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An efficient and stable Cu/SiO₂ catalyst for the syntheses of ethylene glycol and methanol via chemoselective hydrogenation of ethylene carbonate

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ABSTRACT

The efficient synthesis of methanol and ethylene glycol via the chemoselective hydrogenation of ethylene carbonate (EC) is important for the sustainable utilization of CO₂ to produce commodity chemicals and fuels. In this work, a series of β-cyclodextrin-modified Cu/SiO₂ catalysts were prepared by ammonia evaporation method for the selective hydrogenation of EC to co-produce methanol and ethylene glycol. The structure and physicochemical properties of the catalysts were characterized in detail by N₂ physisorption, XRD, N₂O titration, H₂-TPR, TEM, and XPS/XAES. Compared with the unmodified 25Cu/SiO₂ catalyst, the involvement of β-cyclodextrin in 5β-25Cu/SiO₂ could remarkably increase the catalytic activity—excellent activity of 1178 mg_{EC} g_{cat}⁻¹ h⁻¹ with 98.8% ethylene glycol selectivity, and 71.6% methanol selectivity could be achieved at 453 K. The remarkably improved recyclability was primarily attributed to the remaining proportion of Cu⁺/(Cu⁰+Cu⁺). Furthermore, the DFT calculation results demonstrated that metallic Cu⁰ dissociated adsorbed H₂, while Cu⁺ activated the carbonyl group of EC and stabilized the intermediates. This study is a facile and efficient method to prepare highly dispersed Cu catalysts—this is also an effective and stable heterogeneous catalyst system for the sustainable synthesis of ethylene glycol and methanol via indirect chemical utilization of CO₂.

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1. Introduction

Utilization of CO₂ as an important C1 building block for syn-thesizing high-value chemicals and liquid fuels has recently gained considerable global attention [1–3]. Various routes have been exploited for the conversion of CO₂ into valuable fuels and

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chemicals such as ethanol [4], carbamic ester [5], ethylene carbonate [6], dimethyl ether [7], methanol [8], etc. Significant efforts have been devoted to transform CO₂ with renewable hydrogen to methanol [9,10] because methanol is not only a key chemical feedstock for producing various valuable chemicals but is also an alternative transportable fuel [11]. Nevertheless, direct hydrogenation of CO₂ to methanol suffers from low reaction efficiency due to its low thermodynamic stability and the severe reaction conditions required to overcome the kinetic inertia of CO₂ [12].

Coupling of energetic compounds can overcome the thermodynamic and kinetic constraints and result in efficient utilization of CO₂. Thus, the efficient hydrogenation of CO₂ to chemicals via indirect pathways can be performed under relatively mild reaction conditions with satisfactory yields [13–15]. Alternatively, indirect hydrogenation of CO₂ via ethylene carbonate (EC) intermediate to co-produce methanol (MeOH) and ethylene glycol (EG) is a promising approach for environmentally friendly syntheses of sustainable chemical feedstocks and fuels (Scheme 1). EC is industrially available from CO₂ and ethylene oxide, and this process is well established. Therefore, more attention has been devoted to developing an effective catalyst for EC hydrogenation.

The hydrogenation of EC can be effectively catalyzed via Ru(II)-PNP complexes as a homogeneous catalyst [16]. Afterwards, Ru(II)-NHC complexes were also reported, and they showed efficient catalytic performance [17]. In terms of the easy catalyst recovery, increasing attention is given to effective heterogeneous catalyst. In recent years, various types of catalysts, e.g. CuCr₂O₄ [18], Cu–SiO₂-PG [19], Cu/HMS [20], Cu/SBA-15 [21], and Cu/SiO₂-AE [14], were reported to catalyze the hydrogenation of EC. The versatile Cu-based catalysts generally exhibited good catalytic activity due to the selective hydrogenation of C=O and C–O bonds without excessive side-reactions [18,22], e.g. the cleavage of C–C bond. Nevertheless, the catalytic performance of Cu-based catalyst still needs improvement because the active Cu particles are readily aggregated, which can lead to irreversible deactivation. In our previous reports [14,21], Cu/SBA-15 and Cu/SiO₂-AE showed relatively high catalytic activities. However, the catalytic activities of these catalysts tend to decline during recycling experiments; the catalyst stability needs to be further improved.

Many efforts have been devoted to improving the catalytic performance and stability of the copper catalyst. In general, the involvement of a second metal to copper catalyst—especially noble metals—is an alternative way to improve the catalytic properties of copper catalysts by forming bimetallic catalysts [23–25]. Nonetheless, the preparation method is relatively complicated, and the involvement of noble metals inevitably results in high costs. In previous reports [26–28], the coating of

a highly branched organic polymer to active catalyst was used to fabricate metal catalysts, e.g. iron oxide, copper-based catalysts. The use of polysaccharides could control the particle sizes and could stabilize the active sites to some degree [27]. The development of a facile method for preparing low-cost catalysts with high catalytic activity and stability for the chemoselective hydrogenation of EC is highly desired.

