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Efficient hydrogenation of CO₂-derived ethylene carbonate to methanol and ethylene glycol over Mo-doped Cu/SiO₂ catalyst

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ABSTRACT

Hydrogenation of ethylene carbonate (EC) to methanol and ethylene glycol is an attractive method for indirect hydrogenation of CO₂ to methanol. Copper-based catalysts have been studied in EC hydrogenation because of their good selective activation ability for carbon-oxygen bonds. Herein, a series of Mo-doped Cu/SiO₂ catalysts were prepared and used for EC hydrogenation. The catalyst with 0.5 wt% Mo dopant exhibited the highest catalytic performance of 80.9 % MeOH yield and 98.6 % EG yield with an excellent stability for at least 140 h. Detailed characterizations revealed that a proper amount of Mo addition could be beneficial to enhancing the copper dispersion and preventing them from aggregation. Moreover, it is demonstrated that the amount of surface Cu⁺ species was increased with some electron-deficient ones generated resulting from the strong interaction between copper and molybdenum species, which may effectively promote the activation of EC. The optimal 0.5 wt% Mo-doped catalyst showed remarkably enhanced efficiency and the apparent activation energy barrier of 115.8 kJ mol⁻¹ is much lower than that of the Mo-free sample in EC hydrogenation. The insights may bring new possibilities to further design efficient copper-based catalysts for the hydrogenation of carbon-oxygen bonds.

1. Introduction

Carbon dioxide (CO₂) is not only a greenhouse gas but also a low-cost, non-toxic and renewable carbon resource. Its conversion and utilization to valuable chemicals and materials is an attractive approach to reduce the negative impact on environment as well as to alleviate the resource shortages [1]. Methanol (MeOH), as a vital chemical feedstock and liquid fuel, has been considered as an important product of CO₂ conversion [2,3]. However, due to the thermodynamically stable and inert property of its carbon-oxygen bonds, direct conversion of CO₂ to MeOH remains a great challenge [4,5]. Harsh reaction conditions are generally required as well as the single-pass conversion in the direct CO₂ hydrogenation is difficult to improve because of the chemical equilibrium [3,6].

Recently, an alternative and indirect method has been brought up for efficient conversion of CO₂ to MeOH under moderate reaction

conditions, which has attracted extensive attention [7]. In this route, ethylene carbonate (EC) is used as an intermediate product due to its efficient synthesis by cycloaddition of CO₂ into ethylene oxide [8,9]. Subsequently, the hydrogenation of EC is conducted under mild conditions to obtain MeOH as well as high value-added ethylene glycol (EG) with 100 % atomic economy [7,10–12]. The EC production via CO₂ reacting with ethylene oxide has been industrialized in the OMEGA process, in which followed by hydrolysis of the carbonate to generate EG and release CO₂ again [1,13]. Thus, combining the OMEGA process with EC hydrogenation step could provide a new way for producing MeOH by utilization of CO₂ and obtaining additional product EG as well (Scheme S1).

Copper-based catalysts have been widely studied in many ester hydrogenation reactions, such as hydrogenation of dimethyl oxalate to EG [14,15], hydrogenation of methyl acetate to ethanol [16], due to their excellent ability in carbon-oxygen bond activation and inertness in C–C

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bondcleavage [17,18]. Li and co-workers used copper chromite catalyst for EC hydrogenation which achieved 60 % and 93 % selectivities to MeOH and EG respectively [12]. Recently, some mesoporous silica supported copper-based catalysts, such as Cu/HMS [19], Cu/MCM-41 [20], have been employed for continuous EC hydrogenation and obtained excellent catalytic performance benefiting from the high specific surface areas and suitable pore structures. The role of copper species of different chemical states as well as the effects of supports and promoters have also been investigated, which exhibit great influence on the catalytic performance in EC hydrogenation [10,21,22]. It has been reported that balanced Cu^+ and Cu^0 species plays a crucial role in enhancing the catalytic ability, where the Cu^0 could activate hydrogen and Cu^+ could function as Lewis acidic sites to polarize the carbon-oxygen bond [23]. Li et al. [24] found introducing suitable amounts of Zr and Mg into Cu/SiO₂ catalyst could decrease copper particle size and increase the amount of Cu^+ , which were helpful for the adsorption and activation of EC and resulted in enhanced catalytic activity and stability of EC hydrogenation. However, due to EC special structure with two adjacent alkoxyl groups, the efficient hydrogenation of carbon-oxygen bond is still challenging [10,25]. Besides copper particle size and valence distribution, the reaction is found to be closely related to the surface acidity and basicity [10,26]. It was found that strong and excessive basicity or acidity of the catalyst could induce the side reactions, such as decarbonylation and decarboxylation, and block active sites by strongly adsorbed reactants, thereby decreasing the EC conversion and product selectivity. Thus, appropriate promoter is of great significance to improve the catalytic performance for EC hydrogenation.

In the pioneering work, Poels et al. [27] studied different promoters in Cu/SiO₂ catalyst for methyl acetate hydrogenolysis and the activity was arranged in the following order: $\text{Mo} > \text{Co} \geq \text{Zn} \geq \text{M} > \text{Fe} > \text{Y} > \text{Ni} \geq \text{Mg}$. Additionally, it was found that the introduction of Mo promoter could help reduce the particle size and promote the active metal dispersion [28]. Recent works also reported that Mo-decorated noble metal catalysts could give enhanced selectivity of C=O bond hydrogenation because of the generated metal-additive interaction [29,30]. These studies suggested that Mo could be an effective promoter to improve the performance of copper-based catalyst in EC hydrogenation, the role of which is worthy for further study.

