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Efficient synthesis of methanol and ethylene glycol via the hydrogenation of CO_{DOL20.1039/D0CY00827C} View Article Online derived ethylene carbonate on Cu/SiO₂ catalysts with balanced Cu⁺-Cu⁰ sites

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Abstract

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Achieving high catalytic performance with Cu-based catalysts is crucial for the hydrogenation of CO₂-derived ethylene carbonate (EC) to yield methanol (MeOH) and ethylene glycol (EG) simultaneously. Although the Cu-based catalysts are widely studied for the target reaction, there are still some issues to be clarified. In this work, we prepared a 29.1 wt% Cu/SiO₂-MHT catalyst by a modified hydrothermal method and applied to the hydrogenation of EC successfully. In comparison with its three analogues with similar Cu loading and comparable Cu particle size but prepared by different methods, we found that the catalytic performance of Cu/SiO₂ catalysts including the activity and the selectivity to MeOH could be tuned by adjusting the Cu⁺/(Cu⁰+Cu⁺) ratio via different preparation methods. As a result, the Cu/SiO₂-MHT catalyst furnished 89% MeOH yield and 37.6 h⁻¹ turnover frequency, which are one of the highest values among all the heterogeneous Cu catalysts up to now to our best knowledge. The results reveal that the cooperative effect exists between Cu⁰ and Cu⁺. When Cu⁰ species are sufficient to activate H₂, the more Cu⁺ species and the higher Cu⁺ surface areas, the more favorable formation of MeOH. Furthermore, more Lewis acid amount on the Cu/SiO₂-MHT catalyst is also beneficial for MeOH formation.

Keywords: ethylene carbonate; hydrogenation; Cu⁺/(Cu⁰+Cu⁺) active sites; methanol; ethylene glycol

Introduction

In recent decades, it has been recognized that emission of large amount of carbon dioxide has caused an intractable environment crisis, which causes melting of glaciers, greenhouse effects and so on.^{1, 2} However, CO₂ can be utilized as an inexpensive and abundant renewable C1 resource. Therefore, it is of great significance to convert CO₂ to significant chemicals such as methanol (MeOH), which can thus alleviate the environmental and resource problems faced by human beings.³⁻⁵ Moreover, MeOH is readily applied to marketing as an important multifunctional chemical intermediate on the basis of a "Methanol Economy" concept.⁶

Conversion of CO₂ to MeOH can be realized either by the direct hydrogenation or the indirect hydrogenation. With regards of the direct hydrogenation of CO₂ to MeOH, it has been studied extensively. However, relatively harsh conditions (250-300 °C, 5-10 MPa) and unsatisfactory MeOH yields hinder the further industrialization.^{7, 8} Alternatively, Ding et al. ⁹ and Rueping et al. ¹⁰ demonstrated a mild and efficient route to convert CO₂ indirectly through the hydrogenation of ethylene carbonate (EC) to MeOH and ethylene glycol (EG) over the homogeneous complex catalysts, where EC was obtained via cycloaddition of CO₂ with ethylene oxide (Scheme 1). As a result, 99% or 92% MeOH yield has been achieved over the homogeneous pincer-type PNP/Ru or Mn-PNN complex catalyst, respectively. Of particular note is that the industrialization of CO₂-derived EC has been achieved through the cycloaddition reaction of EO and CO₂.¹¹ Nonetheless, due to the difficulty of product-catalyst separation in practical application for the homogeneous catalysts, heterogeneous catalysts are eager to be explored for the catalytic hydrogenation of EC to MeOH and EG.

Among the heterogeneous catalysts, Cu-based catalysts have been paid much attention to owing to the superior performance in C-O bond cleavage and thus in catalytic hydrogenation

of esters to alcohols.¹²⁻¹⁵ With regards of the catalytic hydrogenation of CO_2 -derived EC to the Article Online MeOH and EG, a pioneered report by Li et al. demonstrated that a heterogeneous $CuCr_2O_4$ catalyst with 28.5 wt% Cu loading gave 60% MeOH selectivity for the hydrogenation of EC. The authors considered metallic Cu species to be active sites.¹⁶ On the contrary, the cooperative effect of Cu⁰ and Cu⁺ has been proposed to enhance the hydrogenation of EC by other groups. Xia et al. found that a 70 wt% Cu/SiO₂-PG catalyst (prepared by a precipitationgel (PG) method) achieved 97% selectivity to MeOH at 6 MPa H₂ pressure. The authors regarded that an appropriate surface Cu⁺/(Cu⁺+Cu⁰) ratio was responsible for the high yield of MeOH.¹⁷ Almost at the same time, Dai et al. demonstrated that a 44.6 wt% Cu/HMS catalyst (prepared by an ammonia evaporation (AE) method) afforded 74% selectivity to MeOH. Based on characterizations, the highest yield of MeOH was originated from the maximum surface Cu⁺/(Cu⁺+Cu⁰) ratio of the 44.6 wt% Cu/HMS catalyst.¹⁸

Later, Li et al. found that a 10 wt% Cu/SBA-15-AE catalyst with the maximum $Cu^+/(Cu^++Cu^0)$ ratio (among those supported on SBA-15, MCM-41 and KIT-6) furnished the highest MeOH selectivity (62.3%).¹⁹ Furthermore, due to the increased Cu⁺/(Cu⁺+Cu⁰) ratio after modification with β -cyclodextrin, the catalytic ability of 26 wt% Cu@SiO₂- β -P-HP (synthesized by one-step hydrolysis precipitation method in the presence of β -cyclodextrin and P123) was also greatly improved, resulting in 71.8% MeOH selectivity. ²⁰ Recently, Yue and coworkers modulated the Cu/Si ratios to influence the Cu⁰/Cu⁺ ratio, as a result, a 33.3 wt% Cu/MCM-41 catalyst containing appropriate Cu⁺/(Cu⁺+Cu⁰) molar ratio, showed highest MeOH selectivity (70%).²¹

In our previous work, we also prepared Cu-based catalysts with different Cu loadings for the hydrogenation of EC. A ca. 60 wt% Cu₈-Mg₁-Zr_{0.47}/SiO₂ catalyst by a DP method with appropriate Cu⁺/(Cu⁺+Cu⁰) molar ratio, a 18.2 wt% Cu₈G₁/SiO₂-AE catalyst (synthesized by an AE method in the presence of glucose (G)) with the maximum Cu⁺/(Cu⁺+Cu⁰) molar ratio

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After a thorough literature survey, there are still some issues to be clarified. Although the synergetic Cu⁰ and Cu⁺ as active sites has been accepted by most people, their respective contributions and the relative Cu⁺/(Cu⁰+Cu⁺) ratios are still a matter of debate. Some authors pointed out that the maximum Cu⁺/(Cu⁺+Cu⁰) ratio had the highest catalytic ability for the EC hydrogenation. ^{18-19, 23, 25-26} However, other authors insisted the appropriate Cu⁺/(Cu⁺+Cu⁰) ratio responsible for the highest catalytic performance.^{17, 20-22, 24, 27} In addition, most studies were focused on the Cu loading effect of the Cu-based catalysts prepared by the same method (DP, PG, AE or HT) on the hydrogenation of EC; whereas the influence of preparation methods for the Cu-based catalyst with similar Cu loadings has been hardly investigated.

