

# One-pot Synthesis of Cyclodextrin Doped Cu-SiO<sub>2</sub> Catalysts for Efficient Hydrogenation of Dimethyl Oxalate to Ethylene Glycol

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**Abstract:** The  $\beta$ -cyclodextrin ( $\beta$ -CD) was successfully applied to synthesize Cu-SiO<sub>2</sub> catalysts by the sol-gel method. The first and most important question addressed was increasing copper loading with higher dispersion in silica support. Another task was to elucidate the structureperformance relationship. Furthermore, the catalysts with various  $\beta$ -CD doping were systematically characterized and employed in the hydrogenation of dimethyl oxalate (DMO) to ethylene glycol (EG). The 0.1CD-Cu-SiO<sub>2</sub> catalyst with 17.39 wt% copper showed 99.9% DMO conversion and the highest EG selectivity of 95.0% at 210 °C, as well a lifetime of over 240 h. The reaction results disclosed that the catalytic performance could be tuned facilely by changing the amount of  $\beta$ -CD doping, which effectively influenced Cu metallic surface area and dispersion.

### Introduction

Hydrogenation of esters has become an increasingly significant process for the production of alcohols,<sup>[1]</sup> especially ethylene glycol (EG) that possesses attractive applications in synthesis of polyester, lubricant and antifreeze.<sup>[2]</sup> Traditionally, EG is mainly produced from petroleum-derived ethylene oxide in the industrial approach.<sup>[3]</sup> With increasing use of EG and petroleum resource shortage in China, production of EG is currently interested in dimethyl oxalate (DMO) hydrogenation and successful industrialization with an annual capacity of 20 million tons in China.<sup>[4]</sup> Generally, versatile Cu-based catalysts are the most extensively used in vapor-phase hydrogenation of oxalates to EG.<sup>[5]</sup>

As we all know, there was a direct approach, namely sol-gel method, to synthesize mesoporous copper silicates based on suitable organic functional silicon alkoxide.<sup>[6]</sup> Zhang et al. prepared Cu-SiO<sub>2</sub> catalysts by ammonia evaporation and sol-gel methods, indicating that the catalyst synthesized by sol-gel method exhibited better catalytic

performance owing to smaller Cu particles size, larger BET surface area, and higher dispersion in silica.<sup>[7]</sup> Nevertheless, this excellent method has a shortcoming, namely low copper loading. In our previous work, pure Cu-SiO<sub>2</sub> catalysts with different copper loadings prepared by sol-gel method exhibited good catalytic performance, but the deficiency was that agglomeration among the copper species was serious when copper loading was higher than 10 wt%.<sup>[8]</sup> Karakassides et al. prepared Cu-MCM-41 containing up to 4.7 wt% copper, resulting in the collapse of the ordered mesoporous framework with Cu content higher than 5 wt%.<sup>[9]</sup>

We have been seeking ways to reduce the amount of agglomeration and enhance copper loading. Fortunately, it was accepted that binuclear copper complex with ßcyclodextrin ( $\beta$ -CD) could be readily synthesized.<sup>[10]</sup> Gupta et al. have employed the Cu(II)-\beta-CD as water soluble green catalyst for the one-pot conversion benzyl halide to benzyl azide and 1,2,3-trizoles at ambient temperature.[11] Kaifer et al. have reported that CD-capped Pd nanoparticles were effective heterogeneous catalysts for the hydrogenation of water-soluble alkenes,<sup>[12]</sup> as well as for the for the Suzuki reaction.<sup>[13]</sup> Meanwhile, Zheng et al. have successfully prepared more ordered mesoporous SiO<sub>2</sub> and TiO<sub>2</sub> materials by introducing  $\beta$ -CD as template with sol-gel method,<sup>[14]</sup> which were mainly attributed to the special cylinder-shaped structure of β-CD. Recently, new kind of non-noble Metal@C nanoparticles were prepared with EDTA or glucose by Liu et al. to selective hydrogenation of substituted nitroarenes to corresponding anilines under mild conditions.<sup>[15]</sup> Thus, these similar organic matters have been widely used in the area of heterogeneous catalysis. Prior to this work, we have also explored the applications of  $\beta$ -CD to Cu-SiO<sub>2</sub> catalysts prepared by ammonia evaporation method. However, β-CD was washed away by distilled water after ammonia evaporation. Furthermore, this method also has some disadvantages, such as more procedures, sensitive to evaporation temperature, and emission of high concentration of ammonia.[16]