In this work, we fabricated a series of Mo-doped Cu/SiO₂ catalysts and optimized its contents for EC hydrogenation to produce MeOH and EG. The conversion of EC and yield of MeOH were remarkably improved on the catalyst doped with an appropriate Mo content. The effects of Mo doping on the structure and physicochemical properties were systematically characterized by N₂ physisorption, XRD, TEM, XPS, in situ FTIR of CO adsorption and so on. It was demonstrated that the addition of Mo promoter could regulate the chemical state and surface composition of copper species, consequently affecting the catalytic performance. We believe these insights of the structure-activity relationship may provide instructive suggestions for the further design of catalyst for the hydrogenation reactions.

2. Materials and methods

2.1. Catalyst preparation

The Cu/SiO₂ catalyst with 30 wt% Cu loading was prepared by the typical ammonia evaporation method [16], briefly described as follows. Firstly 26.3 g of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ was dissolved in 100 mL of deionized water, then 90 mL of aqueous ammonia solution (25 wt%) was added. After the mixture was stirred for 30 min, 44.5 mL of silica sol (30 wt%) was added dropwise to the above solution. The initial pH value of the suspension was maintained at 11–12 and stirred for 4 h at room temperature. Next, the suspension was heated to 80 °C for ammonia evaporation. This process was terminated when the pH value was decreased to 6–7. The precipitate was separated by filtration, then washed with deionized water three times and dried at 110 °C overnight.

Finally, the catalyst was calcined at 450 °C for 4 h, pressed, crushed, and sieved to 40–60 mesh.

The Mo doped Cu/SiO₂ catalysts were prepared by incipient wetness impregnation (IWI) method using Cu/SiO₂ powder with aqueous solution of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$. Then the catalysts were dried at room temperature for 24 h and calcined at 500 °C for 4 h. These samples were noted as xMo-Cu/SiO₂ where x represented the weight percentage of Mo in the catalyst. For comparison, 1.0Mo/SiO₂ was also prepared by above method.

2.2. Catalyst characterization

The contents of copper and molybdenum of the samples were determined by the inductively coupled plasma optical emission spectrometer (ICP-OES, Varian Vista-MPX). First, the catalyst was completely dissolved with HF solution and then a saturated boric acid solution was added before analysis.

N₂ adsorption-desorption isotherms were measured at –196 °C by using a Micromeritics Tristar 3000 apparatus. Before testing, the sample was degassed at 300 °C for 4 h. The specific surface area was calculated by the Brunauer–Emmett–Teller (BET) method, and the pore size distribution was calculated by the Barrett–Joyner–Halenda (BJH) method.

X-ray diffraction (XRD) was conducted on Rigaku Model C/max-2500 diffractometer with Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$). The catalyst for testing was reduced at 300 °C for 4 h in H₂ flow. The pattern was acquired from 10° to 90° with a rate of 8°/min.

Transmission electron microscopy (TEM) image was obtained by using a JEM-2100 F system electron microscope. The catalyst was first reduced at 300 °C for 4 h in H₂ flow and then was cooled to room temperature. The reduced powder was added to ethanol and dispersed with sonication. Finally, the solution was dropped onto a copper-grid-supported carbon membrane, dried and tested immediately.

The H₂ temperature-programmed reduction (H₂-TPR) was performed on the Micromeritics Autochem II 2920 equipped with a thermal conductivity detector (TCD). Firstly, 50 mg catalyst was pretreated in the quartz tube under He flow at 200 °C for 2 h and then cooled to room temperature. Finally, the catalyst was heated to 800 °C in 10 % H₂/Ar with a heating rate of 10 °C/min.

N₂O titration was operated on Autochem II 2920 apparatus to determine metallic copper surface area and copper dispersion. In brief, 50 mg of the sample was firstly pretreated in Ar for 1 h at 200 °C, then 10 % H₂/Ar flow was introduced to reduce the catalyst for 2 h at 300 °C. Next, the sample was cooled to 90 °C in Ar flow and then exposed to N₂O for 1 h, ensuring the surface metallic copper was entirely oxidized to Cu₂O. After purged for 30 min with Ar flow, the sample was reduced again at 300 °C by pulse injection of 10 % H₂/Ar.

Raman spectra were collected at room temperature by a Renishaw inVia reflex system. A laser of 532 nm was employed as the spectral excitation line. The catalyst used for the test was firstly reduced at 300 °C for 4 h in H₂ flow and then tested immediately.

X-ray photoelectron spectra (XPS) and Auger electron spectra (AES) were treated on Perkin-Elmer PHI 1600 ESCA equipped with a monochromatic Al K α X-ray source ($h\nu = 1486.6 \text{ eV}$) to detect surface Cu species. First, the catalyst was reduced at 300 °C for 4 h and then cooled to room temperature in the H₂ flow. Next, the catalyst was placed into centrifuge tube and sealed with Ar. Then the sample was transferred to the holder immediately and outgassed in the chamber. The analysis was taken under a vacuum of 1×10^{-8} Torr. The binding energy was calibrated using the C1s peak at 284.6 eV as the reference. The experimental error was within $\pm 0.2 \text{ eV}$.

