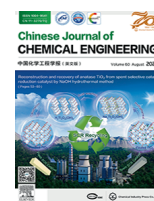




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Full Length Article

Ultra-stable Cu-based catalyst for dimethyl oxalate hydrogenation to ethylene glycol

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ABSTRACT

Dimethyl oxalate (DMO) hydrogenation is a crucial step in the coal to ethylene glycol (CTEG) process. Herein, Cu catalyst supported on fibrous mesoporous silica (Cu/FMS) was synthesized *via* liquid phase deposition technique and applied for the DMO hydrogenation to EG. The catalyst exhibited a remarkable EG selectivity of 96.95% and maintained its activity without deactivation for 1000 h. Fibers of FMS support and liquid phase deposition technology cooperated to give high dispersion of Cu species in the Cu/FMS catalyst, resulting in a high Cu surface area. The formation of Si–O–Cu during catalyst preparation process increased the Cu⁺/(Cu⁰ + Cu⁺) ratio and enhanced the thermal and valence stability of Cu species. The high Cu⁺ surface area and Cu stability (thermal and valence stability) of the Cu/FMS catalyst were key factors for achieving superior EG selectivity and ultra-high stability.

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1. Introduction

Ethylene glycol (EG) has gained considerable attention due to its widespread applications, such as solvent, antifreeze agent, surface active agent, dyestuff and raw material for the synthesis of polyester fibers [1–5]. Coal to ethylene glycol (CTEG) is frequently employed in China due to the current energy structure of rich coal and lean oil [6]. The CTEG process predominantly consists of the following procedures: converting coal to syngas, coupling CO with methanol to form dimethyl oxalate (DMO), and then hydrogenating DMO to EG [7]. However, this industrial process still has some drawbacks. Particularly for the DMO hydrogenation reaction, the limited service life of catalyst hinders the long-term and full-capacity operation of the device [2,8,9]. Therefore, it is essential to develop a catalyst with excellent catalytic activity and stability for DMO hydrogenation.

Extensive research has been conducted on Cu-based catalyst for vapor-phase hydrogenation processes due to their superior activity [10,11]. Cu sites are responsible for the selective hydrogenation of carbon–oxygen bonds but not for the hydrogenolysis of carbon–carbon bonds [12,13]. Therefore, Cu-based catalyst is the ideal

option for DMO hydrogenation. However, the loss of active Cu surface caused by Cu particles aggregation and the valence change of Cu species under reaction conditions, are the primary reasons for the short lifespan of Cu-based catalyst [14]. A general consensus is that catalytic stability can be successfully improved by confining/embedding Cu species into morphologically well-defined inorganic cavities or channels. This confinement effect increases the surface area of Cu species and constrains their movement, resulting in improved stability. Various types of confinement structures have been developed, including core–shell, core–sheath, mesopore, and lamellar structure. Wang *et al.* [15] created a 30Cu@CeO₂ catalyst with a core–shell structure by using the sol–gel process. The catalyst demonstrated long-term stability (160 h), significantly higher than that of the 30Cu/CeO₂-IM catalyst made *via* impregnation, which deactivated quickly after only 10 h. The high dispersion of Cu⁰ nanoparticles (NPs) and the surface enrichment of Cu⁺ species were likely to be responsible for the improved stability of Cu-based catalysts. In previous work of our group, a practical impregnation approach was used to confine the Cu NPs into the nano-channels of carbon nanotubes (CNTs) [16]. The developed Cu@CNTs-500 catalyst outperformed the traditional Cu/SiO₂ catalyst in terms of ethanol yields and stability. Ma *et al.* [17] enclosed the CuO NPs in a highly ordered MCM-41 mesoporous material with Cu loading as high as 20%. The 20Cu-MCM-41 catalyst achieved almost complete DMO conversion, with ethanol selectivity reaching 92%. Shi *et al.* [18] presented a simple co-precipitation

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technique to confine Cu species in the layered double hydroxide for DMO hydrogenation to ethanol. The resulting CuMgAl-LDH-1.25 catalyst had a regular lamellar structure, extensively distributed Cu active sites, and moderately acidic sites. These properties worked in concert to produce a consistent performance with DMO conversion of around 100% and ethanol selectivity reaching 83%.

Ordered mesoporous silica (e.g., MCM-41, SBA-15 and HMS) with abundant mesopores [19,20], regular channels and high surface area, has been successfully used as support for Cu-based catalysts to improve Cu dispersion [21] and restrain agglomeration of Cu NPs through spatial confinement of regular channels [7]. However, majority of the mesoporous silica supports utilized in Cu-based catalysts for DMO hydrogenation possess cylindrical channels, which may lead to inefficient utilization of active sites and poor transfer of reactants and products due to channels blockage by Cu NPs. Fibrous mesoporous silica (FMS) has a peculiar center-radial conical pore structure, with pore sizes gradually increasing from the center to the surface [22–24]. The unique channels of FMS confer high exposure [25,26] and accessibility [27] to the loaded Cu NPs, facilitating the diffusion of reactants and products. More importantly, the independent conical channels are not only conducive to the dispersion of loaded Cu NPs [28], but can also exert certain spatial confinement effect on Cu species to improve catalyst stability [29].

In this work, FMS with peculiar center-radial conical pore structure was facilely synthesized by hydrothermal method and employed as support for Cu-based catalyst *via* liquid phase deposition technique. The resulting Cu/FMS catalyst exhibited superior catalytic activity and ultra-high stability for DMO hydrogenation to EG. The catalyst and a reference catalyst prepared by impregnation method were characterized systematically. The results showed that the high activity of Cu/FMS catalyst was attributed to the Cu⁺ surface area, and the ultra-high stability was due to the high thermal stability and valence stability of Cu species.