Herein, we prepared a Cu/SiO₂ catalyst with ca. 30 wt% Cu loading using a modified hydrothermal (MHT) method for the hydrogenation of EC under mild conditions. For comparison, the Cu/SiO₂ catalysts with similar Cu loading were also prepared using other three methods. As a result, the Cu/SiO₂-MHT catalyst afforded 99% selectivity to EG and 89% selectivity to MeOH at near full conversion of EC in a batch reactor. The results showed that the preparation methods had a strong influence on the Cu⁺/(Cu⁺+Cu⁰) ratio, Cu species surface areas and surface acidity even with the similar Cu loadings and comparable Cu particle sizes and thus the catalytic performance. Furthermore, the aforementioned issues were attempted to explore in combination with detailed characterization.

Experimental

Catalyst preparation

Chemical reagents including Cu(NO₃)₂·3H₂O (Sinopharm, 99%), NH₄Cl (Aladdin, View Article Online 99.8%), ammonia solution (Sinopharm, 25%-28%), NaOH (Sinopharm, 96%) and colloidal silica (Sigma-Aldrich, Ludox-HS, 40 wt.%) were purchased from commercial suppliers and used as received.

The **Cu/SiO₂-MHT** catalyst with nominal Cu loading of 30 wt% was prepared by a modified hydrothermal (MHT) method. Briefly, 1.57 g of Cu(NO₃)₂·3H₂O and 1.39 g of NH₄Cl were dissolved in deionized water (60 mL) firstly. Next, 5 mL of ammonia solution was dropwise added and stirred for 20 min. Then, silica sol with required amount was added into the above solution. After stirring at RT for additional 3 h, the blue mixture was transferred into a Teflon-lined autoclave and maintained in an oven at 200 °C for 48 h. Finally, the resulting solid were collected by filtration and washed with plenty of water, followed by drying in a vacuum oven at 60 °C overnight and calcination at 450 °C for 4 h to obtain the Cu/SiO₂-MHT catalyst precursors.

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For comparison, the Cu/SiO₂ catalysts with ca. 30 wt% Cu loading were also prepared by other methods. The Cu/SiO₂-AEH catalyst was prepared by an ammonia evaporation hydrothermal (AEH) method. In brief, 3.24 g of Cu(NO₃)₂·3H₂O was dissolved in 60 mL of deionized water, and 5 mL of ammonia solution was dropwise added to the above solution under vigorous stirring. Then, 5 g of silica sol was added to the above solution and the initial pH value was adjusted to 11~12 by additional ammonia solution. After stirring at RT for 4 h, the mixture was heated to 80 °C to evaporate ammonia until the pH value of the suspension decreased to 6-7. Subsequently, the mixture was hydrothermally treated at 200 °C for 12 h. Finally, the products were collected by filtration, followed by drying and calcination using the same procedures as above mentioned. The Cu/SiO₂-AEH except that there was no further

hydrothermal process. The Cu/SiO₂-PG catalyst was prepared by a PG method. Briefly, 39700 CY00827C g of Cu(NO₃)₂·3H₂O was firstly dissolved in 50 mL of deionized water. Next, an aqueous solution of NaOH (2 mol·L⁻¹) was dropwise added till the initial pH value reached above 11. Then, silica sol was added to the above solution. After that, the mixture was aged at 100 °C for 4 h. The precipitate was separated by hot filtration, followed by drying and calcination as the former Cu/SiO₂ catalysts.

Catalyst characterizations

Inductively coupled plasma atomic emission spectrometry (ICP-AES) was adopted to measure the actual Cu contents in the Cu/SiO₂ catalysts on a Thermo IRIS Intrepid II XSP. A Bruker D8 ADVANCE powder diffractometer with Cu K α radiation (λ =0.15418 nm) was applied to record the X-ray diffraction (XRD) patterns of samples at 25 mA and 35 kV. N₂ adsorption isotherms at 77 K of the samples was measured on a Quantachrome Autosorb-3B system after the samples were outgassed under vacuum at 200 °C for 2 h. The specific surface area of samples was calculated according to the Brunauer-Emmet-Teller (BET) equation from adsorption branch. Transmission electron microscopy (TEM) images of samples were taken by an FEI Tecnai G2-TF30 microscope at 300 kV. Fourier transform infrared (FT-IR) spectra of the as-calcined samples were performed on a NEXUS 870 spectrometer with a spectral resolution of 4 cm⁻¹ and 64 scans at RT.

The *in situ* FTIR spectroscopy was adopted to investigate the CO chemisorption, MeOH adsorption and pyridine adsorption on the samples with a Nicolet iS50 FTIR spectrometer. The sample was pressed into a self-supported wafer and placed into an *in situ* IR cell, followed by an *in situ* reduction in a hydrogen flow (30 mL min⁻¹) at 350 °C for 1 h and then cooled to RT with a N₂ flow (30 mL min⁻¹), and then the background spectrum was collected.

After that, various adsorbates were introduced separately for adsorption under different. View Article Online conditions. For MeOH adsorption, the temperature firstly increased from RT to 180 °C with N_2 flow. Then, MeOH was introduced to the IR cell by passing the H₂ flow (30 mL min⁻¹) through a MeOH bubbler kept at 0 °C for 20 min. Then, the IR spectrum was recorded at 180 °C. For pyridine adsorption, the sample was evacuated for 30 min, and then exposed to pyridine vapor at 30 °C for 10 min. Subsequently, the IR cell was evacuated at 150 °C for 20 min. After that, the spectrum was measured in the range of 1400-1700 cm⁻¹. For CO adsorption, the samples were exposed to CO (30 ml min⁻¹) for 10 min. Then, the sample was purged by N₂ (30 ml min⁻¹) for another 30 min. Finally, the spectra were recorded.

The *in situ* FTIR spectroscopy during the EC hydrogenation was also conducted using a Nicolet iS50 FT-IR spectrometer. Prior to the measurement, the sample was pressed into a 30 mm self-supported wafer, then the wafer was cut into two 13 mm self-supported wafers. The one was placed into an *in situ* IR cell and reduced in a flow of H₂ (99.999% purity, 30 mL min⁻¹) at 350 °C for 4 h just for the purpose of taking the background spectrum. The other one was reduced in a specially designed quartz tube similarly. Then, the reduced sample was transferred to a 1,4-dioxane solution containing 10 wt% EC without further exposure to air and soaked overnight to pre-adsorb EC. Subsequently, the sample with pre-adsorbed EC was placed into the *in situ* IR cell and increased to 180 °C with a flow of H₂ (30 mL·min⁻¹). The spectra were collected every 10 min at 180 °C.