The in situ FTIR of CO adsorption was performed on the Nicolet 6700 spectrometer. Briefly, self-supporting wafer was made by about 20 mg sample and placed in the in situ cell. Next, the sample was reduced at 300 °C for 1 h under 10 % H₂/Ar and cooled down to 30 °C under He flow to obtain the background spectrum. Then CO gas was introduced

for 30 min. Finally, the spectra were scanned and recorded again under He flow until they appeared unchanged.

2.3. Catalytic activity

The catalytic activity for the hydrogenation of EC was investigated in a stainless-steel fixed-bed reactor with a thermocouple inserted into the catalyst bed to monitor the reaction temperature. The catalyst pellets (40–60 mesh) were loaded into the reactor and reduced in H₂ flow (3 MPa, 100 mL/min) at 300 °C for 4 h at a temperature ramping rate of 2 °C/min from room temperature. After reduction, the catalyst was cooled down to the reaction temperature. Then, the EC solution (10 wt% in 1,4-dioxane) was injected continuously from the top of the reactor through a high-pressure pump and was vaporized in the stream of H₂ gas.

The liquid products were condensed and analyzed off-line with an Agilent Micro GC 6820 instrument with an HP-INNOWAX capillary column (Hewlett-Packard, 30 m × 0.32 mm × 0.50 μm). To ensure the accuracy and repeatability of the results, 2–3 samples were measured under each reaction condition. For the catalyst stability test, the reaction was performed continuously and the sample was collected every 2 or 3 h.

3. Results and discussion

3.1. Textural properties of Cu/SiO₂ and xMo-Cu/SiO₂ catalysts

The metal contents of the as-prepared catalysts measured by ICP-OES are listed in Table 1. The copper loadings of all catalysts are about 30 wt %, while molybdenum loadings vary in the range of 0.1–1.0 wt% as designed. The N₂ adsorption-desorption isotherms and pore size distributions are displayed in Fig. S1. All the samples possess Langmuir type IV isotherms with hysteresis loops, corresponding to the typical mesoporous structure [14]. As shown in Table S1, texture parameters for all catalysts are close to each other. The specific surface areas are over 440 m²/g and average pore sizes are around 6.7 nm, indicating that the introduction of molybdenum species has no significant effect on the porosity of the catalyst.

XRD patterns of the reduced catalysts are presented in Fig. S2. The broad peak that appears at 2θ of 22° in all samples is attributed to amorphous silica. The characteristic peak at 36.4° belongs to Cu₂O phase (JCPDS 65-3288), and the peaks centered at 43.3° and 50.5° could be ascribed to metallic Cu phase (JCPDS 04-0836). No obvious diffraction peaks of Mo species could be observed, indicating the presence of highly dispersed Mo species on the catalysts. When the Mo addition is increased to 0.5 wt%, the characteristic diffraction peaks of

metallic Cu become broader and weaker. Correspondingly, the particle size calculated by the Scherrer equation (Table S2) decreases from 4.4 nm to 3.9 nm, suggesting that the addition of Mo species could reduce the Cu particle size [14]. The copper crystallite size of 1.0Mo-Cu/SiO₂ catalyst is 4.3 nm, similar to the Mo-free Cu/SiO₂ catalyst. Combining the fact that the Mo-modified catalysts were calcined again at a higher temperature (500 °C), it is demonstrated that a proper amount of molybdenum addition could alleviate the thermal migration and aggregation of copper species during the high-temperature calcination and reduction processes [14].

TEM images of the reduced Cu/SiO₂ and xMo-Cu/SiO₂ catalysts are shown in Fig. 1. It is noted that all catalysts have similar morphologies. The particle size distribution (inset) of Cu/SiO₂ catalyst displays a wide range with the average diameter at 5.2 nm. After Mo doping, the mean particle size is reduced to 4.9 nm and 4.6 nm for 0.1Mo-Cu/SiO₂ and 0.5Mo-Cu/SiO₂ catalysts respectively with narrowed distributions, while the average size is 6.1 nm of 1.0Mo-Cu/SiO₂ and some large particles appears, in agreement with the XRD results.

In order to identify the existence states of molybdenum species, Raman spectra of the reduced catalysts were collected [31,32], and the results are illustrated in Fig. 2. An obvious and broad peak at 893 cm⁻¹ is observed in the 1.0 wt% Mo-doped catalyst, which could be ascribed to the vibrational of Mo-O/Mo = O bond in the oligomeric MoO_x domains [32,33]. Notably, as the Mo loading decreases, the peak intensity is dramatically declined. It implies that Mo species is highly dispersed on the catalyst surface when the Mo dopant is less than 1.0 wt%, consistent with the results of no observable Mo species in XRD and TEM. The distinct peak at 1.0 Mo-Cu/SiO₂ suggests that molybdenum species has accumulated to some extent, which maybe not able to effectively separate the copper species and result in the aggregation [14,34].

We further measured the metallic copper surface area (S_{Cu}⁰) and copper dispersion (D_{Cu}) by N₂O titration. As shown in Table 1 and Table S2, with the increasing Mo loading, S_{Cu}⁰ and D_{Cu} are first increased and then decreased and the highest D_{Cu} (14.6 %) is obtained on 0.5Mo-Cu/SiO₂ catalyst, in line with the XRD and TEM results. Notably, the S_{Cu}⁰ of 1.0Mo-Cu/SiO₂ is found smaller than that of the Mo-free Cu/SiO₂ catalyst, indicating that some surface copper particles were aggregated or covered by excessive Mo species [14].