2. Experimental

2.1. Catalyst preparation

2.1.1. Preparation process of FMS support

FMS was synthesized based on a typical hydrothermal method reported by Soltani and co-workers [30]. Aqueous phases were created by dissolving hexadecylpyridinium bromide (CPB, 4.00 g) and urea in deionized water (120.00 g). The mixture of ethyl silicate (TEOS, 10.00 g), cyclohexane (93.60 g) and *n*-amyl alcohol (4.92 g) were stirred to create an oil phase. These two phases were mixed and stirred at room temperature for 45 min. The mixture was then placed into a Teflon-sealed autoclave reactor and heated to 120 °C for 5 h. The precipitate was separated by centrifugation at 5500 r·min⁻¹, washed with acetone and distilled water, dried overnight in air at 100 °C to obtain FMS precursors. Finally, the precursor was calcined under air atmosphere for 5 h at 550 °C to yield fine white powders of FMS.

2.1.2. Preparation of Cu/FMS and Cu/FMS-I catalysts

0.70 g of FMS was dissolved in 200 ml of ethanol and sonicated for 15 min to scatter it at room temperature. Aqueous ammonia (25% (mass)) was added dropwise to the solution until the pH reached 11, followed by the addition of 1.14 g of Cu(NO₃)₂·3H₂O and 1 ml of deionized water under stirring at room temperature. The mixture was then heated to 80 °C and stirred for 8 h to evaporate the ethanol and ammonia. This resulted in the deposition of Cu species onto the support and the solidification of the final prod-

uct. After drying overnight at 100 °C, the solid product was calcined in a muffle furnace at 400 °C for 4 h.

The Cu/FMS-I catalyst was synthesized utilizing the impregnation method. 1.14 g of Cu(NO₃)₂·3H₂O was dissolved in 1 ml of water. Under the condition of ultrasonic assistance, the solution was dripped into an evaporating dish containing 0.70 g of FMS. In the process of dripping, constant stirring was required, and all the liquid was dripped within 30 min. The resulting mixture was vacuum dried overnight at 120 °C, aged at room temperature for 3 h, and finally calcined at 400 °C for 4 h.

2.2. Characterization

The texture parameters of the sample were evaluated *via* nitrogen adsorption method at -196 °C with a BELSORP mini-II physical adsorption apparatus made by MicrotracBEL Japan. Prior to measurement, the sample was degassed for 3 h at 200 °C under vacuum. The pore size distribution was determined using the Barrett-Joyner-Halenda (BJH) method, and the surface area was calculated using the Brunauer-Emmett-Teller (BET) method.

The dispersion and surface area of Cu species were determined by N₂O chemisorption at 50 °C. Briefly, 50.00 mg of catalyst was reduced in 5%H₂-95%Ar at 350 °C for 30 min, with the amount of hydrogen consumed denoted as X. The sample was then cooled to 50 °C and pure N₂O was introduced at a rate of 30 ml·min⁻¹ for 1 h to ensure that the surface Cu atoms were completely oxidized according to the reaction 2Cu(s) + N₂O → Cu₂O(s) + N₂. The sample was then purged with He gas for 30 min. Next, 5%H₂-95%Ar with a rate of 30 ml·min⁻¹ was introduced, and the sample was heated to 350 °C at a rate of 10 °C·min⁻¹ and reduced for 30 min, with the amount of hydrogen consumed denoted as Y. The Cu surface area was calculated as follows: $S = 2 \times Y \times N_{av} / (X \times M_{Cu} \times 1.4 \times 10^{19})$ (N_{av} represented Avogadro's constant, M_{Cu} was relative atomic mass of Cu). The Cu⁺ surface area of the reduced catalysts was determined by CO chemisorption. The catalyst was reduced for 30 min at 350 °C under a 5%H₂-95%Ar atmosphere. After purging with Ar for 30 min, a 10% CO/He stream was injected for 1 h, followed by He stream purging for 30 min. Finally, the desorbed CO was quantified using TCD.

The X-ray diffraction (XRD) patterns were obtained using Cu K_α radiation ($\lambda = 0.15406$ nm) on a Rigaku D/max-2500 X-ray diffractometer. The current was 30 mA, and the voltage across the tube was 40 kV. The XRD data was gathered at a scan speed of 8 (°)·min⁻¹, between $2\theta = 5^\circ$ – 90° . Scanning electron microscopy (SEM) images of the support and catalyst were taken by an FEI Model SIRION-100 scanning electron microscope. Transmission electron microscopy (TEM) was carried out using a Japan JEM-2010 transmission electron microscope outfitted with a Gatan-794MSC CCD camera system. The sample powder was dispersed by ultrasonic scattering in ethanol solution at room temperature, and the resulting material was then placed on the microgrid for TEM inspection. Fourier-transform infrared (FT-IR) was conducted using a Thermo IS10 spectrophotometer with a spectral resolution of 4 cm⁻¹ from 4000 to 400 cm⁻¹. The spectral resolution was 2 cm⁻¹, and each spectrum was recorded with 32 scans after the sample was coarsely powdered, mixed with KBr, and tabled.