A powerful and unique ligand is needed for coordination to transition metals. Examples include copper and β-cyclodextrin with cyclic oligosaccharides of D(+)-glucopyranosyl units linked by α-1,4-glycosidic bonds. The β-cyclodextrin is environmentally friendly, low-cost and has unique coordination ability. This makes it a good precursor for preparing modified copper catalysts. Here, a series of β-cyclodextrin-modified Cu/SiO₂ catalysts were prepared via the ammonia evaporation (AE) method. The as-prepared copper catalysts were employed in the hydrogenation of EC to co-produce methanol and EG. The textural and structural properties of the as-prepared catalysts were systematically characterized by N₂ physisorption, X-ray diffraction (XRD), temperature programmed reduction of H₂ (H₂-TPR), N₂O titration, high resolution transmission electron microscopy ((HR)TEM), and X-ray photoelectron spectroscopy/Auger electron spectroscopy (XPS/XAES). Moreover, the catalytic performance of the as-prepared catalysts and reusability were studied. In addition, density functional theory (DFT) calculation was performed to identify the unique roles of Cu species with different valence states on the catalytic performance. A plausible mechanism was proposed based on these results.

2. Experimental

2.1. Materials

Cu(NO₃)₂·3H₂O (>99%), β-cyclodextrin (>99%), and p-xylene (98.85%) were purchased from Sinopharm Chemical Reagent Co., Ltd., China. Ethylene carbonate (99%) was commercially available from Alfa Aesar. Ammonia aqueous solution (25 wt%) and tetrahydrofuran (THF, 99.8%) were purchased from Xilong Chemical Co., Ltd., China. Hydrogen (99.999%) was purchased from Beijing Haikeyuan Chang Practical Gas Co., Ltd., China. Aqueous colloidal silica sol (mSiO₂·nH₂O, 30 wt%) was obtained from Qingdao Haiyang Chemical Co., Ltd., China. Other reagents were of analytical grade and used as received.

2.2. Catalyst preparation

The xβ-25Cu/SiO₂ catalysts (Cu loading and β-cyclodextrin loading (x) were based on the total weight of the catalyst) were prepared by a one-step AE method described as follows. Briefly, the required amounts of Cu(NO₃)₂·3H₂O and β-cyclodextrin were dissolved in 150 mL deionized water under stirring and ultrasonication (313 K) for 15 min. Subsequently, ammonia aqueous solution (25–28 wt%, 30 mL) was gradually added for 45 min. Then, the required amounts of aqueous colloidal silica sol were added into the suspension with vigorous stirring. The resulting suspension was continuously stirred for 4 h. Thereaf-

Scheme 1. The syntheses of EG and methanol via hydrogenation of EC derived from CO₂.

ter, the suspension was heated at 363 K to evaporate ammonia. During the process, the copper species were successfully deposited on SiO₂ when the pH value of the suspension decreased to 6–7. After that, the suspension was filtered and washed with deionized water and ethanol in sequence five times. The filtered solid was dried at 363 K overnight and calcined at 723 K in N₂ for 4 h. The as-calcined xβ-25Cu/SiO₂ catalysts were obtained after calcination and denoted as xβ-25Cu/SiO₂-C. Finally, xβ-25Cu/SiO₂-C catalysts were further reduced in 10 vol% H₂/N₂ at 623 K for 4 h. The compositions of xβ-25Cu/SiO₂ catalysts were adjusted by varying β-cyclodextrin loadings from 0 to 8%, while maintaining the Cu loadings constant at 25%. The as-prepared catalysts were denoted as xβ-25Cu/SiO₂ (25 and x represent the weight percentage of Cu and β-cyclodextrin, respectively).

2.3. Catalyst characterization

The N₂ physisorption measurements were conducted on Quantachrome Autosorb-1 at liquid nitrogen temperature (77 K) after the samples were outgassed at 573 K in vacuum for 3 h to remove physically adsorbed species. The surface areas (*A*_{BET}) were calculated according to the Brunauer-Emmett-Teller (BET) equation. The average pore diameter was estimated by the Barrett-Joyner-Halenda (BJH) method according to the desorption branch of the isotherms. The total pore volumes (*V*_{pore}) were obtained from the adsorbed N₂ volume at a relative pressure of 0.99.

Copper loading in the catalyst was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) on a PerkinElmer Optima 5300DV. The N₂O titration was performed on a Micromeritics Autochem 2920 with a TCD to determine the Cu dispersion and the metallic Cu-specific surface area of catalysts. About 100 mg catalyst was first outgassed at 473 K under He for 1 h. After cooling to ambient temperature under He, the gas was switched to 10 vol% H₂/Ar mixture stream (30 mL min⁻¹). Then, the sample was heated to 623 K at a ramping rate of 10 K min⁻¹ and retained 623 K for 2 h. The reduced sample was cooled to 363 K, isothermally purged with He for 1 h, and then exposed to pure N₂O (30 mL min⁻¹) for 1 h to ensure complete oxidation of the naked metallic copper. The sample was then flushed with He to remove N₂O and cooled to room temperature. Finally, the gas was switched to 10 vol% H₂/Ar mixture stream (30 mL min⁻¹), and the sample was heated to 623 K at a ramping rate of 10 K min⁻¹. The amount of consumed H₂ during the reduction steps was monitored by TCD. The Cu dispersion (*D*_{Cu}) and the metallic Cu specific surface area (*S*_{Cu}) were calculated as described elsewhere [29].

Powder XRD patterns of samples were obtained using a PANalytical Empyrean diffractometer with Cu K_α radiation (λ = 0.15406 nm) over the 2θ range of 10°–90°. The H₂-TPR experiments were used to evaluate the catalysts on a Quantachrome Chembet pulsar TPR/TPD instrument. The as-calcined catalysts (30 mg) were pretreated under He flow for 1 h at 473 K and then cooled to room temperature before reduction. Temperature programmed reduction was performed from 323 to 803 K at a heating rate of 10 K min⁻¹ in 10 vol% H₂/N₂.

