)₄]²⁺) can be well pre-distributed in the ordered mesoporous silica during the aging stage and reacted with the silica during the evaporation stage, leading to the formation of more copper phyllosilicate. Thus the surface areas of Cu⁰ and Cu⁺ were significantly improved in the final reduced catalyst. The appropriate pH value was the key factor to reserve the ordered mesoporous structure during the aging stage. The catalyst with optimized copper loading presented higher copper dispersion, larger copper surface areas and proper ratio of Cu⁺/ (Cu⁺+Cu⁰), which showed remarkable low-temperature catalytic performance with more than 98% yield of EG at 453K. These findings and synthesized strategy showed a prospective future in fabricating a catalyst with higher loading of active component.

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Tables of content

Table 1. Textural Parameters of xCu/OMS Catalysts and support

Table 2. Characterization of Cu Species and space time yield of EG of the catalysts

Figure 1. (A) N₂ adsorption–desorption isotherms, (B) pore-size distribution curves.

(a)10Cu/OMS,(b)15Cu/OMS,(c)20Cu/OMS,(d)25Cu/OMS,(e)30Cu/OMS,(f)OMS

(signal of f in figure1B was attenuated to 1/5).

Figure 2. The TEM images of the calcined xCu/OMS catalysts and support. (a)10Cu/OMS, (b)15Cu/OMS, (c)20Cu/OMS, (d)25Cu/OMS, (e)30Cu/OMS, (f)OMS.

Figure 3. The TEM images of the reduced xCu/OMS catalysts. (a)10Cu/OMS, (b)15Cu/OMS, (c)20Cu/OMS, (d)25Cu/OMS, (e)30Cu/OMS.

Figure 4. XRD patterns of the xCu/OMS catalysts (A) calcined and (B) reduced. (a)10Cu/OMS, (b)15Cu/OMS, (c)20Cu/OMS, (d)25Cu/OMS, (e)30Cu/OMS.

Figure 5. (A) FT-IR spectra (B) $I_{670/800}$ of the calcined xCu/OMS catalysts. (a)10Cu/OMS, (b)15Cu/OMS, (c)20Cu/OMS, (d)25Cu/OMS, (e)30Cu/OMS.

Figure 6. The TPR profiles of the xCu/OMS catalysts. (a)10Cu/OMS, (b)15Cu/OMS, (c)20Cu/OMS, (d)25Cu/OMS, (e)30Cu/OMS.

Figure 7. (A) Cu 2p XPS spectra (B) Cu LMM Auger spectra of the reduced xCu/OMS catalysts. (a)10Cu/OMS, (b)15Cu/OMS, (c)20Cu/OMS, (d)25Cu/OMS, (e)30Cu/OMS.

Figure 8. The catalytic performance and stability of the catalysts. Reaction condition: p = 2.5 MPa, T = 453 K, $H_2/DMO = 80$. (A) conversion of DMO, (B) selectivity of EG, (C) selectivity of MG. (a)10Cu/OMS, (b)15Cu/OMS, (c)20Cu/OMS,

(d)25Cu/OMS, (e)30Cu/OMS. (D) Stability of 20Cu/OMS. Reaction condition: p = 2.5 MPa, T = 453 K, H₂/DMO = 80, WHSV=1.0h⁻¹.

Figure 9. Relationship between STY_{EG} and $Cu^{0}(A)$ and $Cu^{+}(B)$ surface area.

Figure 10. (A) N₂ adsorption-desorption isotherms, (B) pore-size distribution curves

(a)20Cu -AGE-2, (b)20Cu-AGE-4, (c)20Cu-EVA-1, (d)20Cu/OMS.

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Figure 11. The TEM images of different samples. (a)20Cu-AGE-2, (b)20Cu-AGE-4,

(c)20Cu-EVA-1, (d)20Cu/OMS, (e)20Cu-AGE-4(12), (f)20Cu/OMS(12).

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Catalyst	Cu	S_{BET}^{b}	V_p^{b}	D_p^{b}	$S_{Cu}^{0 c}$	Cu	Crystallite
	loading ^a					dispersion ^c	Size ^d
	(%)	(m^2/g)	(cm^3/g)	(nm)	(m^2/g)	(%)	(nm)
OMS	-	1019	1.10	2.7	-	-	-
10Cu/OMS	10.7	394	0.51	6.0	17.8	27.6	2.08 ± 0.29
15Cu/OMS	15.8	426	0.85	6.2	20.8	22.5	2.12 ± 0.25
20Cu/OMS	20.5	518	1.06	6.9	36.9	21.9	2.33±0.30
25Cu/OMS	25.2	527	1.07	7.0	34.9	18.6	2.74 ± 0.22
30Cu/OMS	29.3	574	1.26	8.4	32.6	16.3	3.16±0.23

Table 1. Textural Parameters of xCu/OMS Catalysts and support

^a Determined by ICP-AES analysis ^b Determined by N₂ isotherm adsorption ^c Determined by the N₂O titration method ^d Determined by the TEM images (counting more than 80 particles).

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Catalyst	$S_{Cu}^{o}(m^2/g)^a$	$X_{Cu}^{+}(\%)^{b}$	$S_{Cu}^{+}(m^2/g)^c$	$STY_{EG}(g_{EG}g_{cat}^{-1}h^{-1})^d$
10Cu/OMS	17.8	36.3	10.1	0.081 ± 0.002
15Cu/OMS	20.8	50.6	21.3	0.209 ± 0.005
20Cu/OMS	36.9	53.0	41.6	0.477 ± 0.009
25Cu/OMS	34.9	45.8	29.5	0.455 ± 0.007
30Cu/OMS	32.6	44.1	25.7	0.424 ± 0.006
$20Cu/SiO_2$	27.3	46.6	23.8	+ <u>-</u>

Table 2. Characterization of Cu Species and space time yield of EG

^a Metallic Cu surface area determined by N₂O titration ^b Cu⁺/(Cu⁺ + Cu⁰) calculated from Cu LMM XAES spectra ^c Cu⁺ surface area based on S_{Cu}^{0} and X_{Cu}^{+} under the assumption that the Cu⁺ ions and the Cu⁰ atoms occupy same areas and have identical atomic sensitivity factors

^d STY_{EG} means space time yield of EG.





