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The reducibility of the as-calcined samples was measured by H_2 temperatureprogrammed reduction (H_2 -TPR) technique on a Micromeritics AutoChem II Chemisorption Analyzer. Typically, 100 mg of sample was pre-treated in a flow of He (30 ml min⁻¹) at 300 °C for 1 h and then cooled down to RT. After that, the sample was reduced in a flow of

H₂-Ar gas (10% H₂, 30 ml min⁻¹) from RT to 600 °C at a rate of 10 °C min⁻¹. The amount $\partial f^{V Article Online}$ H₂ consumption was determined by a thermal conductivity detector (TCD).

The surface acidity of samples was determined by temperature-programmed desorption of NH₃ (NH₃-TPD) on a Micromeritics AutoChem II Chemisorption Analyzer as well. 150 mg of the catalyst precursors was reduced in H₂-Ar gas (10% H₂, 30 ml min⁻¹) at 350 °C for 4 h firstly, and then cooled to 40 °C under a He flow (30 ml min⁻¹). Then, the sample adsorbed NH₃ in a 10% NH₃-He flow (30 ml min⁻¹) for 30 min. Subsequently, the sample was purged by He flow (30 ml min⁻¹) at 100 °C for 40 min. After that, the NH₃-TPD signal was recorded in a He flow by a TCD detector from 100 to 850 °C at a heating rate of 10 °C min⁻¹. In order to determine the acid amount quantitatively, the peak area of NH₃-desoprtion was calibrated with the given NH₃ volume, and then the surface acidity can be expressed as the desorbed NH₃ volume using this datum as a calculation standard. In addition, XPSPEAK41 software was adopted to deconvolute the desorbed NH₃ peaks and the amount of acid contained in each peak was calculated based on the area ratio of the total peak areas.

In order to understand the surface electronic properties of samples, the X-ray photoelectron spectroscopy (XPS) were performed on a Thermo Fisher Scientific ESCALAB 250Xi spectrometer with an Al K α radiation (1486.6 eV) after the sample was pretreated *in situ* under H₂ (>99.999%, 30 mL min⁻¹) at 350 °C for 4 h in a reactor attachment of the XPS spectrometer. All binding energies (BEs) were corrected using Si 2p peak at 103.5 eV of SiO₂ as reference.

The Cu/SiO₂ catalysts were also characterized by N₂O chemisorption and H₂-TPR method using a Quantachrome chemisorption apparatus (ChemBET 3000, USA) with a TCD. Firstly, 50 mg of sample was pretreated in a He flow at 200 °C for 1 h, followed by reduction in a H₂-N₂ mixed flow (10% H₂, 30 ml min⁻¹) at 350 °C for 2 h and then cooled to 90 °C under a He flow (30 ml min⁻¹). Next, 10% N₂O-90% He (30 ml min⁻¹) was introduced at 90 °C for 1

h to oxidize Cu to Cu₂O. Then, H₂-TPR was conducted in H₂-N₂ mixed gas (10% H₂, 30 mH <sup>Article Online min⁻¹) from 30 °C to 350 °C, and kept at 350 °C for 1 h.
The charge distribution were calculated at B3LYP/6-311+G(d,p) level by means of the natural bond orbital (NBO) program within the Gaussian 03 package.²⁸
Catalytic reaction
The liquid-phase hydrogenation of EC was carried out in a 50 mL stainless-steel
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autoclave (Anhui Kemi Machinery Technology Co., LTD.). Prior to reaction, 100 mg of ascalcined catalyst precursor was reduced in a specially-designed quartz tube in a flow of H₂ (99.999%, 30 ml min⁻¹) at 350 °C for 4 h and then cooled down to RT. Next, 10 mL of 10 wt% EC in 1,4-dioxane solution was injected into the specially-designed quartz tube under H₂ atmosphere to protect the catalyst from exposure to air. Subsequently, the mixture was immediately transferred into the autoclave. After flushed with 2 MPa of H₂ for five times, the autoclave was charged with 4 MPa H₂. Then, the reactor was heated. Once the temperature reached 180 °C, the hydrogenation was started with a magnetic stirring of 700 rpm. After a proper time, the reaction was stopped and the products were analyzed by a TECHCOMP GC-700 Plus GC equipped with a flame ionization detector and an DM-5 capillary column (30 m × 0.32 mm × 1µm). For recycling experiments, the catalyst was recovered by centrifugation and washed with plenty of solvent to remove the adsorbed reactants or products, and then submitted to the next run with fresh reactant and solvent.

EC conversion and product selectivity were defined as follows:

Conversion (%) =
$$\frac{\text{mol of reactant charged - mol of reactant left}}{\text{mol of reactant charged}} \times 100\%$$

Selectivity (%) = $\frac{\text{mol of product generated}}{\text{mol of reactant charged - mol of reactant left}} \times 100\%$

General characterizations

Fig. 1 shows the N₂ adsorption-desorption isotherms and the pore-size distributions of the Cu/SiO₂ catalysts. All the catalysts exhibited type-IV isotherms with an H1 or H3-type hysteresis loops at high pressures, demonstrating the mesoporous characteristics (Fig. 1A). For the Cu/SiO₂-MHT catalyst, it might contain some micropores as well. The pore size distribution curves (Fig. 1B) displayed a different peak centered at 3-40 nm for the Cu/SiO₂ catalysts. According to the literature, appearance of the pore centered at 3.3~3.6 nm was a hint of the formation of copper phyllosilicate.²⁹⁻³⁰ For clarity, Table 1 summarizes the physicochemical properties of various Cu/SiO₂ catalysts. The actual Cu contents for the Cu/SiO₂ catalysts prepared by different methods were very close to the nominal values (30%). Cu/SiO₂-MHT, Cu/SiO₂-AEH and Cu/SiO₂-AE had higher specific surface area (374, 445 and 438 m²/g, respectively) than Cu/SiO₂-PG (176 m²/g), while the average pore diameters of the former three Cu catalysts were smaller than that of Cu/SiO₂-PG.