XPS and XAES were carried out under an ultrahigh vacuum using an ESCALAB 250Xi spectrometer with Al K_α radiation (1486.6 eV) and a multichannel detector. The collected binding energies were calibrated using the C 1s peak at 284.6 eV as the reference.

Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were obtained on a microscope (JEOL, JEM-2100F) operating at an acceleration voltage of 200 kV to characterize the morphologies and the crystal structures of the Cu nanoparticles supported on SiO₂. The catalyst samples were ultrasonically dispersed in ethanol at room temperature for 20 min. The as-obtained solution was then dropped onto copper grids supported by holey carbon films.

2.4. Catalyst performance tests

Hydrogenation of EC used a 50-mL stainless steel batch reactor equipped with a magnetic stirrer. In a typical experiment, 10 mmol EC, 20 mL THF, and 0.176 g catalyst were loaded into the reactor. In addition, 100 μL of p-xylene was also added to the autoclave as an internal standard. The autoclave was then flushed with 2 MPa H₂ for five times and charged with 5 MPa H₂ at room temperature. The reactor was then heated to the reaction temperature with 550 r min⁻¹ magnetic stirring. After completion of the hydrogenation reaction, the autoclave was completely cooled in an ice-water bath. The residual H₂ was released carefully. The reaction mixture was quantitatively analyzed using p-xylene as the internal standard on a Shimadzu GC-2014 with a GsBP-1 column (30 m × 0.32 mm × 1.0 μm) and a flame ionization detector (FID).

The calculation method of the conversion of EC, selectivity of methanol, and EG are described as follows:

$$\text{Conv.}(\text{EC})(\%) = \frac{n_0(\text{EC}) - n(\text{EC})}{n_0(\text{EC})} \times 100\%$$

$$\text{Sel.}(\text{MeOH})(\%) = \frac{n(\text{MeOH})}{n_0(\text{EC}) - n(\text{EC})} \times 100\%$$

$$\text{Sel.}(\text{EG})(\%) = \frac{n(\text{EG})}{n_0(\text{EC}) - n(\text{EC})} \times 100\%$$

The abbreviations are as follows:

*n*₀(EC): mol of EC charged, *n*(EC): mol of EC unreacted, *n*(MeOH): mol of MeOH generated, *n*(EG): mol of EG generated.

In the catalyst reusability test, the catalysts were centrifuged after the reaction was finished, washed with THF, and then directly used in the next cycle with fresh reactants. The reaction conditions followed the same procedure mentioned before.

2.5. Computational methods and models

All DFT calculations were performed using the Dmol3 program available in Materials studio 6.1 package [30]. The generalized gradient approximation (GGA) with the Perdew-Wang 1991 function was used [31,32]. The following thresholds were used for the geometry optimization: 1 × 10⁻⁵ Hartree for the maximum energy change, 2 × 10⁻³ Hartree Å⁻¹ (1 Å = 0.1 nm) for the maximum force, and 5 × 10⁻³ Å for the maximum dis-

placement. The doubled numerical basis set with a set of polarization functions (double numerical plus polarization (DNP)) was used—this is comparable to Gaussian 6–31G** [33]. Vibrational frequencies were calculated at the optimized geometries to identify the nature of the stationary points (no imaginary frequency).

The optimized initial geometries of the Cu(111) surface, EC, and H₂ molecules are shown in Fig. 1. All the subsequent calculations were based on these configurations. Both Cu(111) and Cu(110) slab models were constructed based on a 4 × 4 unit cell. The Cu(111) slab model consists of four metal layers and seven equivalent vacuum layers (> 0.16 nm). The two uppermost layers of the slab were allowed to relax to their lowest energy configuration, while the atoms of the bottom layer were fixed to the bulk positions keeping their optimized lattice constants. The slab model was relaxed until the forces were convergent to 0.01 eV Å⁻¹. Surface adsorption occurs on the top-most layer of the slab. All adsorbate atoms were allowed to relax to their optimized positions. The adsorption energy, E_{ads} , is given by the following equation:

$$E_{\text{ads}} = E_{\text{slab/ads}} - E_{\text{slab}} - E_{\text{gas}}$$

Here, $E_{\text{slab/ads}}$ is the total energy of the slab with adsorbates, E_{slab} is the energy of the slab, and E_{gas} is the energy of the adsorbates in the gas phase.

3. Results and discussion

3.1. Textural properties of the catalysts

Fig. 2 presents N₂ adsorption-desorption isotherms of a series of $x\beta$ -25Cu/SiO₂ catalysts; the corresponding textural properties are also summarized in Table 1. The actual copper loadings were determined by ICP-AES, and the results showed that the actual Cu contents were essentially close to the nominal value. The N₂ physisorption isotherms of $x\beta$ -25Cu/SiO₂ catalysts exhibited type IV isotherms with an H1-type hysteresis loop [34] indicating that the mesoporous structures were formed. Table 1 shows that the unmodified 25Cu/SiO₂ had a

Fig. 1. (a) DFT optimized surface layer geometry of the Cu(111) slab. (b) DFT optimized geometry of EC in the gas phase. Red, gray, and white spheres represent oxygen, carbon, and hydrogen atoms, respectively. (c) DFT optimized surface layer geometry of H₂.