3.2. Chemical states of copper species of Cu/SiO₂ and xMo-Cu/SiO₂ catalysts

H₂-TPR profiles of the as-prepared catalysts were performed to investigate the reducibility of copper species. As shown in Fig. 3, it is observed that the reduction peak of Cu/SiO₂ catalyst is mainly concentrated at 216 °C, which is attributed to the overlapped reduction peaks of the well-dispersed CuO to Cu⁰ species and copper phyllosilicate to Cu⁺ species [35]. With the increase of Mo content, the reduction temperature is gradually decreased and then increased, consistent with the copper dispersion [36]. Moreover, the peaks of the Mo-doped catalysts are more symmetrical and sharper compared with the Mo-free Cu/SiO₂ catalyst, suggesting narrower size distribution and more uniform dispersion of copper particles. Additionally, a weak peak at 290 °C is observed on Cu/SiO₂ catalyst, corresponding to the reduction of large CuO particles [35]. The broad shoulder peak around 273 °C on 1.0Mo-Cu/SiO₂ could be ascribed to the overlapped reduction peaks of large CuO particles, and some of which may interact with molybdenum species [37]. The weak peak of 1.0Mo-Cu/SiO₂ above 600 °C may be attributed to the reduction of molybdenum oxides. For comparison, the 1.0Mo/SiO₂ sample was prepared, which showed a wide range of reduction temperature at 400–650 °C. It has been reported that highly dispersed molybdenum oxides could be reduced at a relatively low temperature, while bulk ones could be reduced at above 600 °C [31]. Thus, it is suggested that excessive Mo species in 1.0Mo-Cu/SiO₂ would agglomerate during the high-temperature treatment, consistent with the Raman spectra.

Table 1
Physicochemical properties of Cu/SiO₂ and xMo-Cu/SiO₂ catalysts.

Catalyst	M _{Cu} ^a (wt%)	M _{Mo} ^a (wt%)	d _{Cu} ^b (nm)	S _{Cu} ⁰ ^c (m ² g ⁻¹ cat)	X _{Cu} ⁺ ^d (%)	S _{Cu} ⁺ ^e (m ² g ⁻¹ cat)
Cu/SiO ₂	31.2	/	5.2	26.1	27.5	9.9
0.1Mo-Cu/SiO ₂	30.6	0.10	4.9	25.2	35.7	14.0
0.5Mo-Cu/SiO ₂	30.2	0.49	4.6	28.0	40.7	19.2
1.0Mo-Cu/SiO ₂	31.7	1.05	6.1	22.3	32.3	10.6

^a Cu and Mo contents obtained by ICP-OES analysis.

^b Cu particle size measured from the TEM image.

^c Metallic Cu surface area (S_{Cu}⁰) obtained from N₂O titration.

^d Cu⁺/(Cu⁺ + Cu⁰) calculated from Cu LMM AES spectra.

^e Cu⁺ surface area (S_{Cu}⁺) estimated on the basis of S_{Cu}⁰ and X_{Cu}⁺ assuming the Cu⁰ and Cu⁺ have the same surface area and atomic sensitivity factor.

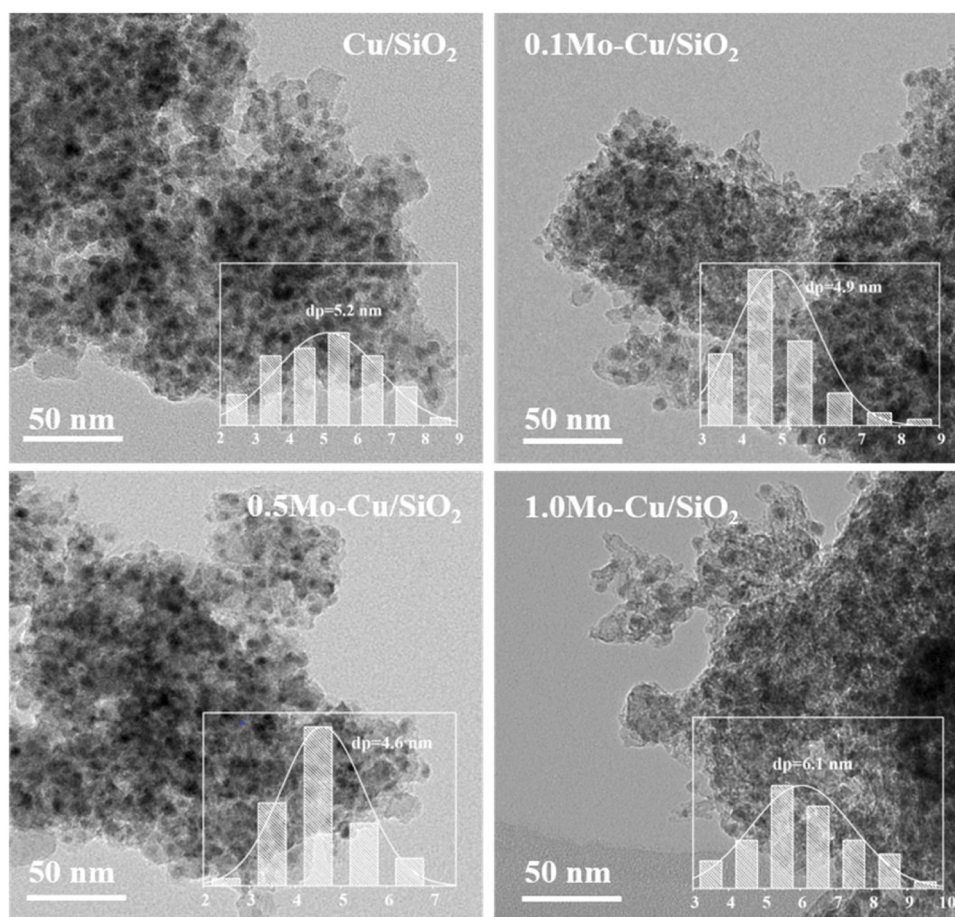


Fig. 1. TEM images of the reduced Cu/SiO₂ and xMo-Cu/SiO₂ catalysts (inset:particle size distribution).