By using a TP-5000 (Xianquan, Tianjin) multi-purpose adsorption equipment, the temperature-programmed reduction (TPR) profiles were obtained. A newly calcined catalyst weighing 50.00 mg underwent a 60 min pretreatment at 150 °C. The catalyst was then purged under an inert gas for 30 min after cooling to 50 °C. A TCD detector was used to measure the amount of hydrogen consumed as the catalyst was heated to 700 °C in 10%H₂/Ar mixed gas at a rate of 10 °C·min⁻¹. The catalyst was analyzed using X-ray photoelectron spectroscopy (XPS) on a Thermo Scientific K-Alpha energy spectrometer with an Al K_α radiation source

(1486.6 eV). The binding energy (BE) of sample was calibrated to the 284.6 eV of the C 1 s line, and the measurement error was ± 0.05 eV.

2.3. Activity test

The activity test was conducted in a stainless steel fixed-bed reactor at a system pressure of 2.5 MPa. To ensure precise temperature control, 0.20 g of the catalyst (0.25–0.42 mm) was packed into the center of reactor prior to the evaluation. A thermocouple was also placed into the catalyst bed. The catalyst was heated to 300 °C for 3 h at a ramping rate of 2 °C·min⁻¹ in an environment of H₂ (99.9% pure). After cooling to the reaction temperature, the catalyst was exposed to 15% (mass) DMO (99% purity) in methanol and pure H₂ (99.9% purity) atmosphere with a H₂/DMO molar ratio of 100. The weight hourly space velocity (WHSV) of DMO was set as 0.4 h⁻¹. Then, the liquid phase product was condensed by the low-temperature circulating cooling pump and analyzed by a gas chromatograph (GC-2014, Shimadzu instrument) equipped with a flame ionization detector (FID) and DB-624 capillary column.

3. Results and Discussion

3.1. Catalytic performance of catalysts

Herein, a Cu-based catalyst with fibrous mesoporous silica (FMS) as support was prepared *via* liquid phase deposition technique and applied for the catalytic hydrogenation of DMO to EG. The hydrogenation performance of Cu/FMS catalyst was compared to Cu/FMS-I reference catalyst prepared *via* simple impregnation method in a fixed-bed reactor. As shown in Fig. 1(a), the Cu/FMS catalyst demonstrated a higher DMO conversion (99.62%) and EG selectivity (96.95%) compared to the Cu/FMS-I reference catalyst, which had a low EG selectivity of 70.34% and a high MG selectivity of 22.54%. This result implied that the catalyst prepared using liquid phase deposition technique was more efficient in promoting the production of EG from DMO. In addition, the long-term stability of the Cu/FMS catalyst was also evaluated (Fig. 1(b)). Despite small fluctuations in its hydrogenation activity over the period of 1000 h reaction period, the ultra-high stability of Cu/FMS catalyst was demonstrated by the fact that no deactivation occurred.

Furthermore, the catalytic performance of Cu/FMS catalyst was evaluated at different WHSV. Table S1 (in Supplementary Material) showed that as the WHSV increased, the DMO conversion and EG selectivity gradually declined while the selectivity of unsaturated hydrogenation product MG steadily increased. This can be attributed to DMO being taken out of the reactor without sufficient contact with the catalyst, resulting in reduced conversion and hydrogenation depth. The stability of Cu/FMS and Cu/FMS-I catalysts was also evaluated at low conversion levels, with the DMO conversion of Cu/FMS and Cu/FMS-I catalyst being 91.43% and 86.14% (Table S2), respectively. As shown in Fig. S1, the Cu/FMS-I catalyst deactivated after 58 h, while the Cu/FMS catalyst started to deactivate after 300 h. Although the stability of Cu/FMS catalyst decreased at high WHSV, the stability difference between these two catalysts still demonstrated the advantage of Cu/FMS catalysts in terms of stability.

3.2. Physicochemical properties of catalysts

To determine the primary cause of the enhanced catalytic activity and stability, the Cu/FMS catalyst and Cu/FMS-I reference catalyst was characterized by N₂ adsorption–desorption isotherms, SEM, TEM, XRD, FT-IR, N₂O chemisorption and XPS. N₂ adsorption–desorption isotherms and pore size distribution curves were given in Fig. S2. The FMS support, Cu/FMS and Cu/FMS-I catalysts displayed a comparable type-IV isotherm with H3 hysteresis loops, indicating that the pore structure of FMS support did not change significantly after Cu loading. The pore size distribution of the catalysts and FMS support was compared in Fig. S2(b). For the FMS support, the pore size distribution was centered at about 3 nm, which was conducive to the dispersion and exposure of Cu species. After loading Cu species, although the pore volume of the Cu/FMS and Cu/FMS-I catalysts decreased due to the blocking of part pores by Cu particles, the pore size distributions of two catalysts were similar to that of FMS support. Therefore, the catalysts with center-radial conical pore still retained enough pores for the diffusion of the reactants and products in the reaction.

The morphology and Cu particle distribution could be more directly observed by TEM. The FMS support, as seen in Fig. 2(a), showed a multitude of microspheres with uniform size and average diameter of around 500 nm, as well as the typical wrinkled structure of fibrous nanosilica. Upon careful inspection, the TEM