Fig. 2. N₂ adsorption-desorption isotherms of the $x\beta$ -25Cu/SiO₂ catalysts.

surface area of 242 m² g⁻¹ with an average pore size of 5.2 nm. In contrast, the surface areas of $x\beta$ -25Cu/SiO₂ ($x = 2, 5, 8$) were 326–351 m² g⁻¹, and the values gradually declined with increasing β -cyclodextrin content. These results indicated that the surface area of 25Cu/SiO₂ could be markedly enhanced via β -cyclodextrin. Meanwhile, the average pore sizes of the $x\beta$ -25Cu/SiO₂ catalysts were primarily distributed in the larger pore regions (5.5–7.5 nm). This is beneficial for mass transfer during the reaction process and could provide abundant easily accessible active sites for hydrogenation. N₂O titration indicated that the introduction of an appropriate amount of β -cyclodextrin could enhance the copper dispersion. Specifically, the maximal metallic Cu surface area of Cu/SiO₂ was 26.8 m² g⁻¹ with a high Cu dispersion of 28.6%. Nevertheless, the introduction of excessive β -cyclodextrin, i.e. 8%, obviously decreased the metallic Cu⁰ surface area (19.7 m² g⁻¹).

3.2. XRD

The XRD patterns of reduced $x\beta$ -25Cu/SiO₂ catalysts are shown in Fig. 3. A diffraction peak at 2θ of 43.3° and two weak diffraction peaks at 50.4° and 74.1° were distinguished—these are ascribed to the (111), (200), and (220) lattice planes of fcc Cu [JCPDS 00–04–0836] [35]. Meanwhile, two characteristic diffraction peaks at 2θ of 36.6° and 61.6° were assigned to Cu₂O [JCPDS 05–0667] [36]. According to the literature [14,21], the Cu⁰ and Cu⁺ species are derived from the reduction of CuO and

Table 1

Physical-chemical properties of $x\beta$ -25Cu/SiO₂ catalysts.

Sample	Cu loading ^a (wt%)	S_{Cu} ^b (m ² g ⁻¹)	D_{Cu} ^b (%)	A_{BET} ^c (m ² g ⁻¹)	V_p ^c (cm ³ g ⁻¹)	D_p ^c (nm)
25Cu/SiO ₂	24.8	22.6	24.1	242	0.46	5.17
2β-25Cu/SiO ₂	25.0	24.3	27.0	351	0.69	5.51
5β-25Cu/SiO ₂	25.0	26.8	28.6	345	1.07	7.46
8β-25Cu/SiO ₂	24.9	19.7	23.4	326	0.91	6.71

^a Determined by ICP-AES. ^b Determined by N₂O titration. ^c Obtained by N₂ physisorption.

Fig. 3. XRD patterns of the reduced $x\beta$ -25Cu/SiO₂ catalyst with different x values. (1) $x = 0$; (2) $x = 2$; (3) $x = 5$; (4) $x = 8$.

copper phyllosilicate, respectively. The presence of Cu₂O is generally attributed to the strong interactions between the copper species and the silica support—these interactions lead to partial reduction of Cu²⁺ to Cu⁺.

In addition—compared with uncoated 25Cu/SiO₂—the intensity of the diffraction peaks did not obviously change at lower β -cyclodextrin contents, e.g. 2% and 5%. On the contrary, the Cu crystallite diffraction peaks became stronger when the β -cyclodextrin content increased to 8%. This observation suggested that copper particles were aggregated into larger sizes at higher β -cyclodextrin amount. These results indicate that Cu⁰ and Cu⁺ species co-existed on the catalyst surface, and Cu particle sizes remained when an appropriate amount of β -cyclodextrin was used.

3.3. H₂-TPR

The TPR profiles of the as-calcined $x\beta$ -25Cu/SiO₂-C catalysts are depicted in Fig. 4. The as-calcined $x\beta$ -25Cu/SiO₂-C catalysts showed a main sharp reduction peak attributable to the overlapped reduction of copper phyllosilicate and bulk CuO parti-

Fig. 4. H₂-TPR profiles of the calcined $x\beta$ -25Cu/SiO₂-C catalyst samples with different x values. (1) $x = 0$, $x = 2$, (3) $x = 5$, (4) $x = 8$.

cles. The $x\beta$ -25Cu/SiO₂-C with 5% and 8% higher β -cyclodextrin content had an additional weak shoulder reduction peaks at lower temperature regions. These are due to the reduction of the well-dispersed CuO nanoparticles [37]. Most Cu²⁺ species in the calcined samples were completely eliminated via reduction pretreatment conditions. The maximum reduction temperature of 623 K used here for catalyst preparation could only reduce copper phyllosilicate to Cu⁺; a higher reduction temperature (> 873 K) is needed for further reduction of Cu⁺ to Cu⁰ [14]. In particular, the reduction peaks shifts toward lower temperature regions (527–537 K), which indicates that coating β -cyclodextrin onto the copper catalyst promotes the reducibility of the oxidized copper species. The combination of β -cyclodextrin improves the dispersion of the Cu species, which is consistent with the N₂O titration results. These data suggest that the modified Cu activates molecular H₂ and supplied more active H-species. This reduces the oxidized copper at relatively lower temperatures. Therefore, the introduction of an appropriate amount of β -cyclodextrin into the copper-based catalyst obviously enhances H₂ activation.

3.4. Surface chemical states

Fig. 5. Cu 2p XPS (a) and Cu LMM XAES (b) spectra of the reduced $x\beta$ -25Cu/SiO₂ catalysts with different x values. (1) $x = 0$, (2) $x = 2$, (3) $x = 5$, (4) $x = 8$.