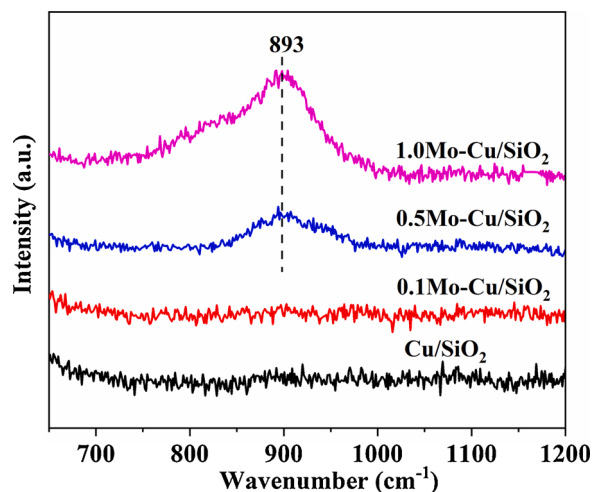


Fig. 2. Raman spectra of the reduced Cu/SiO₂ and xMo-Cu/SiO₂ catalysts.

XPS was carried out to investigate surface chemical state of copper species of the reduced catalysts. As shown in Fig. 4(a), there are two peaks at binding energies of 932.4 eV and 952.5 eV, typically assigned to Cu 2p_{3/2} and Cu 2p_{1/2} peaks respectively [14]. The absence of Cu 2p satellite peak at 942–944 eV indicates that the Cu²⁺ species has been completely reduced to Cu⁺ and Cu⁰ under the reduction condition [16], as shown by XRD. Further, a slight shift of Cu2p_{3/2} peak to higher binding energy is observed after doping Mo species, suggesting the strong interaction and charge transfer between copper and molybdenum

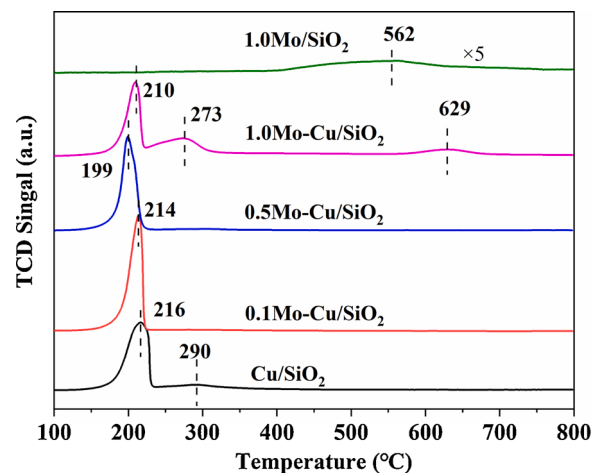


Fig. 3. H₂-TPR profiles of the calcined Cu/SiO₂ and xMo-Cu/SiO₂ catalysts.

species [34].

Since Cu⁰ and Cu⁺ species have rather similar binding energies, Cu LMM AES spectra were detected to determine the different copper species [36]. As shown in Fig. 4(b), the broad and asymmetric peak presented on Cu/SiO₂ catalyst is deconvoluted into two symmetrical peaks centered at 569.7 eV and 572.7 eV, which are attributed to Cu⁰ and Cu⁺, respectively [35]. Notably, as the Mo content increases, the binding energy of Cu⁺ gradually shifts to higher value and arrives at 573.1 eV, further indicating the charge transfer from copper to molybdenum species [14]. It is demonstrated that the addition of Mo species could

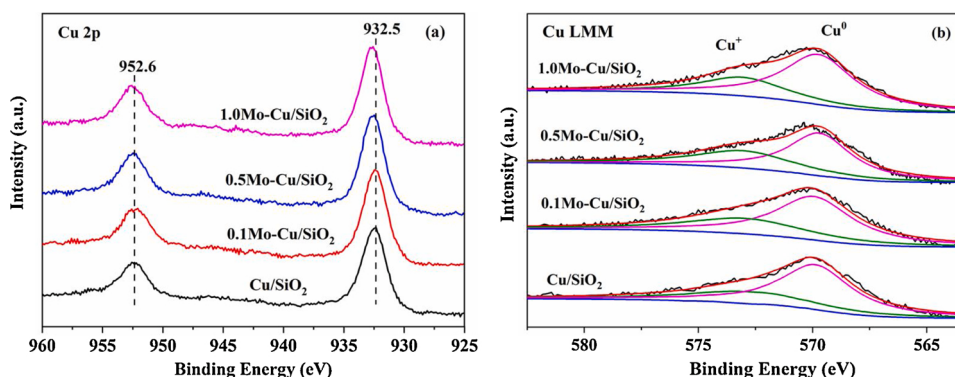


Fig. 4. Cu2p XPS spectra (a) and Cu LMM AES spectra (b) of the reduced Cu/SiO₂ and xMo-Cu/SiO₂ catalysts.

decrease the electron density of Cu⁺ species resulting from the strong interaction. The similar electronic interaction was reported on Mo promoted Ir-based catalyst [30].