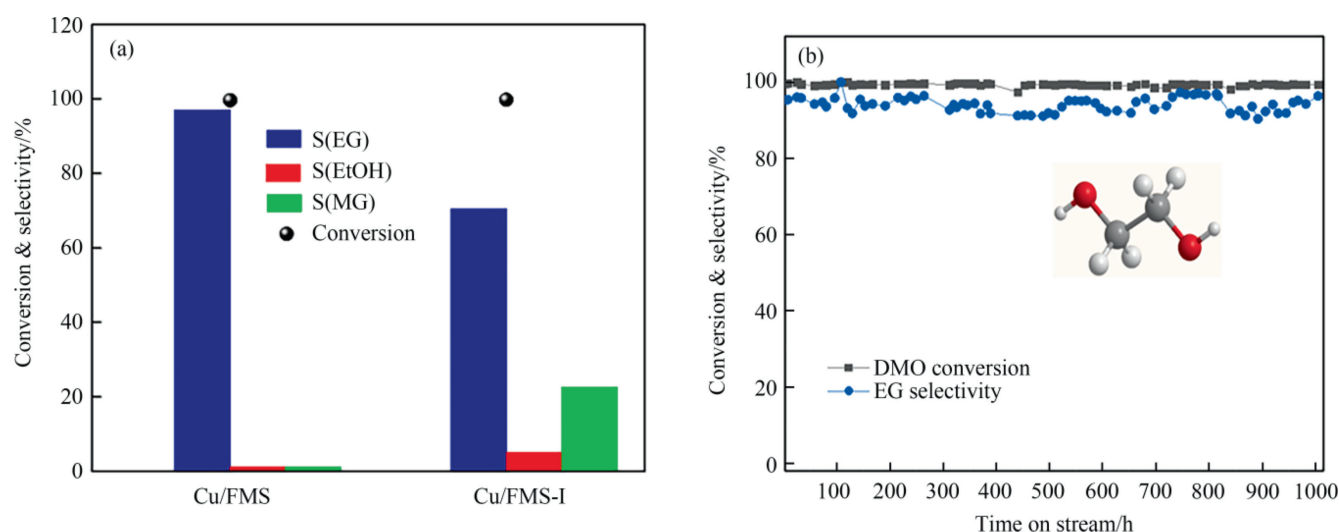


Fig. 1. DMO conversion and product selectivity of Cu/FMS catalyst and Cu/FMS-I reference catalyst (a) and stability test over Cu/FMS catalyst (b). Reaction condition: $T = 245$ °C, $P(\text{H}_2) = 2.5$ MPa, H_2/DMO molar ratio = 100, $\text{WHSV} = 0.4$ h⁻¹.

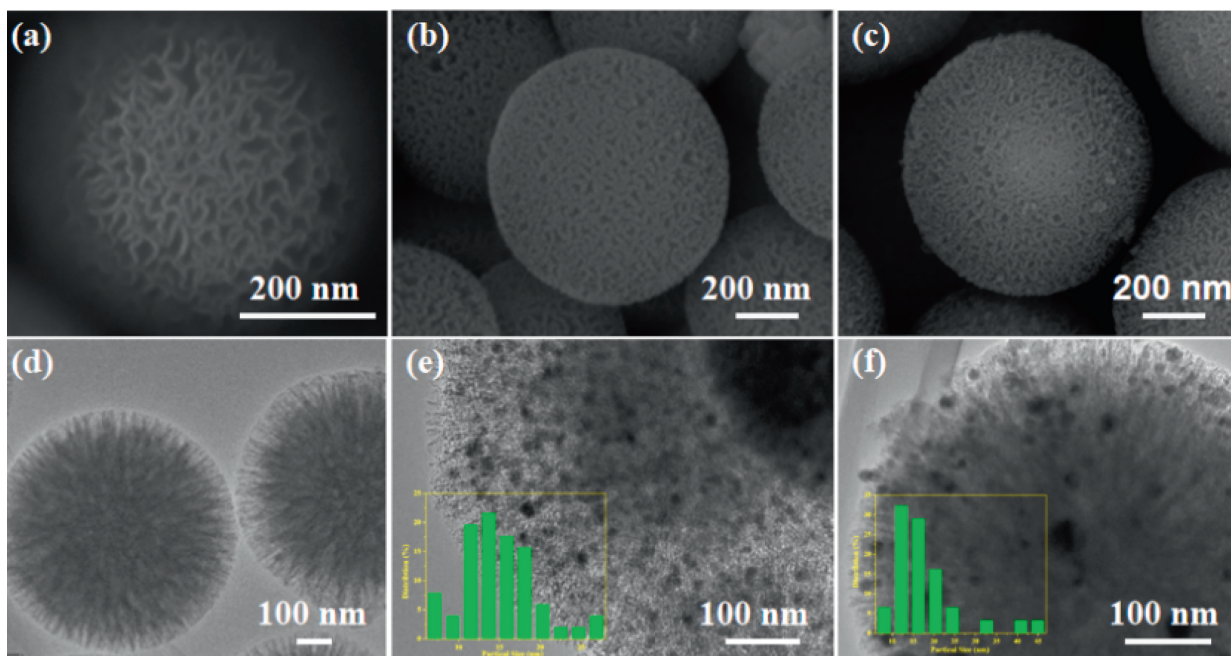


Fig. 2. SEM images of FMS support (a), Cu/FMS (b) and Cu/FMS-I (c) catalysts; TEM images of FMS support (d), calcined Cu/FMS (e) and Cu/FMS-I (f) catalysts.