Herein, a series of  $\beta$ -CD doped Cu-SiO<sub>2</sub> catalysts with higher copper loading were prepared via a one-pot synthesis approach based on sol-gel method. Copper-based catalysts with introduction of  $\beta$ -CD were highly efficient in the vaporphase hydrogenation of DMO to EG due to the enhanced dispersion of copper species and formation of defects. A probable formation mechanism of  $\beta$ -CD doped Cu-SiO<sub>2</sub>

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catalysts was obtained, as well as deep insight into the relationship between copper species and catalytic performance.

## **Results and Discussion**

### Catalytic activity and stability

The gas-phase hydrogenation of DMO was performed on a fixed-bed reactor at different temperature to discover the catalytic activities of xCD-Cu-SiO<sub>2</sub> catalysts. Many excellent studies describing DMO hydrogenation comprises several continuous reactions (Scheme 1), also producing several byproducts including 1,2-butanediol (1,2-BDO) and 1,2-propanediol (1,2-PDO).<sup>[16b, 17]</sup> An obvious feature of the DMO hydrogenation on Cu-based catalyst is that the product can be significantly influenced by reaction temperature, generally producing more MG under low temperature (~ 190 °C) and

alcohol byproducts under high temperature (~ more 240 °C).  $^{[18]}$  As shown in Figure 1A, the 0.1CD-Cu-SiO\_2 catalyst exhibited 99.9% DMO conversion and the highest EG selectivity of 95.0% at 210 °C. It should be pointed out that the Selec.<sub>EG</sub> was only 58.4% with 95.0% Conv.<sub>DMO</sub> for pure Cu-SiO<sub>2</sub> catalyst at 210 °C and the optimal reaction temperature for it was 240 °C. Catalytic performance (T= 210 °C) over xCD-Cu-SiO<sub>2</sub> catalysts with different mass fraction of β-CD introduction are displayed in Figure 1B. Along with the increase of doping  $\beta$ -CD, the selectivity of EG showed volcanic variation, and the highest selectivity of EG was obtained over the 0.1CD-Cu-SiO<sub>2</sub> sample. More details about DMO conversion and product selectivity as a function of reaction temperature over other xCD-Cu-SiO<sub>2</sub> catalysts can be found in Figure S1. This result indicated that the introduction of  $\beta$ -CD had significant effect on the catalytic performance.



**Figure 1.** (A) DMO conversion and product selectivity as a function of reaction temperature over the 0.1CD-Cu-SiO<sub>2</sub> catalyst. (B) Catalytic performance over xCD-Cu-SiO<sub>2</sub> catalysts with different mass fraction of  $\beta$ -CD introduction at 210 °C. Reaction conditions: P(H<sub>2</sub>)= 2.0 MPa, WHSV<sub>DMO</sub>= 0.72 g g<sub>-catal</sub><sup>-1</sup> h<sup>-1</sup>, H<sub>2</sub>/DMO= 50.

Table	1. Ph	vsicochemical	pro	perties	of the	xCD-	Cu-SiO <sub>2</sub>	catal	vsts.
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Catalysts	Cu loading (wt%) <sup>ª</sup>	C loading (wt%) <sup>b</sup>	N loading (wt%) <sup>b</sup>	S <sub>BET</sub> (m² g <sup>-1</sup> ) <sup>c</sup>	V <sub>p</sub> (cm <sup>3</sup> g⁻¹) <sup>d</sup>	D <sub>p</sub> (nm) <sup>e</sup>	S <sub>Cu</sub> (m² g⁻¹) <sup>f</sup>	Cu dispersion (%) <sup>f</sup>
Cu-SiO <sub>2</sub>	17.14	0.85, <0.3	4.44, <0.3	319.0	0.17	2.7	13.5	12.2
0.05CD-Cu-SiO <sub>2</sub>	17.78	1.52, <0.3	3.39, <0.3	275.6	0.19	3.2	15.2	13.3
0.1CD-Cu-SiO <sub>2</sub>	17.39	2.72, <0.3	2.04, <0.3	324.5	0.18	2.7	18.4	16.5
0.2CD-Cu-SiO <sub>2</sub>	16.03	6.65, <0.3	0.63, <0.3	294.8	0.12	2.2	15.4	14.9
0.3CD-Cu-SiO <sub>2</sub>	15.56	8.99, 5.53	0.41, 0.36	227.8	0.11	2.5	8.7	8.6