Fig. 2 displays the XRD patterns of the as-calcined and the reduced catalysts. For the ascalcined catalysts (Fig. 2A), Cu/SiO₂-MHT, Cu/SiO₂-AEH and Cu/SiO₂-AE showed the characteristic diffraction peaks centered at 2θ = 30.8°, 35.0°, 57.5°, 62.3° and 71.2°, assignable to the copper phyllosilicate phases (JPCDS N0 027-0188).³¹ Moreover, no obvious CuO diffraction peaks were observed for as-calcined Cu/SiO₂-MHT, Cu/SiO₂-AEH and Cu/SiO₂-AE, suggesting that there was no CuO or CuO was highly dispersed. After reduction, the Cu/SiO₂ catalysts (MHT, AEH and AE) showed an intense diffraction peak at 36.5° along with several weak peaks at 42.2°, 61.5° and 73.6°, characteristic diffractions of Cu₂O phase (JCPDS 05-0667) (Fig. 2B). On the contrary, CuO diffraction peaks at 2 θ of 34.9°, 38.7°, 48.8°, 57.8°, 61.5°, 66.6° and 74.6° were obviously detected for as-calcined Cu/SiO₂-PG (JPCDS 05-0661). After reduction, the Cu/SiO₂-PG catalyst showed three typical $\underbrace{Cu}_{10.1039/DOCY00827C}$ diffraction peaks at 20 of 43.4°, 50.1° and 74° (JCPDS 04-0836) besides the characteristic diffraction peaks at 20 of 36.5° and 61.5° of Cu₂O phase.²¹ This indicates that the Cu/SiO₂ catalysts prepared by various methods resulted in different Cu species and thus different Cu⁺/(Cu⁰+Cu⁺) ratios, which might lead to different catalytic behaviors towards the hydrogenation of EC. Besides, the average Cu grain size and dispersion were calculated based on the diffraction peak at 20 of 36.5° according to the Scherrer equation. The Cu/SiO₂ catalysts had an average Cu particle size of 3.0-3.6 nm with the corresponding dispersion of 33.3%-27.8%, which are also listed in Table 1.

To deeply understand the dispersion and morphology, the Cu/SiO₂ catalysts were characterized by TEM (Fig. 3). All the Cu/SiO₂ catalysts had similar morphologies and the Cu particles were uniformly and highly dispersed. According to the statistic results, the Cu grain sizes for all the Cu/SiO₂ catalysts were comparable in the range of 3.4-4.2 nm with the relevant dispersion of 29.4%-23.8% (Table 1), in good agreement with the XRD results.

Additionally, N₂O titration is a typical technique for Cu-based catalysts to get the information about Cu dispersion. However, due to that three Cu/SiO₂ (AE, AEH and MHT) catalysts contained predominantly Cu₂O even after reduction, which made the hydrogen consumption too small during the N₂O titration, so that the calculated Cu dispersions deviated seriously from the real value (Table 1 and Fig. S1). Therefore, the Cu dispersions obtained from the TEM results were taken for the relevant calculations.

Catalytic performance of the Cu/SiO₂ catalysts

With these findings at hand, the Cu/SiO_2 catalysts were investigated for the liquid-phase hydrogenation of EC in a batch reactor (Fig. 4A). Under the conditions including 180 °C, 4

MPa of H₂ and 4 h, EC was almost completely converted over Cu/SiO₂-AE, Cu/SiO₂-AEHew Article Online and Cu/SiO₂-MHT, while that over Cu/SiO₂-PG was only 88.5%. About 99% selectivity to EG was obtained over all the Cu/SiO₂ catalysts. Interestingly, the selectivity to MeOH obtained with various Cu/SiO₂ catalysts was quite different. The selectivity to MeOH over Cu/SiO₂-PG, Cu/SiO₂-AE and Cu/SiO₂-AEH were 58.0%, 68.5% and 75.0%, respectively. To our delight, the Cu/SiO₂-MHT catalyst afforded MeOH selectivity of 88.9%, superior to other three analogues.

We noticed that MeOH selectivity was lower than that of EG; while the selectivity to MeOH should be equal to that to EG theoretically. As well known, EC can be easily hydrolyzed to EG, CO and CO₂, which is rather difficult to completely restrict due to that trace water in the reactants such as EC, solvent and hydrogen cannot be absolutely removed.¹⁸ Moreover, we analyzed the gas-phase products after reaction. Correspondingly, CO and CO₂ were detected, which were originated from the hydrolysis of EC.^{18, 24} In addition, MeOH would inevitably decompose to CO, which was confirmed by the *in situ* FTIR spectra of MeOH adsorbed on the Cu/SiO₂-MHT catalyst (Fig. S2).

In order to compare the catalytic ability of the Cu/SiO₂ catalysts prepared by different methods more fairly, we calculated the TOF values (defined as the moles of formed MeOH per mole of surface Cu sites per hour). As listed in Table 1, the Cu/SiO₂-MHT catalyst showed the highest TOF (22.4 h⁻¹) among the four Cu/SiO₂ catalysts, while the Cu/SiO₂-PG catalyst gave the lowest TOF (14.3 h⁻¹). That is, the preparation methods for the Cu/SiO₂ catalysts affected the MeOH selectivity remarkably although they had similar Cu loadings and comparable Cu particle sizes.

Based on the above discussions, the Cu/SiO_2 -MHT catalyst was the most active and selective among all the Cu/SiO_2 catalysts in this study. In order to explore the superiority of the Cu/SiO_2 -MHT catalyst to the greatest extent, the influence of reduction temperature for

the Cu/SiO₂-MHT catalyst precursors was studied in the range of 250-400 °C. As shown if the value of the Cu/SiO₂-MHT catalyst precursors was studied in the range of 250-400 °C. As shown if the value of the temperature is the temperature is the temperature of the temperature is the temperature is the temperature. It increased with the reduction temperature initially till the reduction temperature reached 350 °C. Further increasing the reduction temperature made the MeOH selectivity decrease instead. As a result, the Cu/SiO₂-MHT catalyst after reduction at 350 °C showed the best catalytic performance. The effect of reduction temperature for the Cu/SiO₂-MHT catalyst will be further discussed in combination with H₂-TPR results in the following part.
Furthermore, the reusability of the Cu/SiO₂-MHT catalyst was also investigated for the hydrogenation of EC. As displayed in Fig. 5A, the Cu/SiO₂-MHT catalyst could be easily

hydrogenation of EC. As displayed in Fig. 5A, the Cu/SiO₂-MHT catalyst could be easily recycled and reused for at least 5 times without any loss in EC conversion or selectivity to MeOH or EG. However, EC conversion declined gradually from 99% to 84.2% during the 6th to the 10th cycles, although the selectivity to MeOH and EG almost remained stable even after the 10th cycle. To reveal the reason for the declining EC conversion during the recycling experiments, the catalyst was weighed firstly after 10 runs. As a result, nearly 30% of the Cu/SiO₂-MHT catalyst was washed off the catalytic system during the 10 recycling processes. Secondly, the Cu particle size was also checked for the spent Cu/SiO₂-MHT catalyst was comparable with the fresh one. This suggests that the Cu/SiO₂-MHT catalyst was stable enough during the recycling processes. The finding was also verified by the TEM image of the used Cu/SiO₂-MHT catalyst (Fig. S4), where many Cu particles with 3-5 nm diameter were detected.