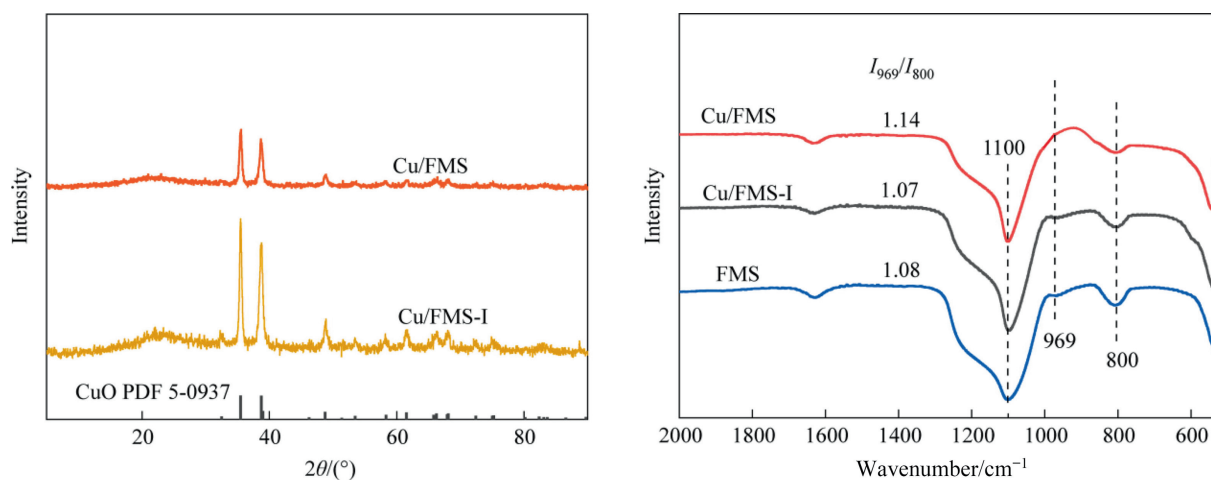


Fig. 3. XRD patterns (a) and FT-IR spectra (b) of calcined catalysts.

image of FMS revealed that wrinkled fibers extended from the center of spheres and were organized outwardly in three dimensions (Fig. 2(d)), greatly increasing the surface area to enhance the dispersion of supported Cu NPs. After Cu loading, Cu/FMS catalyst and Cu/FMS-I reference catalyst retained the spherical morphology and wrinkled structure of FMS support (Fig. 2(b) and (c)). Further comparing the TEM images of the calcined catalysts, it was evident that the Cu dispersion of Cu/FMS catalyst (Fig. 2(e)) was better than that of Cu/FMS-I catalyst (Fig. 2(f)).

Subsequently, the wide-angle powder XRD patterns of calcined catalysts were acquired to determine the diameters of Cu crystallites (Fig. 3(a)). The diffraction peak intensity of Cu/FMS catalyst was significantly weaker than that of Cu/FMS-I catalyst, indicating that the former had smaller Cu particle size and higher Cu dispersion. According to the Scherrer equation, the Cu particle size of Cu/FMS catalyst was about 16.00 nm, while that of Cu/FMS-I catalyst

was about 19.00 nm (Table 1). Additionally, these two catalysts exhibited obvious diffraction peaks of CuO, indicating that the Cu species in the catalysts existed in the form of CuO.

To get insight into the Cu species present on the calcined catalysts, the FMS support and catalysts were characterized by FT-IR (Fig. 3(b)). The symmetric and asymmetric ν_{SiO} bands of amorphous silica were observed at 800 cm^{-1} and 1100 cm^{-1} , respectively. The peak at 969 cm^{-1} was attributed to the Si–O stretching of the Si–OH structure. The development of Si–O–Cu, where the Si–O was still there but the H was replaced by Cu, caused the peak at 969 cm^{-1} to become less obvious [17]. Compared to FMS support, the peak at 969 cm^{-1} of Cu/FMS catalyst disappeared, indicating the formation of Si–O–Cu. In contrast, for Cu/FMS-I catalyst, the change in peak at 969 cm^{-1} was very weak relative to FMS support, indicating Si–O–Cu bonds were hardly formed. This phenomenon demonstrated that the liquid phase