<sup>a</sup> Determined by ICP-OES.

<sup>b</sup> Determined by EA for the catalyst precursors: the former for the dried samples and the latter for the calcined ones.

<sup>c</sup> BET specific surface area for the calcined samples.<sup>d</sup> Total pore volume. <sup>e</sup> BJH desorption average pore diameter.

<sup>f</sup> Cu metallic surface area and dispersion determined by N<sub>2</sub>O titration.

	+ 2H <sub>2</sub>	CH₂OH	+ 2H <sub>2</sub>	CH₂OH	+ H <sub>2</sub>	CH <sub>3</sub>
соосн3	- CH <sub>3</sub> OH	COOCH3	- CH <sub>3</sub> OH	└ СН₂ОН	- H <sub>2</sub> O	с́н₂он
DMO		MG		EG		EtOH

**Scheme 1.** Reaction pathway for the hydrogenation of DMO to MG, EG, and EtOH.



**Figure 2.** DMO conversion and EG selectivity vs time on stream over the Cu-SiO<sub>2</sub> and 0.1CD-Cu-SiO<sub>2</sub> catalysts. Reaction conditions: T= 210 °C,  $P(H_2)$ = 2.0 MPa, WHSV<sub>DMO</sub>= 0.72 g g<sub>-catal</sub><sup>-1</sup> h<sup>-1</sup>, H<sub>2</sub>/DMO= 50.

To investigate the long-term stability of the 0.1CD-Cu-SiO<sub>2</sub> catalyst, comparison of catalytic activity and selectivity to EG as a function of time on stream for the pure Cu-SiO<sub>2</sub> catalyst are displayed in Figure 2. The  $\beta$ -CD-free Cu-SiO<sub>2</sub> catalyst showed an obvious deactivation within 80 h. On the contrary, the 0.1CD-Cu-SiO<sub>2</sub> catalyst displayed excellent performance in both DMO conversion (~ 99.9%) and selectivity to EG (~ 95.0%), which was stable for 240 h under identical reaction conditions. This suggests its promising applications in industrial catalyst and the inherent reasons will be further discussed below.

### Physiochemical properties of the catalysts

### **Chemical compositions**

The real copper loading of the flesh catalysts were determined by ICP-OES, as shown in Table 1. The preset values were calculated as the mass of Cu divided by the total mass of CuO and SiO<sub>2</sub>. It is clear that the copper loading was about 17 wt%, which was a little less than the theoretical copper loading (22 wt%). This indicated that the catalyst precursors still contained a certain amount of hydroxyl groups after calcination (300 °C).<sup>[8]</sup> The 0.3CD-Cu-SiO<sub>2</sub> catalyst exhibited the lowest copper loading (15.56 wt%), which was probably because that some  $\beta$ -CD was not

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completely decomposed after calcination. The C content for the calcined 0.3CD-Cu-SiO<sub>2</sub> sample was 5.53 wt%, which was much higher than other catalysts. Notably, the pure dried Cu-SiO<sub>2</sub> sample showed a 0.85 wt% C loading, indicating that some TEOS was not completely hydrolyzed and was coated by the gel. When the  $\beta$ -CD increased, the C content was effectively increased while N content was decreased from 4.44 wt% to 0.41 wt%. The only nitrogen source was from NO<sub>3</sub><sup>-</sup> group, thus the dried catalyst precursors exhibited some NO<sub>3</sub><sup>-</sup> group.