Subsequently, the kinetic behaviors were investigated over Cu/SiO₂-MHT catalyst as well (Fig. 5B). With the reaction going on, EC conversion increased steadily and smoothly. As a result, full conversion of EC was realized within 3 h. A linear correlation was obtained between lnC_0/C_t with reaction time, indicating the first order reaction with respect to EC (see

Besides, in order to further understand the Cu/SiO₂-MHT catalyst, we also compared the Cu/SiO₂-MHT catalyst with the heterogeneous Cu catalysts applied to the hydrogenation of EC in a batch reactor in the literature. Accordingly, the mass specific activity (MSA, defined as converted EC in gram per gram of Cu per hour) and TOF were calculated according to the original data in the literature, which are summarized in Table 2 for convenience. Clearly, the CuCr₂O₄ catalyst and the Cu/SiO₂-PG catalyst gave an MSA of 1.2-1.5 g_{EC} g_{Cu}⁻¹ h⁻¹ and 7.0-10.1 h⁻¹ TOF, respectively.¹⁶⁻¹⁷ The Cu/SBA-15-AE catalyst, the Cu/SiO₂-AE catalyst and the S-1@Cu catalyst exhibited a higher MSA of 7.2-7.8 g_{EC} g_{Cu}⁻¹ h⁻¹, with the TOF ranging from 12.3 to 18.1 h⁻¹.^{19, 24, 27} In our previous studies, the Cu₈G₁/SiO₂-AE catalyst realized an MSA of 13.2 g_{EC} g_{Cu}⁻¹ h⁻¹ with a TOF value of 38.7 h⁻¹.²³ With regards of the Cu/SiO₂-MHT catalyst in this work, according to the kinetic results that the EC conversion of 88.6% was achieved at 2.2 h, the MSA of 15.5 g_{EC} g_{Cu}⁻¹ h⁻¹ and a TOF value of 37.6 h⁻¹ were furnished, which are one of the highest values among all the heterogeneous Cu catalysts up to now to our best knowledge. Regarding of the MeOH selectivity furnished by the Cu/SiO₂-MHT catalyst, it is

Characterization of Cu species

In this work, the Cu/SiO₂ catalysts prepared by different methods gave very different catalytic performance, particularly for the MeOH selectivity (Fig. 4A). The ICP-AES and TEM results showed that the four Cu/SiO₂ catalysts have comparable Cu loadings and similar Cu particle size. Hence, these factors can be ignored in the following discussion. To deeply

comprehend the influence of preparation methods, the surface Cu species on the Cu/SiQ_{39/D0CY00827C} catalysts were further characterized using a series of techniques.

Based on the XRD patterns (Fig. 2A), copper phyllosilicate is predominant for the ascalcined Cu/SiO₂ (MHT, AEH and AE). In order to characterize the amount of copper phyllosilicate in the as-calcined catalyst, the as-calcined catalyst was evaluated by FTIR firstly (Fig. 6). The bands at 1100 cm⁻¹ and 800 cm⁻¹ are attributed to the asymmetric and symmetric stretching vibration of Si-O-Si in SiO₂, respectively. Moreover, the δ_{OH} vibration at 670 cm⁻¹ and the v_{SiO} should r peak at 1040 cm⁻¹ confirms the formation of copper phyllosilicate in as-calcined Cu/SiO₂ (MHT, AEH and AE). ³²⁻³³ However, these two typical IR bands were not clearly observed for as-calcined Cu/SiO₂-PG, suggesting that no plenty of copper phyllosilicate was likely formed in as-calcined Cu/SiO₂-PG. Nevertheless, a new band at approximately 969 cm⁻¹ appeared for as-calcined Cu/SiO₂-PG, indicating the formation of Cu-O-Si species.³⁴⁻³⁵ Thence, in combination with the XRD results, as-calcined Cu/SiO₂ (MHT, AEH and AE) had much copper phyllosilicate and a little highly dispersed CuO, while as-calcined Cu/SiO₂-PG contained CuO and Cu-O-Si units predominantly. In addition, the relative amount of copper phyllosilicate in as-calcined Cu/SiO₂ was also determined using the peak area ratio I_{670}/I_{800} at 670 cm⁻¹ and 800 cm⁻¹.¹⁸ As a result, the relative amount of copper phyllosilicate (I₆₇₀/I₈₀₀) followed an order of Cu/SiO₂-PG < Cu/SiO₂-AE < Cu/SiO₂-AEH < Cu/SiO₂-MHT (see the inset of Fig. 6).

After reduction, Cu⁰ and Cu⁺ coexisted for all the catalysts (Fig. 2B), which can be verified by H₂-TPR and XPS. As displayed in Fig. 7 for the H₂-TPR profiles of the ascalcined catalysts, all of them presented one reduction peak at around 220 °C, ascribe to the reduction of highly dispersed small CuO particles.^{21, 36} This indicates that four Cu/SiO₂ catalysts had uniform particle size distribution, in accordance with XRD and TEM results. According to the literature, either the reduction of highly dispersed CuO to Cu⁰ or the

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reduction of copper phyllosilicate to Cu⁺ occurs at approximately 240 °C. ^{33, 37} Further View Article Online View Article reduction of the Cu⁺ species derived from copper phyllosilicate to Cu⁰ needs much higher temperature of around 600 °C, while the reduction of bulk CuO particles to Cu⁰ takes place at slightly higher temperature (273 °C). ³⁷⁻³⁹ Therefore, the asymmetric peak at around 260 °C for Cu/SiO₂-PG could be the combined contribution from the reduction of highly dispersed CuO to Cu⁰ and Cu-O-Si to Cu⁺-O-Si.³⁴ As for Cu/SiO₂-MHT, Cu/SiO₂-AEH and Cu/SiO₂-AE, the main peak at around 220 °C was attributed to the combined reduction of well-dispersed CuO to Cu⁰ and copper phyllosilicate to Cu⁺. Nevertheless, there was a slight shift in the dominant reduction peak for Cu/SiO₂-MHT, Cu/SiO₂-AEH and Cu/SiO₂-AE, probably due to different amount of copper phyllosilicate. In addition, a small peak centered at around 300 °C for Cu/SiO₂-AEH and Cu/SiO₂-MHT was attributed to the reduction of the well-dispersed Cu species with stronger interaction with SiO₂.^{22, 40} This suggests that the Cu/SiO₂-MHT catalyst had the strongest Cu-SiO₂ interaction probably produced during the hydrothermal process. This can also explain the reduction temperature effect for the Cu/SiO₂-MHT catalyst in Fig. 4B. When the reduction temperature is below 350 °C, the Cu/SiO₂-MHT catalyst cannot be completely reduced; whereas at higher reduction temperatures, Cu particles would unavoidably aggregate.