The molar proportion of surface Cu⁺ (X_{Cu}^+) calculated from the AES deconvolution result is listed in Table 1. It can be seen that the X_{Cu}^+ of Mo doped catalysts is increased compared with the Mo-free Cu/SiO₂ catalyst and reaches the maximum value of 40.7 % at 0.5 wt% Mo dopants. By assuming the Cu⁰ and Cu⁺ species have the same surface area and atomic sensitivity factor, the surface area of Cu⁺ (S_{Cu}^+) could be estimated on the basis of S_{Cu}^0 and X_{Cu}^+ [16]. Correspondingly, the S_{Cu}^+ is varied with the Mo loading as well. The S_{Cu}^+ is first increased and obtained the maximum value of 19.2 m²/g when the Mo content is increased to 0.5 wt%, and then sharply decreased with further increase of Mo species (Table 1).

In situ FTIR spectra of CO adsorption could be also used to detect the surface Cu species [14,38]. As shown in Fig. 5, the asymmetric CO absorption peak with a weak shoulder one is observed in the all reduced Cu/SiO₂ and Mo-modified catalysts. Since no CO adsorption is found on 1.0Mo/SiO₂, the peaks are attributed to the CO adsorption at copper sites. Generally, the CO adsorption on Cu²⁺ and Cu⁰ sites is considered to disappear after purge at room temperature because of the weak interaction [16]. But it has been observed that some detectable CO adsorption could occur at 27 °C in small Cu⁰ crystallites, which would disappear when further increasing the temperature [38]. Then in order to identify the peaks in FTIR spectra of CO adsorption, we tested one sample purged under different temperatures (Fig. S3). It is obvious that the band at 2080 cm⁻¹ disappears when the temperature is increased to 50 °C, whereas the asymmetric band is remained and accompanied with a shoulder peak, suggesting the former is the peak of Cu⁰-CO adsorption

and the latter is Cu⁺-CO adsorption domain. Further increasing the temperature to 100 °C, the band around 2108 cm⁻¹ is sharply reduced, while that around 2124 cm⁻¹ comes out (Fig. S3), indicating the stronger CO adsorption at 2124 cm⁻¹ [14].

Based on above discussion, the asymmetric peaks in Fig. 5 could be deconvoluted into three symmetrical peaks centered at 2080 cm⁻¹, 2108 cm⁻¹ and 2124 cm⁻¹, respectively. The 0.5Mo-Cu/SiO₂ catalyst is given the largest Cu⁰-CO adsorption at 2080 cm⁻¹, indicating that it has the highest metallic copper dispersion, in line with the TEM and TPR results. The FTIR of CO adsorption could be used to verify the amount of surface Cu⁺ species as well [39]. The integral area of Cu⁺-CO band (A_{Cu}^+ , Table S2) and the S_{Cu}^+ of these reduced catalysts as the function of Mo loading (Fig. S4) exhibit good consistency, and both of them reach the highest value at the 0.5 wt% Mo-doped sample, which confirms the accuracy and reliability on the quantitative measurement of the copper species [16]. In addition, compared to the Mo-free sample, the vibration bands of Cu⁺-CO adsorption are gradually blue-shifted with the Mo addition, suggesting the decreasing electronic density of surface Cu⁺ species [14,30]. Correspondingly, the integral area ratio under the peaks of 2124 cm⁻¹ and 2108 cm⁻¹ displays a volcano-trend change as the Mo loading increases, and maximizes the value of 1.64 at 0.5 wt% Mo content (Table S2), indicating the change of electronic density of Cu⁺ species, agreed with the AES analysis.

Thus, it could be concluded that an appropriate amount of Mo dopant could not only enhance the dispersion of copper active species, but also facilitate the generation of more electron-deficient Cu⁺ sites because of the strong interaction between copper and molybdenum species. However, when the Mo content is increased to 1.0 wt%, the promoting effects drops sharply due to the agglomeration of Mo species and its coverage on active sites.

3.3. Catalytic performance

The catalytic performances were tested over Cu/SiO₂ and xMo-Cu/SiO₂ catalysts to investigate the effect of Mo content on vapor-phase EC hydrogenation to MeOH and EG. As shown in Fig. 6, the EC conversion and products yields could be significantly improved by introducing suitable amount of Mo dopants. For comparison, 1.0Mo/SiO₂ was also tested but there was barely EC converted (not given). Under the WHSV (weight hourly space velocity) of EC at 0.75 h⁻¹, all catalysts exhibit 100 % EC conversion and >97.5 % EG yield, while the MeOH yield is remarkably changed with the different Mo loadings. It maybe because the generation of CO or CO₂ via the decarbonylation and decarboxylation reactions [12,26], which would reduce the yield of MeOH. The possible reactions are shown in the supporting information (Eq.S1-S6). The high yield of EG could be ascribed to few by-products of C₃₋₄ alcohols, such as 1,2-propanediol and 1,2-butanediol, formed by the Guerbet reactions. The few surface basic sites of SiO₂ support, as well as the relative low reaction temperature of 180 °C could both effectively