### SBET and SCu

Table 1 also lists the textual properties of xCD-Cu-SiO<sub>2</sub> catalysts with different  $\beta$ -CD amount. It was found that the Cu-SiO<sub>2</sub> catalyst prepared by the sol-gel method possessed a relatively high S<sub>BET</sub> of 319.0  $m^2 g^{-1}$  and a small V<sub>p</sub> of 0.17  $cm^3 g^{-1}$ . The S<sub>BET</sub> and V<sub>p</sub> of xCD-Cu-SiO<sub>2</sub> catalysts varied from the  $\beta$ -CD doping. With the increment of  $\beta$ -CD introduction from 0.1 to 0.3, both the  $S_{\text{BET}}$  and  $V_{\text{p}}$  decreased from 324.5 to 227.8 cm<sup>3</sup> g<sup>-1</sup>, 0.18 to 0.11 cm<sup>3</sup> g<sup>-1</sup>, respectively. The excrescent  $\beta$ -CD loading probably made the copper species cover the surface and plug some pores, resulting in a decrease of SBET and Vp. The N2 adsorptiondesorption isotherms of calcined samples was illustrated in Figure S2, as well as their pore size distribution curves. The samples presented Langmuir type IV isotherms with H1-type hysteresis loops, suggesting that they were mesoporous materials.<sup>[19]</sup> This phenomenon was in agreement with other mesoporous Cu-SiO<sub>2</sub> catalysts prepared by ammoniaevaporation method, independent of promoters.<sup>[4a, 16b, 20]</sup> All the Dp were about 2.7 nm, which indicated that Cu-SiO<sub>2</sub> catalyst doping with β-CD would not influence the pore shape. In addition, Cu surface area and Cu dispersion of xCD-Cu-SiO<sub>2</sub> catalysts were summarized in Table 1. Chemisorption of N<sub>2</sub>O further showed slightly higher Cu dispersion (16.5%) and more active Cu surface area (18.4 m<sup>2</sup> g<sup>-1</sup>) for 0.1CD-Cu-SiO<sub>2</sub> catalyst. However, when excess amount of β-CD was introduced, the metallic copper would be agglomerated.

### **TEM** images

Figure 3 shows the TEM images of xCD-Cu-SiO<sub>2</sub> catalysts to clarify their morphology. In the calcined samples (Figure 3A-D), no lamellar structure of copper phyllosilicate could be observed. Inversely, some bulk copper species unevenly dispersed on the silica support over pure Cu-SiO<sub>2</sub> catalyst (Figure 3A). As the 0.1CD-Cu-SiO<sub>2</sub> precursor doped proper amount of  $\beta$ -CD, which was decomposed after calcination. Some stacking fault was found in the calcined 0.1CD-Cu-SiO<sub>2</sub> sample (Figure 3B-C), as well as in the calcined 0.2CD-Cu-SiO<sub>2</sub> catalyst (Figure S3A-B). With more  $\beta$ -CD

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introduction, we cannot observe this stacking fault in 0.3CD-Cu-SiO<sub>2</sub> sample (Figure 3D). After reduction at 350 °C, highly dispersed Cu particles with a mean size of 4.7 nm and 3.3 nm were observed for Cu-SiO<sub>2</sub> and 0.1CD-Cu-SiO<sub>2</sub> catalysts, respectively. For the reduced 0.3CD-Cu-SiO<sub>2</sub> sample, it apparently exhibited a non-homogenous

dispersion of copper species with larger particle sizes (Figure S3C-D). This confirmed again that copper species were more uniformly dispersed on the SiO<sub>2</sub> matrix for 0.1CD-Cu-SiO<sub>2</sub> sample. An excess amount of  $\beta$ -CD loading (x≥ 0.2) would lead to serious agglomeration, which was in agreement with the results from N<sub>2</sub>O chemisorption.



Figure 3. TEM images of (A) calcined Cu-SiO<sub>2</sub>, (B) calcined 0.1CD-Cu-SiO<sub>2</sub>, (C) enlargement of ellipse region in (B), (D) calcined 0.3CD-Cu-SiO<sub>2</sub>, (E) Cu-SiO<sub>2</sub>-Reduced, and (F) 0.1CD-Cu-SiO<sub>2</sub>-Reduced.