To examine the surface chemical states of Cu species on the Cu/SiO₂ catalyst surface, Cu 2p XPS spectra were recorded after *in-situ* pretreated in a hydrogen flow. As shown in Fig. 8A, two distinct peaks at around 932.5 and 952.4 eV for all the samples were attributed to Cu $2p_{3/2}$ and Cu $2p_{1/2}$ of Cu⁰/Cu⁺ species, respectively. ⁴¹⁻⁴² It seemed that Cu²⁺ species were completely reduced to Cu⁺/Cu⁰ species because no Cu²⁺ satellite peak was detected.³⁷ Moreover, Cu LMM electron spectra were measured as a supplement in that Cu2p XPS spectra was hard to distinguish Cu⁺ and Cu⁰ species due to their similar BEs. All the catalysts exhibited a broad and asymmetric peak, which was deconvoluted to four peaks using

Lorenz/Gaussian of 1/99 (Fig. 8B).^{17, 24} The peaks at approximately 918.6 and 916.5 eV, were reference online assigned to Cu⁰ and Cu⁺ species, respectively, which were adopted to calculate the Cu⁺/(Cu⁺+Cu⁰) ratios.^{17, 41, 43-44} As a result, the Cu⁺/(Cu⁺+Cu⁰) ratios for Cu/SiO₂-PG, Cu/SiO₂-AE, Cu/SiO₂-AEH and Cu/SiO₂-MHT were 22.8%, 36.6%, 48.4% and 55.6%, respectively. Additionally, the surface area of Cu⁺ (S_{Cu}⁺) was also estimated in combination with Cu⁰ surface area (S_{Cu}⁰) and the ratio of Cu⁺/(Cu⁺+Cu⁰) from the Cu LMM analysis, where S_{Cu}⁰ was calculated according to 649×D_{Cu}×Cu loading (wt%).^{17, 21} For clarity, Table 3 summarizes the relevant parameters for Cu species. The S_{Cu}⁺ also followed the sequence of Cu/SiO₂-PG < Cu/SiO₂-AE < Cu/SiO₂-AEH < Cu/SiO₂-MHT. It is notable that the Cu/SiO₂-MHT catalyst had the highest Cu⁺/(Cu⁺+Cu⁰) ratio and the largest S_{Cu}⁺, in good accordance with the largest amount of copper phyllosilicate in as-calcined Cu/SiO₂-MHT (Fig. 6).

Subsequently, the *in situ* CO-FTIR spectroscopy was applied to further probe the surface Cu species in the Cu/SiO₂ catalysts (Fig. 9A).¹² Considering that CO adsorption on Cu²⁺ or Cu⁰ sites is weak and no Cu²⁺ species existed after reduction, the band at 2126 and 2112 cm⁻¹ should be ascribed to Cu⁺-CO species.^{12, 41, 45-46} Hence, the normalized integral areas of the bands at 2126 and 2112 cm⁻¹ can be correlated qualitatively to the relative amounts of Cu⁺ in the Cu/SiO₂ catalysts (Table 3), which increased by the order of Cu/SiO₂-PG < Cu/SiO₂-AE < Cu/SiO₂-AEH < Cu/SiO₂-MHT, in good agreement with the observation from the Cu LMM results (Fig. 8B). The normalized integral areas of Cu⁺-CO IR peak A_{Cu}^+ *versus* S_{Cu}^+ derived from Cu LMM spectra shows a good linear correlation (Fig. 9B), indicating that the results are reasonable and reliable.

Characterization of surface acidity

Additionally, it is apparent that the acidity of the Cu-based catalysts also played an important role in MeOH selectivity. Based on the literature, Cu⁺ species act as strong Lewis

acid sites to polarize the C=O groups, and thus facilitate the EC activation. ^{18, 47} In order to warticle Online understand the surface acidity of the Cu/SiO₂ catalysts, the NH₃-TPD technique was adopted (Fig. 10A). All the samples showed an intense NH_3 -desorption peak in 100-400 °C, indicating the existence of the weak and medium acidity.^{28, 48} The origin of the catalyst surface acidity might be traced back to the Cu⁺ species.¹⁷⁻¹⁸ Moreover, the quantitative calculation demonstrated that Cu/SiO₂-MHT had the highest surface acidity among the four Cu/SiO₂ catalysts. The total surface acidity follows the sequence of Cu/SiO₂-PG (0.64 mmol g^{-1}) < Cu/SiO_2 -AE (1.13 mmol g⁻¹) < Cu/SiO_2 -AEH (1.28 mmol g⁻¹) < Cu/SiO_2 -MHT (1.37 mmol g⁻¹) ¹). Deconvolution of the broad peak resulted in two peaks at weak acidity region ($\leq 200 \text{ °C}$) and medium acidity region (200-400 °C), respectively. The acid strength of the Cu/SiO₂ catalysts followed the sequence of Cu/SiO₂-PG \approx Cu/SiO₂-AE < Cu/SiO₂-AEH \approx Cu/SiO_2 -MHT at the medium acidity region, because the NH₃ desorption peaks from the Cubased catalysts gradually shifted to higher temperatures. Additionally, we performed a curve fitting on the acid amount and the sum copper specific surface areas $(S_{Cu}^{+}+S_{Cu}^{0})$, which showed a quasi-linear correlation (Fig. S5), suggesting that the acidity of the catalyst is derived from Cu species.

Furthermore, to distinguish the types of the surface acidity of the Cu/SiO₂ catalysts, the pyridine-FTIR spectroscopy was applied (Fig. 10B). All the Cu/SiO₂ catalysts showed three IR bands centered at about 1450, 1490 and 1607 cm⁻¹. The bands at 1450 and 1607 cm⁻¹ are attributed to pyridine adsorbed on Lewis acid sites (LAS) while the one at 1490 cm⁻¹ is assigned to the combinational contribution of pyridine adsorbed on both Lewis and Brönsted acid sites.⁴⁹⁻⁵¹ No typical IR band at 1540 cm⁻¹, characteristic of pyridine adsorbed on Brönsted acid sites, was detected for all samples, indicating that only LAS existed on all the Cu/SiO₂ catalysts.

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Further discussions

Based on the catalytic performance and characterization results, different preparation methods led to different Cu species in the as-calcined samples and thus different $Cu^{+}/(Cu^{+}+Cu^{0})$ ratios in the reduced Cu/SiO₂ catalysts. More copper phyllosilicate resulted in higher Cu⁺/(Cu⁺+Cu⁰) ratio and thus higher S_{Cu⁺}. The Cu⁺/(Cu⁺+Cu⁰) ratios and Cu species surface areas greatly influenced both the catalyst activity and MeOH selectivity. Two-site mechanism is usually proposed that Cu⁰ species activate H₂ and facilitate the hydrogenation reaction, while the Cu⁺ species adsorb and activate the carbonyl group.^{32, 52} According to the reaction results, EC conversion increased as a sequence of Cu/SiO₂-PG (88.5%) < Cu/SiO₂-AE \approx Cu/SiO₂-AEH \approx Cu/SiO₂-MHT \approx 99%. However, S_{Cu}⁰ increased as an order of Cu/SiO₂-PG < Cu/SiO₂-MHT < Cu/SiO₂-AE < Cu/SiO₂-AEH. Interestingly, the MeOH selectivity increased with a different sequence of Cu/SiO₂-PG < Cu/SiO₂-AE < Cu/SiO₂-AEH < Cu/SiO₂-MHT, which had the same trend as Cu⁺/(Cu⁺+Cu⁰) ratio and S_{Cu⁺}, suggesting that when the amount of Cu^0 species is sufficient, the higher $Cu^+/(Cu^++Cu^0)$ ratio and S_{Cu^+} , the more favorable formation of MeOH. To visually understand the correlation between the reaction results and Cu⁰ or Cu⁺ species, we attempted to correlate the EC conversion and MeOH selectivity with Cu^0 surface area or $Cu^+/(Cu^++Cu^0)$ ratio separately (Fig. 11). Remarkably, such a MeOH selectivity ascending trend is also consistent with the increasing acidity of the Cu/SiO₂ catalysts. This implies that more Lewis acid amount is favorable for MeOH formation in weak and medium acidity region.