Table 1

Physicochemical properties of support and catalysts

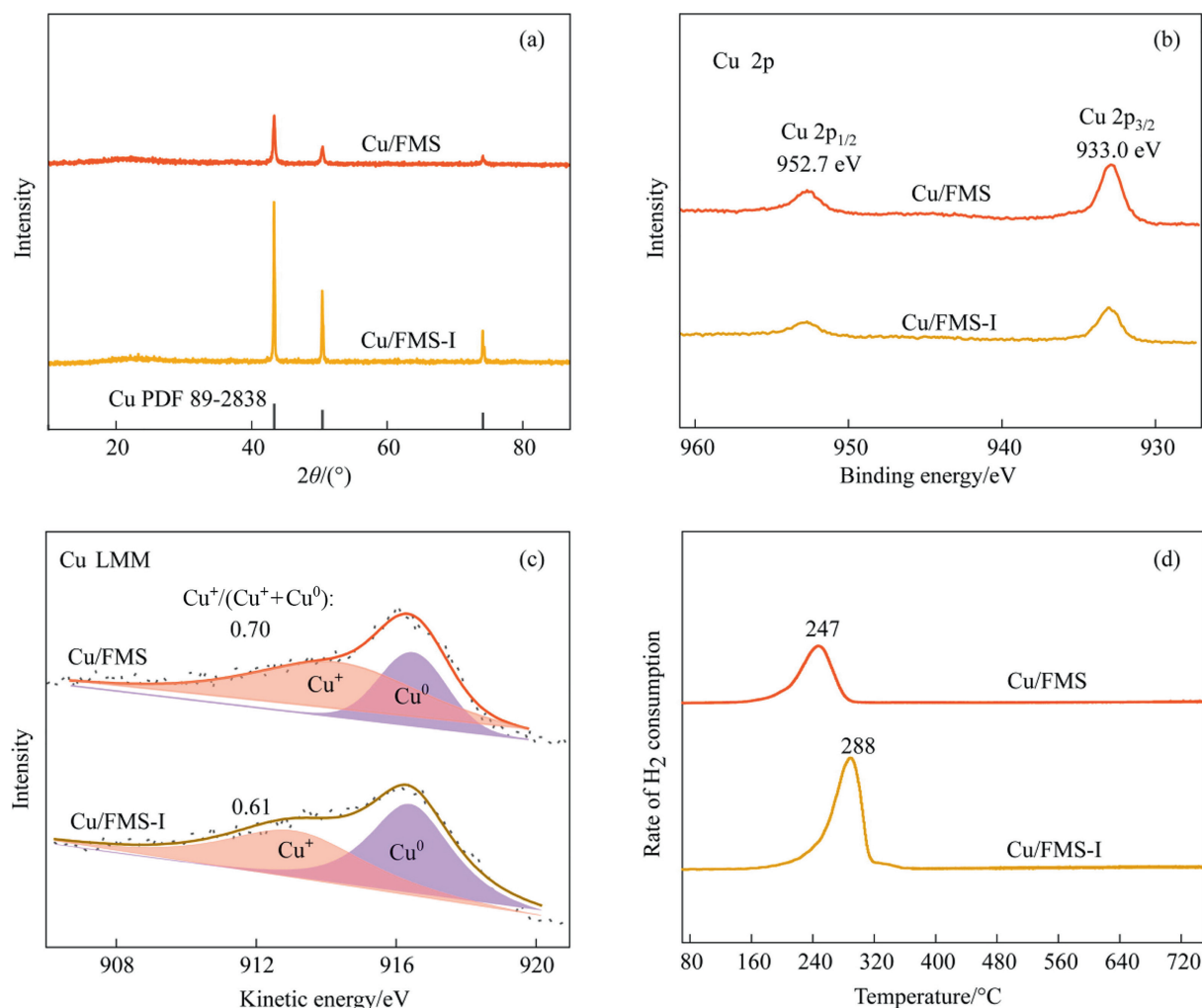
Sample	$S_{\text{BET}}^{\text{①}}/\text{m}^2\cdot\text{g}^{-1}$	$V_p^{\text{②}}/\text{cm}^3\cdot\text{g}^{-1}$	$d_p^{\text{③}}/\text{nm}$	$d_p^{\text{④}}/\text{nm}$	$S_{\text{Cu}}^{\text{⑤}}/\text{m}^2\cdot\text{g}^{-1}$	$S_{\text{Cu}^+}^{\text{⑥}}/\text{m}^2\cdot\text{g}^{-1}$	Cu^+ ratio ^⑦	$S_{\text{Cu}^+}^{\text{⑧}}/\text{m}^2\cdot\text{g}^{-1}$
FMS	269.08	0.35	—	—	—	—	—	—
Cu/FMS	106.53	0.14	16.00	20.00	52.39	34.39	0.70	36.67
Cu/FMS-I	195.16	0.17	19.00	46.00	43.55	27.24	0.61	26.57

① BET specific surface area;

② Pore volume at $P/P_0 = 0.99$;

③ Average diameter of CuO particle size calculated from the XRD data based on Scherrer equation;

④ Average diameter of Cu particle size calculated from the XRD data based on Scherrer equation;

⑤ Cu surface area per gram of Cu determined by N_2O pulse adsorption;⑥ Cu^+ surface area per gram of Cu determined from CO chemisorption;⑦ $\text{Cu}^+/(\text{Cu}^0 + \text{Cu}^+)$ ratio determined by XAES;⑧ Cu^+ surface area per gram of Cu obtained from XAES spectra and N_2O chemisorption.**Fig. 4.** XRD patterns (a), Cu 2p spectra (b) and Cu LMM spectra (c) of reduced catalysts at 300 °C; H₂-TPR profiles of calcined catalysts (d).

deposition technique favored the formation of Si—O—Cu, resulting in a robust interaction between supported Cu NPs and FMS support. This strong interaction would not only improve the sintering resistance of Cu NPs, but also inhibit the reduction of CuO to Cu⁰.

However, XRD result of the reduced Cu/FMS catalyst showed that the diffraction peaks of CuO disappeared, and only the diffraction peaks of Cu⁰ existed (Fig. 4(a)). The smaller the Cu NPs, the lower the intensity of XRD diffraction peaks. In order to further confirm whether there was Cu⁺ in the reduced catalyst, XPS mea-

surement with X-ray induced Auger electron spectroscopy (XAES) were carried out. The Cu2p_{3/2} and Cu2p_{1/2} peaks with binding energy of 952.7 and 933.0 eV strongly indicated that the Cu²⁺ species were reduced to Cu⁰ and/or Cu⁺ after reduction at 300 °C (Fig. 4 (b)). Two discernible peaks with Auger kinetic energy of 913.5 eV and 917.5 eV [31] provided evidence of the coexistence of Cu⁰ and Cu⁺ species on reduced catalyst (Fig. 4(c)), demonstrating the existence of Cu⁺ in reduced Cu/FMS catalyst. Peak deconvolution was employed to determine the relative amount of Cu⁰ and Cu⁺

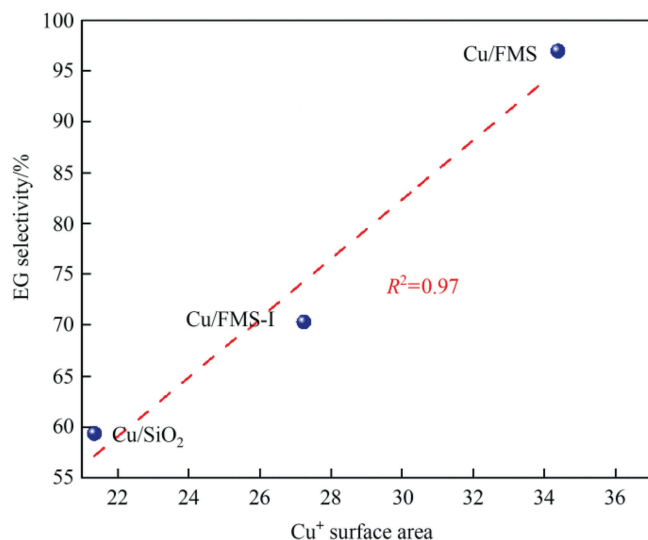


Fig. 5. Correlation of EG selectivity with Cu⁺ surface area determined from CO chemisorption.