**Figure 4.** XRD patterns of (A) the pure CD, (B) the dried catalyst precursors, (C) the calcined catalyst precursors, and (D) the fresh reduced catalysts: (a) Cu-SiO<sub>2</sub>; (b) 0.05CD-Cu-SiO<sub>2</sub>; (c) 0.1CD-Cu-SiO<sub>2</sub>; (d) 0.2CD-Cu-SiO<sub>2</sub>; (e) 0.3CD-Cu-SiO<sub>2</sub>.

### Copper species on the catalysts

### **XRD** analysis

The XRD patterns of the pure  $\beta$ -CD and all the catalyst samples are shown in Figure 4. The  $\beta$ -CD template displayed strong characteristic peaks from 20 of 5° to 45° (Figure 4A), which were not observed on the dried catalyst precursors. As clearly depicted in Figure 4B, all the samples exhibited a broad and diffuse peak at 22°, which was attributed to the feature peak of amorphous  $SiO_2$ .<sup>[2a, 21]</sup> Besides, only the dried Cu-SiO<sub>2</sub> and 0.05CD-Cu-SiO<sub>2</sub> samples were composed of a strong phase of Cu<sub>2</sub>(OH)<sub>3</sub>NO<sub>3</sub> as evidenced by obvious reflection at 20 of 12.8° and 25.8° (JCPDS 75-1779),<sup>[22]</sup> indicating the poor dispersion of copper species in Cu-SiO<sub>2</sub> catalyst. But luckily for more β-CD doped Cu-SiO<sub>2</sub> samples, no crystalline characteristic peaks were observed, suggesting better dispersion of  $\beta$ -CD and copper species. Interestingly, an characteristic diffraction peak of Cu<sub>2</sub>O at 20 of 36.4°(JCPDS 05-0667) was observed for the dried 0.3CD-Cu-SiO<sub>2</sub> (Figure 4B-e).

Figure 4C presents the XRD patterns of the xCD-Cu-SiO<sub>2</sub> catalysts before reduction. Except for the characteristic peak of silica, more and more weak diffraction peaks of CuO at 20 of 35.5° and 38.7°(JCPDS 05-0661) were observed when  $x \le 0.2$ . A weakly diffraction peak of some residual Cu<sub>2</sub>(OH)<sub>3</sub>NO<sub>3</sub> at 20 of 12.8° could still be found over the calcined 0.05CD-Cu-SiO<sub>2</sub> (Figure 4C-b). However, with the continuous increment in  $\beta$ -CD doping, the peaks of CuO were disappeared while the peaks of Cu<sub>2</sub>O and Cu were arisen. It was interesting that the auto-reduction was occurred on 0.3CD-Cu-SiO<sub>2</sub> catalyst. Ai et al. reported that the auto-reduction of copper oxides with carbon nanotubes could directly realize, owing to the interaction of copper species with electron deficient interior surface of CNTs.<sup>[3]</sup> After reduction (Figure 4D), the strong diffraction peak at 20 of 43.3° along with two small ones at 50.4° and 74.1° were assigned to Cu species (JCPDS 04-0836), while the weak diffraction peak at 36.4° was characteristic of Cu<sub>2</sub>O.<sup>[18]</sup> Therefore, the reduced xCD-Cu-SiO<sub>2</sub> catalysts exhibited crystalline Cu and well dispersed Cu<sup>+</sup> species, especially for 0.1CD-Cu-SiO<sub>2</sub> catalyst.

### H<sub>2</sub>-TPR and NH<sub>3</sub>-TPD analysis



Figure 5. (A)  $H_2$ -TPR and (B)  $NH_3$ -TPD profiles of the calcined xCD-Cu-SiO<sub>2</sub> catalysts.