As a result, the preparation methods for the Cu/SiO₂ catalysts affected the surface $Cu^+/(Cu^++Cu^0)$ ratios strongly, so that the copper species surface areas and surface acidity were influenced correspondingly. The Cu/SiO₂-MHT catalyst, prepared by a modified hydrothermal method, had the highest $Cu^+/(Cu^++Cu^0)$, the largest Lewis acidity, the highest 20

 S_{Cu^+} among the four Cu/SiO₂ catalysts, which were definitely helpful for the hydrogenation of the contract of the con

Possible reaction pathways

In order to explore the reaction pathway of EC hydrogenation, the evolution of the EC adsorbed on the Cu-SiO₂-MHT catalyst in flowing H₂ was studied using the *in-situ* FTIR spectroscopy (Fig.12). Two main bands at 1798 and 1770 cm⁻¹ were observed for EC adsorbed on the Cu-SiO₂-MHT catalyst, assignable to the C=O stretching vibration of the EC molecules.^{24, 53} After switching H₂ flow, the C=O stretching vibration gradually decreased with time. Meanwhile, some new broad bands appeared (the coloured regions), which are highly consistent with the vibration bands of EG and MeOH, proving that the hydrogenation of EC to MeOH and EG indeed occurs on the Cu-SiO₂-MHT catalyst surface. Additionally, we analyzed the charge distributions of the EC molecule by DFT calculation (Fig. S6). The charge density of O atom attached to the C=O group was -0.326 eV. In contrast, the charge density of the O atom connected to the C-O group was -0.155 eV. The results implied that the O atom on C=O could preferentially interact with the acid sites (as electron acceptors).

Based on the findings at hand, we proposed two possible pathways for the EC hydrogenation to MeOH and EG (Scheme 2). The surface Cu⁰ species dissociatively adsorb H₂ firstly, leaving two ·H bonded to Cu⁰ surface. Meanwhile, the surface Lewis acidic Cu⁺ sites adsorb and polarize the O atoms in carbonyl O=C groups with p- π conjugated effect.⁵⁴ For pathway A, ·H attacks C-O bond and effectively destroys the C-O bond, forming an EG molecule and leaving an intermediate ·CH₂O bonded to the Cu⁺ species via Cu⁺-O bond. Then, the ·CH₂O is further hydrogenated to MeOH. For pathway B, the reaction process is similar expect that the ·H attacks C=O firstly, followed by attacking C-O secondly with simultaneous formation of MeOH and EG.

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Conclusions

In summary, the Cu/SiO₂-MHT catalyst with ca. 30 wt% Cu loading was prepared by a modified hydrothermal method for the liquid-phase hydrogenation of EC to yield MeOH and EG simultaneously. For comparison, the Cu/SiO₂ catalysts with similar Cu loading were also prepared by different methods such as PG, AE and AEH. Interestingly, the Cu/SiO₂ catalysts had similar Cu particle size despite of the preparation methods. However, when submitted to the hydrogenation of EC, the Cu/SiO₂-MHT catalyst showed superior catalytic performance to its three analogues, furnishing 99% EG selectivity and 89% MeOH selectivity at nearly complete EC conversion. A 37.6 h⁻¹ turnover frequency of MeOH formation was reached on the Cu/SiO₂-MHT catalyst, one of the highest values among all the heterogeneous Cu catalysts up to now to our best knowledge. Furthermore, the Cu/SiO₂-MHT catalyst can be easily recycled and reused for at least 10 times without obvious loss in EC conversion or MeOH selectivity. In combination with the detailed characterization results, the preparation methods influenced strongly the $Cu^+/(Cu^++Cu^0)$ ratio and Cu^+ surface areas S_{Cu^+} , and thus the catalytic performance. When the amount of Cu⁰ species is sufficient, the higher surface $Cu^{+}/(Cu^{+}+Cu^{0})$ ratio and $S_{Cu^{+}}$, the more favorable formation of MeOH. In addition, more Lewis acid amount and stronger Lewis acid site of the Cu/SiO₂-MHT catalyst is also helpful for MeOH formation. The findings in this study may provide some fundamental insights into the design and preparation of effective Cu-based catalysts for the hydrogenation of esters.

Conflict of interest

There are no conflicts to declare.

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Catalyst	Cu loading	S _{BET}	Av. Pore	V _{pore}	D _{Cu} ^b	D _{Cu} ^c	$D_{Cu}^{\ \ d}$	TOF _{MeOH} ^e	Crystallite Size (nm)	
	(wt%) ^a	(m^2g^{-1})	size (nm)	$(cm^3 g^{-1})$	(%)	(%)	(%)	(h ⁻¹)	by XRD ^f	by TEM
Cu/SiO ₂ -MHT	29.1	374	9.5	0.83	29.4	27.0	70.4	22.4	3.1	3.7
Cu/SiO ₂ -AEH	27.7	445	9.2	1.02	33.3	29.4	77.5	18.2	3.0	3.4
Cu/SiO ₂ -AE	28.3	438	7.7	0.78	32.3	28.6	65.6	16.6	3.1	3.5
Cu/SiO ₂ -PG	30.2	176	28.1	1.20	27.8	23.8	29.3	14.3	3.6	4.2

Table 1 Physicochemical properties of various Cu/SiO₂ catalysts.

^a Determined by ICP-AES.

^b Cu dispersion obtained by D_{Cu} (%) = 1.0/d_{Cu} (nm) (d_{Cu}: mean Cu particle size from XRD results).

^c Cu dispersion obtained by D_{Cu} (%) = 1.0/d_{Cu} (nm) (d_{Cu}: mean Cu particle size based on TEM results).

^dCu dispersion obtained by N₂O titration.

^e TOF_{MeOH} (turnover frequency, defined as the moles of formed MeOH per mole of surface Cu sites per hour).

^f Cu crystallite size was calculated by the Scherrer equation.