Table 2

Assignments of copper species in $\alpha\beta$ -25Cu/SiO₂ catalysts derived from Cu LMM XAES.

Catalyst	Binding energy (eV)		Kinetic energy (eV)		Cu ⁺ /(Cu ⁺ +Cu ⁰)* (mol ratio)
	Cu 2p _{3/2}	Si 2p	Cu ⁺	Cu ⁰	
25Cu/SiO ₂	933.8	103.2	912.0	916.0	0.46
2 β -25Cu/SiO ₂	933.8	103.5	911.9	916.1	0.47
5 β -25Cu/SiO ₂	933.8	103.4	912.0	916.1	0.51
8 β -25Cu/SiO ₂	933.9	103.1	912.0	916.0	0.43

* Calculated from Cu LMM XAES spectra.

The surface chemical states and surface compositions of the reduced $\alpha\beta$ -25Cu/SiO₂ catalysts were investigated via XPS and XAES. The XPS spectra of Cu 2p are shown in Fig. 5, and the corresponding quantitative data are listed in Table 2. In general, the binding energy of Cu 2p_{3/2} was centered at 933.8 eV, and Cu 2p_{1/2} was centered at 953.8 eV—these peaks were assigned to Cu⁰ and/or Cu⁺ species, respectively.

The proportion of Cu⁰ and Cu⁺ was further distinguished via the LMM XAES. In the Cu LMM XAE spectra (Fig. 5), asymmetric and broad peaks are deconvoluted into two symmetric peaks with kinetic energies centered at 916.0 and 912.0 eV corresponding to Cu⁰ and Cu⁺, respectively [38,39]. A weak 2p→3d satellite peak was attributed to oxidized Cu species from 942–945 eV (Fig. 5(a)). The weak satellite peaks imply a small amount of Cu²⁺ [21]. The presence of oxidized copper species detected in $\alpha\beta$ -25Cu/SiO₂ catalysts is probably due to the potential oxidation of copper species with lower valence states when the catalysts are exposed to the atmosphere. These data suggest that while a small amount of oxidized copper species could not be completely excluded, Cu⁺ and Cu⁰ were likely the majority species and co-existed on the catalyst surface. This agrees with the XRD and H₂-TPR results.

Table 2 shows that the distribution of Cu⁺ and Cu⁰ species was influenced by the amount of β -cyclodextrin content. With increasing β -cyclodextrin into the Cu/SiO₂ sample, the proportion of surface Cu⁺/(Cu⁺+Cu⁰) first increases and then decreases. The maximum Cu⁺/(Cu⁺+Cu⁰) was 0.51, and it could be obtained for 5 β -25Cu/SiO₂. The Cu⁺ proportion remarkably decreased to 0.43 when introducing excessive β -cyclodextrin. Consequently, adding β -cyclodextrin played an important role in modulating the Cu⁺/(Cu⁺+Cu⁰) ratio.

3.5. TEM images

The (HR)TEM images and EDS mappings are illustrated in Fig. 6. The metal particles were highly dispersed on SiO₂ support of $\alpha\beta$ -25Cu/SiO₂ catalysts. The unmodified Cu/SiO₂ has an average copper particle size of about 3.8 nm confirming that ultrasmall Cu nanoparticles were formed. The modified $\alpha\beta$ -25Cu/SiO₂ catalysts with increased of β -cyclodextrin contents have average particle sizes of 3.3 to 4.2 nm. The clear lattice fringes with an interplanar spacing of 0.210 nm were attributed to Cu(111) for 5 β -25Cu/SiO₂ [23] implying the formation of Cu crystallite, which agrees with the XRD results.

We conclude that this preparation method is an effective approach for highly dispersed active copper species. The particle size can be finely controlled during the process. In addition, the morphologies of the $\alpha\beta$ -25Cu/SiO₂ catalysts became more compact at higher β -cyclodextrin contents suggesting that there are strong interactions between the residual carbon and the silica-supported Cu species. A previous study [26] found that the agglomeration of Cu nanoparticles could be retarded by tiny amounts of carbon during the reaction.

Next, we used EDS to better identify the chemical composition and elemental distribution of the 5 β -25Cu/SiO₂ catalyst (Fig. 6). The Si, O, C, and Cu species are distributed uniformly. This indicates that the Cu components are highly dispersed in the material. In addition, the Cu coincided with carbon indicating the formation of homogeneous domains of carbon-modified Cu—the residual carbon originates from β -cyclodextrin during calcination in inert atmosphere. We conclude from TEM and EDS that the catalysts prepared by the ammonia evaporation method were well-dispersed Cu; the appropriate amount of β -cyclodextrin inhibited copper agglomeration.

3.6. Catalytic performance

The catalytic performance of $\alpha\beta$ -25Cu/SiO₂ catalysts for the hydrogenation of EC was investigated at 453 K for 4 h (Table 3). The unmodified 25Cu/SiO₂ catalyst had 83.7% EG yield and 60.2% methanol yield (entry 1). In contrast, 2 β -25Cu/SiO₂ had 85.8% of EG yield and 60.7% methanol yield, which was slightly higher than the unmodified catalyst (entry 2). Interestingly, the 5 β -25Cu/SiO₂ with a medium amount of β -cyclodextrin exhibited a much higher catalytic performance—there was

Table 3

Catalytic performance of the $\alpha\beta$ -25Cu/SiO₂ catalysts.