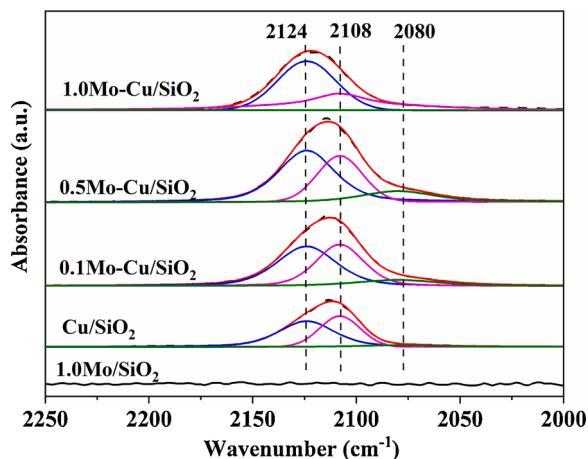


Fig. 5. In situ FTIR spectra of CO absorption of the reduced Cu/SiO₂ and xMo-Cu/SiO₂ catalysts.

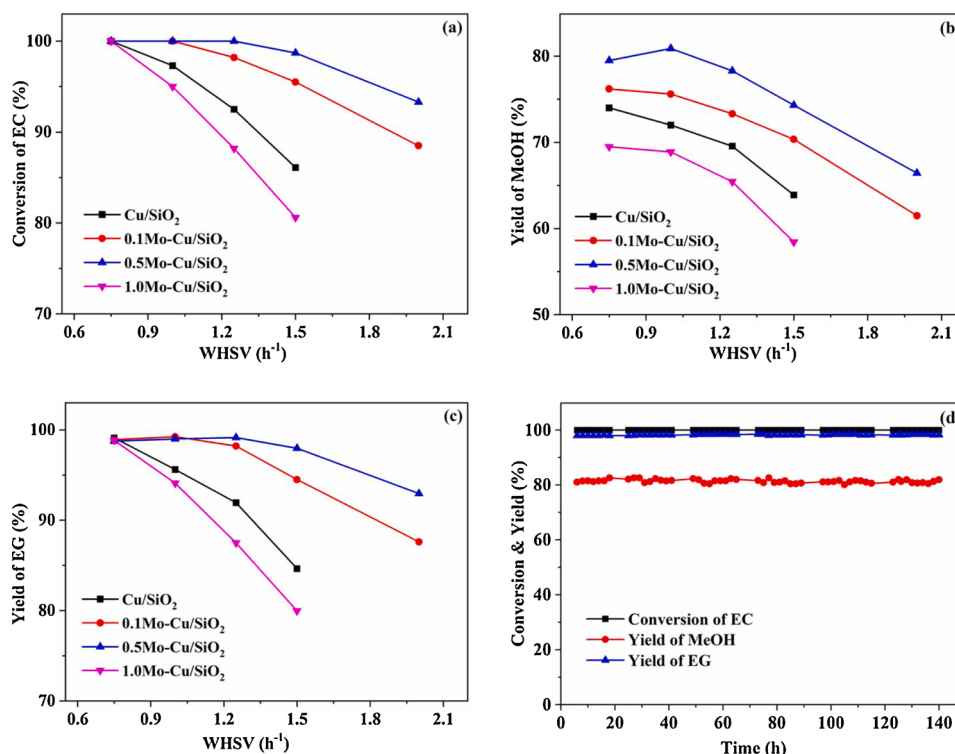


Fig. 6. The catalytic performance of Cu/SiO₂ and xMo-Cu/SiO₂ catalysts: conversion of EC (a), yields of MeOH (b) and EG(c) (Reaction conditions: 180 °C, 3 MPa, H₂/EC = 180 mol/mol), (d) stability test of the 0.5Mo-Cu/SiO₂ catalyst (WHSV = 1.0 h⁻¹).

reduce the Guerbet reactions. Similar results were reported in the literatures using Cu/SiO₂ for EC hydrogenation [40,41]. When the WHSV increases, the EC conversion of Cu/SiO₂ decreases rapidly, whereas that of 0.5Mo-Cu/SiO₂ could maintain 93.3 % at 2.0 h⁻¹. The optimal performance of 80.9 % yield of MeOH and 98.6 % yield of EG is obtained at 1.0 h⁻¹ WHSV on the 0.5 wt% Mo-doped sample. When Mo content is increased to 1.0 wt%, the catalytic activity becomes even worse than the blank one due to the partial coverage and aggregation of active species. Moreover, we selected the best-performing 0.5Mo-Cu/SiO₂ catalyst to further evaluate the long-term stability in EC hydrogenation. The result in Fig. 6(d) exhibits that the 0.5 wt% Mo doped catalyst possesses excellent lifespans. The conversion of EC maintains constant at about 100 % and stable yields of MeOH and EG are also observed during 140 h of time on stream.

3.4. The role of Mo dopant

In order to better understand the role of Mo in the Cu/SiO₂ catalyst for EC hydrogenation, we further employed Arrhenius plots to analyze the apparent activation energy barriers (E_a) of Cu/SiO₂ and 0.5Mo-Cu/SiO₂ catalysts. As shown in Fig. 7, the E_a of Cu/SiO₂ catalyst is 153.7 kJ mol⁻¹, while that for the 0.5Mo-Cu/SiO₂ catalyst is 115.8 kJ mol⁻¹, suggesting Mo dopant could greatly reduce the E_a and enhance the catalytic efficiency. In fact, some studies have reported that Mo-doped Ru-based catalyst is beneficial for activating carbonyl-containing compounds and increasing selectivity of C=O hydrogenation [29]. It is also found that Mo-decorated Ir-based catalyst could form Ir-MoO_x interface via the interaction between Ir and MoO_x species, which could promote adsorption and activation of aldehyde group [30]. The carbon-oxygen bonds of EC is quite stable and difficult to be activated because of the resonance stabilization effect of two adjacent alkoxy groups [10,25]. Therefore, the decrease of E_a may result from the promoted adsorption and activation of carbon-oxygen bonds of EC due to the introduction of Mo dopant.