		Т	P _{H2}	t	Cu loading	EC Conv.	MSA ^d	Sel. (·%)	TOF _{MeOH} ^e	
Entry Catalyst	Catalyst	(°C)	(MPa)	(h)	(wt%)	(%)	$(g_{EC} g_{Cu}^{-1} h^{-1})$	МеОН	EG	(h ⁻¹)	Ref.
1	CuCr ₂ O ₄	180	5	3	28.5	75.0	1.5	60.0	93.0	10.1	16
2 ^a	Cu-SiO ₂ -PG	160	6	10	70.0	99.0	1.2	97.0	98.0	7.0	17
3 ^b	Cu/SBA-15-AE	180	5	4	10.0	62.1	7.8	50.7	98.1	12.3	19
4	Cu/SiO ₂ -AE	180	5	6	9.5	83.5	7.3	71.5	98.2	16.3	27
5°	$Cu@SiO_2-\beta-P-HP$	210	5	4	26.0	97.4	1.2	71.8	97.8	3.9	20
6	5β - $25Cu/SiO_2$	180	5	4	25.0	94.2	4.7	71.6	98.8	8.1	26
7	Cu_8G_1/SiO_2 -AE	180	4	2.5	18.2	96.0	13.2	86.0	99.0	38.7	23
8	S-1@Cu	180	4	4	21.4	98.0	7.2	74.0	99.0	18.1	24
9	Cu/SiO ₂ -MHT	180	4	2.2	29.1	88.6	15.5	90.0	99.0	37.6	This work

Table 2 Catalytic properties of the second seco	ne Cu/SiO ₂ catalysts	for the selective hydrogenation	of EC in a batch reactor.
		for the serective hydrogenation	

^a Prepared by a precipitation-gel (PG) method. ^b Prepared by ammonia evaporation (AE) method. ^c Prepared by hydrolysis precipitation (HP) method. ^d Mass specific activity (MSA) was defined as converted EC in gram per gram of copper per hour. ^e TOF_{MeOH} (turnover frequency, defined as the moles of formed MeOH per mole of surface Cu sites per hour).

Catalyst	$S_{Cu^0}{}^a$	$X_{Cu^{^{+}}}{}^{b}$	$S_{Cu^+} {}^{c}$	$A_{Cu}{}^{\!$	Acid amount ^e	
Catalyst	(m ² g ⁻¹)	(%)	(m^2g^{-1})	(area/g)	(mmol g ⁻¹)	
Cu/SiO ₂ -MHT	51.0	55.6	63.9	629.2	22.4	
Cu/SiO ₂ -AEH	52.9	48.4	49.6	478.0	18.2	
Cu/SiO ₂ -AE	52.5	36.6	30.3	189.5	16.6	
Cu/SiO ₂ -PG	46.6	22.8	13.8	108.5	14.3	

Table 3 Characterization of Cu species for the Cu/SiO₂ catalysts

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^a $S_{Cu^0} = Cu^0$ Surface area, calculated according to 649× D_{Cu} ×Cu loading (wt%)

^b X_{Cu^+} represents Cu⁺/(Cu⁺+Cu⁰) ratio calculated from Cu LMM spectra.

^c $S_{Cu^+} = Cu^+$ Surface area, calculated on the basis of X_{Cu^+} and S_{Cu^0} .

^d Normalized integral area of the peaks of CO chemisorbed on active Cu⁺ in *in-situ*

FT-IR spectra.

^e Quantitatively calculated from NH₃-TPD



Scheme 1 Indirect conversion of CO2 to MeOH and EG via the hydrogenation of

CO₂-derived EC.





Scheme 2 Proposed reaction pathways for the hydrogenation of EC over the Cu/SiO₂ catalysts.

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Fig. 1 (A) N₂ adsorption-desorption isotherms and (B) pore size distributions of various Cu/SiO₂ catalysts.



Fig. 2 XRD patterns of (A) as-calcined and (B) reduced Cu/SiO₂ catalysts.

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Fig. 3 TEM images of the reduced Cu/SiO₂ catalysts.



Fig. 4 (A) Catalytic performance of the Cu/SiO₂-PG, Cu/SiO₂-AE, Cu/SiO₂-AEH, and Cu/SiO₂-MHT catalysts in the hydrogenation of EC to MeOH and EG. (B) The influence of reduction temperature for the Cu/SiO₂-MHT catalyst precursor on the EC hydrogenation. Reaction conditions: 10 mL of 10 wt% EC in 1,4-dioxane, 100 mg of Cu/SiO₂ catalyst, 180 °C, 700 rpm, 4 MPa of H₂, 4 h.



Fig. 5 (A) The kinetic profile of EC hydrogenation over the Cu-SiO₂-MHT catalyst.
(B) The reusability of the Cu/SiO₂-MHT catalyst in EC hydrogenation. Reaction conditions: 10 mL of 10 wt% EC in 1,4-dioxane, 100 mg of Cu/SiO₂ catalyst, 180 °C, 700 rpm, 4 MPa of H₂, 4 h.



Fig. 6 FT-IR spectra of as-calcined Cu/SiO₂ prepared by different methods (The inset shows the I_{670}/I_{800} (R) intensity ratio for various catalysts).

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Fig. 7 H₂-TPR profiles of as-calcined Cu/SiO₂ catalysts.



Fig. 8 (A) The *in situ* Cu 2p XPS spectra and (B) Cu LMM Auger spectra of (a) Cu/SiO₂-MHT, (b) Cu/SiO₂-AEH, (c) Cu/SiO₂-AE and (d) Cu/SiO₂-PG.



Fig. 9 (A) *In situ* FTIR spectra of CO adsorbed on the Cu/SiO₂ catalysts. (B) The correlation of the estimated Cu⁺ specific surface area (S_{Cu}^+) derived from Cu LMM spectra and the integral area (A_{Cu}^+) of the peaks from the *in situ* FTIR spectra of CO chemisorption.



Fig. 10 (A) NH₃-TPD profiles of the Cu/SiO₂ catalysts and (B) *in situ* FTIR spectra of pyridine adsorbed on (a) Cu/SiO₂-MHT, (b) Cu/SiO₂-AEH, (c) Cu/SiO₂-AE and (d) Cu/SiO₂-PG.



Fig. 11 The correlation of EC conversion or MeOH selectivity with Cu^0 specific surface area or $Cu^+/(Cu^++Cu^0)$.



Fig. 12 FTIR spectra of *in-situ* EC hydrogenation on the Cu/SiO₂-MHT catalyst in flowing hydrogen at 180 °C.

View Article Online DOI: 10.1039/D0CY00827C Efficient synthesis of methanol and ethylene glycol via the hydrogenation $_{DOf:} CO_{29/D0CY00827C}^{View Article Online}$ derived ethylene carbonate on Cu/SiO₂ catalysts with balanced Cu⁺-Cu⁰ sites

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The preparation method for Cu/SiO_2 catalysts had a great impact on the Cu^+/Cu^0 ratio and thus the catalytic performance.