Entry	Catalyst	T (K)	t (h)	Conv. (%) EC	Yield (%)		Sel. (%)		Activity (mg _{EC} g _{cat} ⁻¹ h ⁻¹)	Ref.
					EG	MeOH	EG	MeOH		
1	25Cu/SiO ₂	453	4	86.7	83.7	60.2	96.6	69.4	1084	This work
2	2 β -25Cu/SiO ₂	453	4	88.1	85.8	60.7	97.3	68.9	1102	This work
3	5 β -25Cu/SiO ₂	453	4	94.2	93.2	67.4	98.8	71.6	1178	This work
4	8 β -25Cu/SiO ₂	453	4	77.4	73.2	47.6	94.6	61.4	968	This work
5	CuCr ₂ O ₄	453	3	75.0	70.0	45.0	93.0	60.0	440	[18]
6	Cu/SiO ₂ -AE	453	6	83.5	82.0	59.7	98.2	71.5	696	[14]
7	Cu/SiO ₂ -PG	433	10	>99.0	97.0	96.0	98.0	97.0	334	[19]
8	Cu/SBA-15	453	4	62.1	60.9	31.5	98.1	50.7	776	[21]

Reaction conditions: 10 mmol EC, 5 MPa H₂, 20 mL THF, 20 wt% catalyst loading (based on the weight of EC).

98.8% EG selectivity and 71.6% of methanol selectivity with 94.2% EC conversion (entry 3). This result indicates that coating β -cyclodextrin onto the copper catalyst is an efficient method to prepare highly active copper catalysts. However, the EG yield rapidly decreased to 73.2% and methanol yield decreased to 47.6% over 8 β -25Cu/SiO₂ (entry 4). We suspect that the excessive residual carbon obviously reduced the exposure of active sites of Cu and partially made the active Cu species inaccessible—presumably due to the lower Cu dispersion as determined by N₂O titration.

The results indicated that the β -cyclodextrin loadings markedly influenced the catalytic behavior. Accordingly, the optimum catalytic performance could be acquired with 5 wt% of β -cyclodextrin. Meanwhile, the selectivity is obviously improved relative to unmodified 25Cu/SiO₂ catalyst. Hence, the 5 β -25Cu/SiO₂ catalyst has a superior catalytic performance.

These results underscored the important role of the Cu⁺/(Cu⁺+Cu⁰) ratio in the catalytic performance as well as the balanced effect of different copper species. This concurs with previous reports [40–43]. It can be inferred that the coexistence of Cu⁺ and Cu⁰ species in a suitable distribution on the catalyst surfaces is essential for effective hydrogenation of EC to MeOH and EG [44,45]. These results confirmed that 5 β -25Cu/SiO₂ catalyst is a good candidate for chemoselective hydrogenation of EC.

According to the experimental results and previous reports [14,19–21], the Cu⁺ and Cu⁰ species were both active sites for the syntheses of methanol and ethylene glycol. The Cu⁰ species is responsible for the dissociation of H₂ and the Cu⁺ species activate the EC carbonyl groups. Moreover, we examined the effect of Cu⁺/(Cu⁺+Cu⁰) on the turnover frequency (activity) in terms of EC in Table 3 in light of the catalytic results. Within the

Fig. 6. TEM images and EDS mapping of the reduced $x\beta$ -25Cu/SiO₂ catalysts. (a) $x = 0$, (b) $x = 2$, (c) $x = 5$, (d) $x = 8$, (e) $x = 5$, EDS-mapping, (f) Cu-mapping, (g) Si-mapping, (h) O-mapping, and (i) C-mapping.

Fig. 7. The reusability of 25Cu/SiO₂ (a) and 5β-25Cu/SiO₂ (b) catalysts. Reaction conditions: 10 mmol EC, 5 MPa H₂, 20 mL THF, 20 wt% catalyst loading (based on the weight of EC), 453 K, and 4 h.

same reaction time of 4 h, the EC activity first increased and then decreased with further increases in Cu⁺/(Cu⁺+Cu⁰) ratio. The activity reaches a maximum value of 1178 mg_{EC} g_{cat}⁻¹ h⁻¹ in the case of Cu⁺/(Cu⁺+Cu⁰) at 0.51, which exhibited much higher catalytic activity than the heterogeneous catalysts reported in prior literature [14,18,19,21]. Thus, we deduced that there is likely a cooperative effect between Cu⁰ and Cu⁺. The amount of β-cyclodextrin is very important for obtaining a robust catalyst and is the vital factor affecting the surface Cu⁺/(Cu⁺+Cu⁰) ratio. Consequently, adding β-cyclodextrin modulates the proportion of surface Cu⁺ and Cu⁰. It is crucial to achieving remarkably enhanced catalytic performance.

3.7. Catalyst reusability

The reusability of 5β-25Cu/SiO₂ and 25Cu/SiO₂ catalysts were preliminarily evaluated, and the results were shown in Fig. 7. The 25Cu/SiO₂ had an EC conversion, EG yield, and MeOH yield that slightly decreased to 82.9%, 80.7%, and 57.5% during the 2nd cycle, respectively. However, when the catalyst was used after the 4th cycle, the EC conversion, EG yield, and MeOH yield dramatically decreased to 35.9%, 34.7%, and 17.3%, respectively. The 25Cu/SiO₂ catalyst deactivated gradually and exhibited poor stability. Importantly, in comparison with 25Cu/SiO₂, the catalytic activity of the 5β-25Cu/SiO₂ cata-

lyst remained almost unchanged during the recycling experiments. The 97.7% EG selectivity and 69.3% methanol selectivity with 92.6% EC conversion could be retained even after the 5th cycle. These data and the characterization results showed that the residual carbon derived from decomposition of β-cyclodextrin likely retarded the possible deactivation of the copper catalyst. Hence, we concluded that the coating of β-cyclodextrin effectively improves the stability of the copper-based catalysts.