It is generally accepted that the synergy of Cu⁺ and Cu⁰ is the key in

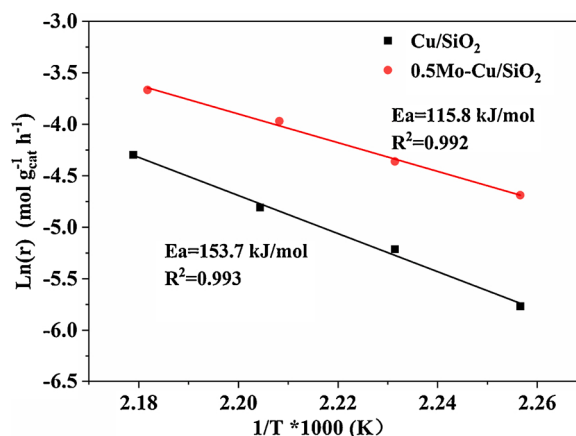


Fig. 7. Arrhenius-type plots for EC hydrogenation of Cu/SiO₂ and 0.5Mo-Cu/SiO₂ catalysts.

catalyzing the ester hydrogenation reactions. In order to get a further insight, catalytic activity and S_{Cu}⁺ as a function of Mo loading was investigated. As shown in Fig. 8, along with the increase of Mo loading, the EC conversion and MeOH yield get improved, which are similar to the change of S_{Cu}⁺. It is implied that the enhancement of Cu⁺ sites could make great contribution to the catalytic performance. Some researchers found that the high proportion of Cu⁺ species could facilitate the conversion of intermediates during the process of EC hydrogenation [40], because Cu⁺ can act as electrophilic or Lewis acidic sites to adsorb and polarize carbo-oxygen groups [14,16]. It is observed that the Mo dopant could increase X_{Cu}⁺ as well as produce the electron transfer from copper to molybdenum due to their strong interaction, which maybe in favor of stabilizing the surface Cu⁺ species [42]. Moreover, the generated electron-deficient Cu⁺ sites are more conducive to the adsorption and activation of the carbon-oxygen group, thus promoting the conversion

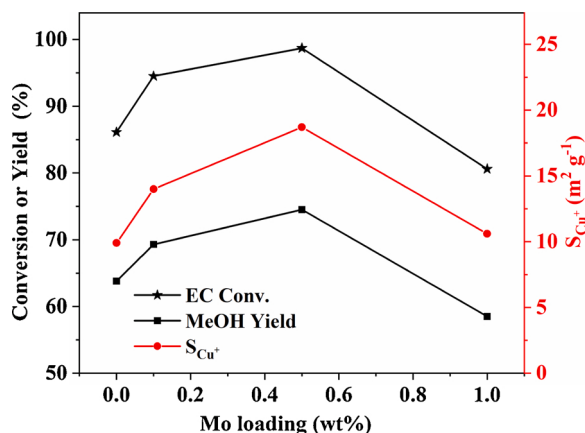


Fig. 8. The variations of EC conversion, MeOH yield and Cu^+ surface area against the Mo loading.

efficiency as confirmed by the significant decrease of E_a . However, excessive Mo addition will deteriorate the catalytic performance. As can be seen, the 1.0Mo-Cu/SiO₂ catalyst and Cu/SiO₂ catalyst have the similar S_{Cu^+} , while the former one displayed lower conversion of EC and yield of MeOH (Fig. 8), which could be ascribed to its smaller S_{Cu^0} causing insufficient hydrogen dissociation [16]. It has been reported that when the amount of surface metallic copper is sufficient, the catalytic activity of ester hydrogenation is primarily related to the area of the surface Cu^+ sites [16]. It is illustrated that the synergy catalysis with a balanced Cu^0 and Cu^+ species is also of great significance in EC hydrogenation, consistent with the reported literatures [19,24].

4. Conclusion

In summary, we found that molybdenum could be an effective dopant to improve the catalytic performance of Cu/SiO₂ catalyst for the hydrogenation of CO₂-derived EC to produce MeOH and EG. The optimal 0.5 wt% Mo-doped Cu/SiO₂ catalyst exhibits remarkable performance of 100 % EC conversion, 98.6 % EG and 80.9 % MeOH yields and shows a excellent stability during the 140 h long-term reaction. But when excessive amount of Mo is introduced, the catalytic performance would be deteriorated due to the surface coverage and aggregation of the active sites. Furthermore, it is demonstrated that with the addition of appropriate Mo species, the aggregation of copper particle is suppressed and the Cu dispersion is promoted. Meanwhile, according to the quantitative characterizations of copper species, the surface area of Cu^+ sites is increased as well as more electron-deficient ones formed benefiting from the strong interaction between copper and molybdenum species, which may effectively decrease the apparent activation energy barrier of the hydrogenation of EC. The insights could enlighten us to further design efficient copper-based catalyst for the hydrogenation of carbon-oxygen bonds.

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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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.cattod.2020.07.070>.

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