species. According to the deconvolution results, the Cu⁰/(Cu⁰ + Cu⁺) ratio of reduced Cu/FMS catalyst was 0.70, higher than that of Cu/FMS-I catalyst (0.61). It was evident that the Si—O—Cu could produce Cu⁺ after reduction [32], leading to a higher proportion of Cu⁺ in the Cu/FMS catalyst.

To further investigate the reducibility and dispersion of Cu species, H₂-TPR was first conducted on Cu/FMS and Cu/FMS-I catalysts (Fig. 4(d)). Both catalysts showed a single reduction peak in the range of 200–300 °C. It has been reported that the reduction peaks of Si—O—Cu to Cu⁺ and CuO to Cu⁰ overlapped each other. Therefore, the reduction peak of Cu/FMS catalyst could be attributed to the reduction of Si—O—Cu to Cu⁺ and CuO to Cu⁰. Since only CuO existed in the calcined catalyst, the reduction peak of Cu/FMS-I catalyst should be ascribed to the reduction of CuO to Cu⁰ and Cu⁺. The size of Cu particles had a significant impact on the reduction temperature of catalyst. The lower reduction temperature peak was attributed to the reduction of highly dispersed Cu_xO, while

the higher reduction temperature originated from the reduction of bulk Cu_xO. It was worth noting that the peak temperature of Cu/FMS catalyst was 247 °C, much lower than that of Cu/FMS-I catalyst (288 °C). This demonstrated that the Cu species on Cu/FMS catalyst dispersed more effectively via the liquid phase deposition technique, which was consistent with XRD result.

Then, N₂O chemisorption of reduced catalysts was conducted to calculate the Cu metallic surface area. As shown in Table 1, the Cu metallic surface area of Cu/FMS catalyst was 52.39 m²·g⁻¹, while that of Cu/FMS-I catalyst was only 43.55 m²·g⁻¹. This result was consistent with the TEM (Fig. S3) and XRD (Fig. 4(a)) results. The higher the Cu dispersion, the greater the Cu surface area. In order to eliminate the possible effect of partial oxidation, the Cu⁺ surface area of catalysts was also determined by CO chemisorption. As shown in Table 1, the data determined by CO chemisorption was slightly different from that obtained from XAES spectra and N₂O chemisorption.

3.3. Discussions

Systematic characterizations were conducted to explore the reason for the excellent DMO hydrogenation activity and stability of Cu/FMS catalyst. The unique structure of FMS support and liquid phase deposition technique allowed for highly dispersed Cu species on FMS support with a robust interaction between them. This strong interaction formed the Si—O—Cu, which could be reduced to form Cu⁺ species. CO chemisorption revealed that the reduced Cu/FMS catalyst had a higher surface area of Cu⁺ species. In DMO hydrogenation, Cu⁰ was responsible for hydrogen dissociation, while Cu⁺ was responsible for adsorption and activation of methoxy and acyl groups of reactants and intermediates. Therefore, the surface area of Cu⁺ played a crucial role in the hydrogenation of DMO to EG. Performance evaluation showed that the EG selectivity of Cu/FMS catalyst was up to 96.95%, while that of Cu/FMS-I reference catalyst was only 70.34%. As shown in Table 1, the Cu⁺ surface area of Cu/FMS catalyst was 34.39 m²·g⁻¹, which was much higher than that of Cu/FMS-I catalyst (27.24 m²·g⁻¹). Therefore, the excellent EG selectivity of Cu/FMS catalyst could be attributed to its high Cu⁺ surface area.

To further confirm the reliability of this result, we prepared SiO₂ supported Cu-based catalyst by liquid phase deposition technique. The physicochemical properties of SiO₂ support and Cu/SiO₂