To illustrate the origins of the stability of the 5β-25Cu/SiO₂ catalyst, XRD, TEM, and XPS were used to study the catalyst after the 5th cycle. Fig. 8(a) shows little change between the diffraction peaks of the reused catalysts and the fresh one indicating that the crystal phases and particle sizes likely remained unchanged. The Cu particle sizes in the used catalyst were ~3.4 nm (Fig. 8(b)). This implies that marginal metal particle size growth occurred in 5β-25Cu/SiO₂ when it was used. Copper particles often aggregate during hydrogenation reactions, but that is not seen here. We suspect that the coherent interactions between Cu and residual carbon originated from β-cyclodextrin and presumably retarded the aggregation of Cu species during the reaction.

The Cu LMM XAES spectra showed that the distribution of Cu⁺ and Cu⁰ on the surface of catalyst changed after the fifth cycle (Fig. 8(c)). The molar ratio of surface Cu⁺/(Cu⁺+Cu⁰) spe-

Fig. 8. XRD patterns (a), TEM image (b), and XAES spectra (c) of fresh (1) and reused (2) 5β-25Cu/SiO₂ catalysts.

Fig. 9. (a) DFT optimized geometry of the EC molecule adsorbed on the Cu(111) surface. Red, gray, and white spheres represent oxygen, carbon, and hydrogen atoms, respectively. (b) DFT optimized geometry of the EC molecule adsorbed on the Cu(111) surface. (c) DFT optimized geometry of the H₂ molecule adsorbed on the Cu(111) surface. (d) DFT optimized geometry of the EC molecule adsorbed on the Cu⁺/SiO₂ surface. (e) DFT optimized geometry of the H₂ molecule adsorbed on the Cu⁺/SiO₂ surface.

cies remained constant, i.e. 0.51 for the fresh sample and 0.50 after the 5th cycle. This shows that there was no distinct variation in Cu⁺ and Cu⁰. Accordingly, the balanced surface distribution of Cu⁺ and Cu⁰ species is important to achieve remarkable catalytic performance. The XRD and TEM results revealed that the crystallite particles did not grow even after the fifth cycle. These results, the stability of 5β-25Cu/SiO₂ catalyst, and the recycling experiments are due to the retained structure and constant ratio of surface Cu⁺/(Cu⁺+Cu⁰). The incorporation of carbon into the copper catalyst prevented Cu aggregation. Importantly, the catalyst recyclability study has provided credible evidence and gave insight into the distribution of different copper valences. This is critical to obtaining higher catalytic performance.

3.8. DFT

DFT calculations showed the configurations of EC and H₂ molecules adsorbed on the of Cu(111) surface (Fig. 9). These surface adsorption energy results are summarized in Table 4. Fig. 9(a) and Fig. 9(b) show the optimized geometries—the carbonyl O is closer to the Cu(111) surface than the ring O suggesting that the interaction between the carbonyl O and the Cu(111) surface is the main contributor to the adsorption. However, the distances were 0.2747 and 0.3004 nm, respectively, which means that the van Edward force was the main type of interaction between two atoms. That is, the EC molecule was not activated by the Cu(111). This was confirmed by comparing the adsorption energy of two similar configurations ((a)

and (b)): Configuration a has a weaker binding strength ($E_{\text{ads}} = -0.921$ and -1.021 kcal mol⁻¹) corresponding to a weaker O-surface interaction.

The H₂ was activated when it adsorbed on the Cu(111) surface. There was a strong H-surface interaction ($E_{\text{ads}} = -2.921$ kcal mol⁻¹) with a H and Cu distance of 0.1573 nm. The DFT calculations also revealed that the H atom moved away from the Cu(111) surface after energy optimization. The distance between the H atoms is 0.1021 nm, which is longer than the initial configurations 0.0707 nm suggesting that the H atoms that interact with the surface are not stable on Cu(111).

The optimized initial geometries of EC and H₂ adsorbed on the Cu⁺/SiO₂ surfaces are shown in Fig. 9(e) and Fig. 9(f). There was a stronger interaction between the carbonyl O and the Cu⁺—the adsorption energy was about -3.071 kcal mol⁻¹. These results indicate that Cu⁺ is the main active site responsible for activating the EC molecule. The activated EC and the dissociated hydrogen atoms then formed new transition states. The Cu⁺ species stabilizes the methoxy and acyl species that are intermediates of the EC hydrogenation. They can also function as electrophilic or Lewis acidic sites to polarize the C=O bond via the electron lone pair in oxygen. This improves the reactivity of the EC ester group.

A catalytic mechanism was proposed based on the experimental results and DFT calculations. Metallic Cu⁰ on the catalyst surface are likely responsible for the dissociative activation of H₂ molecules, while the neighboring Cu⁺ sites are responsible for the adsorption of EC molecules. The oxidized Cu⁺ species could stabilize the carbonyl groups in EC; electrophilic sites polarize the C=O bond of the intermediates and lower the activation barriers. Therefore, these results show the coexistence of Cu⁺ and Cu⁰ species in a suitable proportion—their synergistic effects on the catalyst surfaces are likely responsible for the higher catalytic activity for hydrogenation of EC to methanol and ethylene glycol. In short, these results indicated that the balanced Cu⁺/(Cu⁰+Cu⁺) remarkably enhanced the catalytic performance.