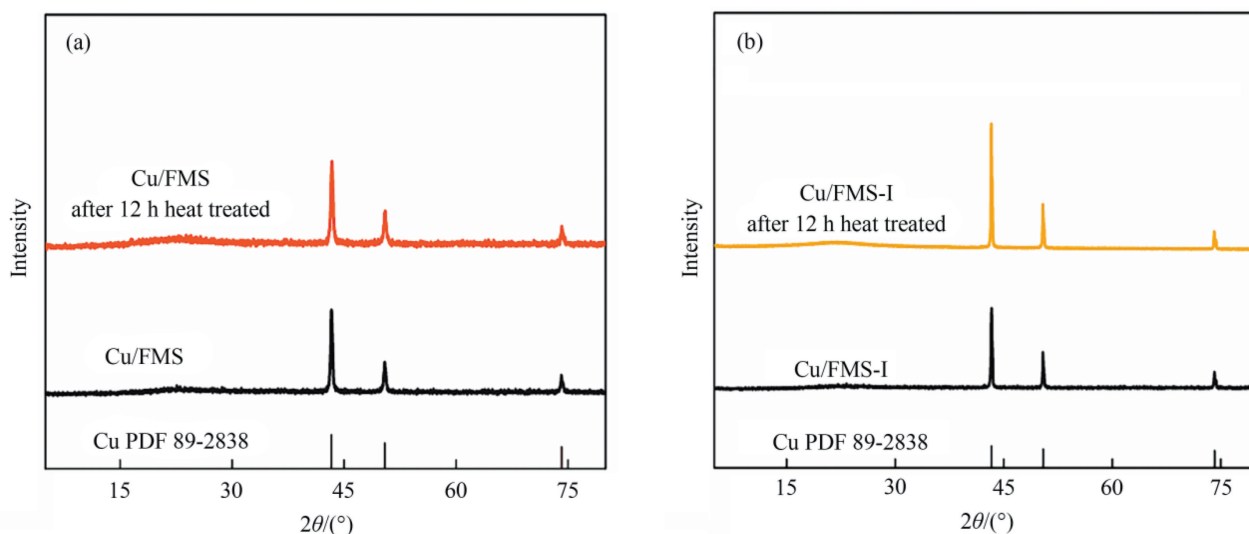


Fig. 6. XRD patterns of Cu/FMS (a) and Cu/FMS-I (b) catalyst before and after 12 h of heat treatment.

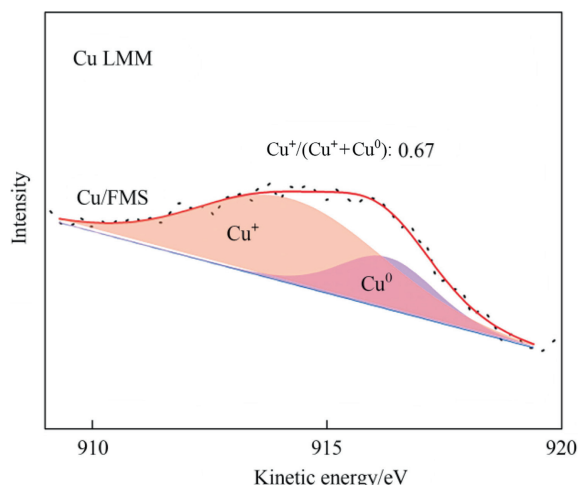


Fig. 7. Cu LMM profiles of spent Cu/FMS catalyst.

catalyst were listed in Table S1. The DMO conversion and product selectivity of Cu/SiO₂ catalyst were shown in Fig. S4. According to N₂O chemisorption and CO chemisorption, the Cu surface area and Cu⁺ surface area of Cu/SiO₂ catalyst were lower than those of Cu/FMS and Cu/FMS-I catalysts. This result confirmed that the unique center-radial conical pores of FMS support were beneficial to the dispersion of Cu species.

Subsequently, we plotted the Cu⁺ surface area determined from the CO chemisorption as the abscissa and EG selectivity as the ordinate. As can be seen from the Fig. 5, there was a positive correlation between these two parameters, indicating that the Cu⁺ surface area was the key factor affecting the selectivity of EG.

According to the performance data, Cu/FMS catalyst also exhibited ultra-high stability, as it could operate stably at 245 °C for 1000 h. To explore the cause for the ultra-high stability of the Cu/FMS catalyst, XRD was conducted on the catalysts after heat treatment. The Cu/FMS and Cu/FMS-I catalysts were first reduced at 300 °C under H₂ for 3 h and then raised to 450 °C under N₂ for 12 h. As seen in Fig. 6, the diffraction peak intensity of Cu/FMS catalyst was almost unchanged, while that of Cu/FMS-I catalyst was significantly stronger. This phenomenon indicated that Cu species of Cu/FMS catalyst had excellent thermal stability. The liquid phase deposition technique allowed for even distribution of Cu species on FMS support, which provided a foundation for maximizing the spatial limitation effect of support and strengthening the metal-support interaction. The synergism of these two factors greatly enhanced the thermal stability of Cu species.

In hydrogenation reactions with excess hydrogen, it was challenging for the Cu⁺ species to exist steadily, leading to a less stable catalyst and changes in the valence state composition. Therefore, we also examined the valence states of Cu species in the spent Cu/FMS catalyst (Fig. 7). Compared with the fresh catalyst, the Cu⁺/(Cu⁰ + Cu⁺) ratio of spent Cu/FMS catalyst decreased slightly, but still maintained a relatively high Cu⁺/(Cu⁰ + Cu⁺) ratio of 0.67 after 1000 h. This may be due to the difficulty of further reducing Cu⁺ species produced by the reduction of Si—O—Cu in the Cu/FMS catalyst. Finally, the combination of excellent thermal and valence stability in the Cu/FMS catalyst resulted in its ultra-high DMO hydrogenation stability.

4. Conclusions

In summary, an ultra-stable Cu-based catalyst with fibrous mesoporous silica as support was synthesized via liquid phase

deposition technique. Excellent dispersion of Cu species was accomplished by taking full advantage of center-radial fibers on FMS support. More importantly, Si—O—Cu chemical bond formed during preparation process of Cu/FMS catalyst enhanced the interaction between Cu species and FMS support. According to the characterizations, Si—O—Cu was not only beneficial to increase the Cu⁺/(Cu⁰ + Cu⁺) ratio, but also enhance the thermal stability and valence stability of Cu species. The high Cu dispersion and Cu⁺/(Cu⁰ + Cu⁺) ratio endowed high Cu⁺ surface area of Cu/FMS catalyst, which was the primary factor for excellent EG selectivity. Ultimately, the Cu/FMS catalyst exhibited superior catalytic activity and ultra-high stability thanks to the high Cu⁺ surface area and Cu stability (thermal and valence stability), with EG selectivity of 96.95% and stability for more than 1000 h.

Data Availability

No data was used for the research described in the article.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary Material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cjche.2023.06.008>.

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