4. Conclusions

Table 4

Calculated surface adsorption energies E_{ads} for EC and H₂ adsorption on Cu(111) surface and Cu⁺/SiO₂.

Geometry	E_{ads} (kcal mol ⁻¹)
a	-0.921
b	-1.021
c	-2.921
d	-3.071
e	-1.002

In summary, a facile ammonia evaporation method was successfully applied to prepare β -cyclodextrin-modified Cu/SiO₂ catalysts. The 5 β -25Cu/SiO₂ exhibited enhanced catalytic activity, i.e. methanol selectivity of 71.6% and EG selectivity of 98.8% with EC conversion of 94.2% after 4 h at 453 K. An excellent activity of 1178 mg_{EC} g_{cat}⁻¹ h⁻¹ could be achieved. Moreover, the formation of well-dispersed Cu species and the appropriate ratio of Cu⁺/(Cu⁰+Cu⁺) were likely responsible for the remarkable enhancement of catalytic activity. The reusability study showed that coating suitable amounts of β -cyclodextrin onto the copper catalyst retarded the aggregation of the Cu species. The modified 5 β -25Cu/SiO₂ exhibited superior stability than the unmodified 25Cu/SiO₂ counterpart. The DFT calculations showed that the catalytic mechanism was primarily Cu⁰-dissociated H₂. The Cu⁺ activated the carbonyl group of EC and promoted the transformation of intermediates. These findings offer insight into effective, stable, and low-cost copper-based catalysts for hydrogenation of EC derived from CO₂.

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Graphical Abstract

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An efficient and stable Cu/SiO₂ catalyst for the syntheses of ethylene glycol and methanol via chemoselective hydrogenation of ethylene carbonate

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β -cyclodextrin modified Cu/SiO₂ catalysts were successfully prepared by ammonia evaporation method. They exhibited high efficiency with excellent stability for synthesizing methanol and ethylene glycol via chemoselective hydrogenation of ethylene carbonate derived from CO₂.

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碳酸乙烯酯选择加氢合成甲醇与乙二醇高效稳定 Cu/SiO₂ 催化剂研究

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摘要: CO₂ 作为重要的碳氧资源, 具有来源丰富、价格低廉、安全等突出优点。近年来, 由于蕴含的巨大利用潜力, CO₂ 间接利用制备基础化学品、能源燃料对于可持续制备大宗化工品中具有重要研究意义, 日益受到研究者和工业界的广泛重视。甲醇与乙二醇是化学工业中的两种重要大宗原料。甲醇不仅是重要的有机化工原料、清洁环保的液体燃料, 同时也是氢气和能量储存的良好载体。乙二醇作为一种重要的有机化工原料, 在聚酯等领域具有广泛应用。CO₂ 经碳酸乙烯酯水解制备甲醇/乙二醇是典型的原子经济反应, 对资源、能源和环境的可持续发展具有重要意义。需要指出的是, CO₂ 与环氧乙烷环加成制备碳酸乙烯酯已具备成熟的工业化技术。因此, 该路线研究重点在于发展碳酸乙烯酯选择加氢联产甲醇和乙二醇高效稳定的催化体系。近年来, 铜基多相催化剂催化碳酸乙烯酯加氢联产甲醇乙二醇得到了广泛重视。由于铜基催化剂存在活性较低、高温易失活等问题, 开发高效且具有良好稳定性的铜基催化剂是目前碳酸乙烯酯加氢研究重点。

本文针对碳酸乙烯酯选择加氢合成甲醇乙二醇新型铜基催化体系构建和构效关系研究, 采用硅溶胶蒸氨法制备高分散 Cu/SiO₂ 过程中引入多羟基β-环糊精修饰催化剂前驱体的合成策略, 并通过惰性气体中煅烧后的积碳有效抑制活性铜物种的团聚, 获得了β-环糊精改性的 Cu/SiO₂ 催化剂。通过 N₂ 吸脱附、XRD、N₂O 滴定、H₂-TPR、TEM 和 XPS 等系统表征, 发现β-环糊精可有效调控催化剂结构和表面不同价态活性铜物种分布。碳酸乙烯酯加氢性能评价结果表明引入适量β-环糊精的 5β-25%Cu/SiO₂ 具有较优催化活性, 乙二醇选择性 98.8% 和甲醇选择性 71.6%, 且相应的催化活性可达 1178 mg_{EC} g_{cat}⁻¹ h⁻¹。高活性的原因很可能归因于不同价态 Cu⁰ 与 Cu⁺ 物种协同催化作用及适宜的 Cu⁺/(Cu⁰+Cu⁺) 比例。结合密度泛函理论模拟计算, 我们提出了 Cu⁰ 促进氢气解离、Cu⁺ 吸附活化碳酸乙烯酯分子中酯羰基的反应机理。催化剂重复使用和表征结果表明, 5β-25%Cu/SiO₂ 具有良好的稳定性, 使用前铜粒子大小和铜物种分布几乎未发生明显变化。本文为解决铜基催化剂高温易烧结等难题提供了简单有效的活性铜物种稳定化方法, 并为 CO₂ 经碳酸乙烯酯绿色合成甲醇、乙二醇高效稳定铜基催化新体系的构筑提供了有益借鉴。

关键词: 碳酸乙烯酯; 加氢; β-环糊精; Cu/SiO₂; 甲醇; 乙二醇

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