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The H<sub>2</sub>-TPR measurements were performed to study the reducibility of the copper species in xCD-Cu-SiO<sub>2</sub> catalyst precursors. It is commonly known that different copper species probably possess different electron density around copper, resulting in distinct reduction temperatures.<sup>[18]</sup> As can be seen in Figure 5A, each calcined sample exhibited at least one hydrogen consumption peak with different shapes at various temperatures. Due to the XRD patterns have already shown the presence bulk CuO in the calcined xCD-Cu-SiO<sub>2</sub> (x $\leq$  0.2) samples, the peaks at lower temperature (~ 210 °C) and higher temperature (~ 230 °C) can be assigned to the reduction of well dispersed CuO including ionexchanged Cu-O-Si units and the reduction of small CuO clusters, respectively.<sup>[5a, 22-23]</sup> The peak centered at 250 °C for pure Cu-SiO<sub>2</sub> catalyst should be attributed to the reduction of larger CuO clusters.<sup>[24]</sup> Furthermore, the T<sub>max</sub> position of second peak was shifting to lower temperature region with the increase of  $\beta$ -CD doping. When the  $\beta$ -CD loading was 0.3, the second reduction peak disappeared and only a peak at 215 °C was observed, which was attributed to reduction of Cu<sub>2</sub>O to Cu. The reduction peaks became narrowing and shifted toward lower temperatures probably because of the decrease in crystallininty of CuO with increase in β-CD introduction as evidenced by XRD results. Besiedes, the calcined 0.3CD-Cu-SiO<sub>2</sub> sample had a 29.4% loss of H<sub>2</sub> consumption compared with Cu-SiO<sub>2</sub> sample (Figure 5A). Thus the self-reduction behavior was happened to it, which was in accordance with the XRD results.

The NH<sub>3</sub>-TPD characterization was performed to evaluate the strength and quantity of acid sites on the xCD-Cu-SiO<sub>2</sub> catalysts. It was observed that a sharp peak centered at 123 °C (weak acid site), a shoulder peak centered at 255 °C (moderate acid site) and a broad weak peak appeared centered at 525 °C (strong acid site) appeared over the xCD-Cu-SiO<sub>2</sub> (x $\leq$  0.1) catalyst surfaces (Figure 5B). However, the middle peak intensity gradually decreased while the strong acid site improved much with more  $\beta$ -CD introduction (x  $\geq$  0.2). Meanwhile, the catalytic activity was increased first and then decreased much. Thus it is inferred that the addition of  $\beta$ -CD was responsible for the surface acidity and EG selectivity.

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**Figure 6.** FT-IR spectra of (A) pure  $\beta$ -CD, (B) the dried samples, (C) the calcined precursors of catalysts with different  $\beta$ -CD loading, and (D) the  $I_{962}/I_{800}$  intensity ratio from picture (C).

### FT-IR analysis

The FT-IR spectrum of pure β-CD is given in Figure 6A. A typical peak at 2923 cm<sup>-1</sup> was attributed to the antisymmetric C-H vibration of -CH<sub>2</sub>, while it was not shown in the dried catalyst precursors with  $\beta$ -CD doping (Figure 6B), as well as other characteristic peaks of  $\beta$ -CD. As shown in Figure 6B, obvious bending absorption of Cu-O-H bond at 679 cm<sup>-1</sup> and a sharp absorption at 1382 cm<sup>-1</sup> related to NO<sub>3</sub><sup>-</sup> groups were first saw for Cu-SiO<sub>2</sub> and 0.05CD-Cu-SiO<sub>2</sub> catalysts. It indicated the presence of Cu<sub>2</sub>(OH)<sub>3</sub>NO<sub>3</sub> as also proved by XRD results. The adsorption band at 945 cm<sup>-1</sup> was assigned to the bond vibration of Cu-O-Si units, which was shifted to 962 cm<sup>-1</sup> after calcination at 300 °C (Figure 6C). The Si-O bonds of amorphous SiO<sub>2</sub> support also showed different adsorption bands at ~ 1095, 800, and 465 cm<sup>-1</sup>. The broad absorption band in the range 3650-3250 cm<sup>-1</sup>, especially for the previous two catalysts, was owing to the overlapping of the OH stretching vibration of adsorbed water, ethanol and silanols (Figure 6B).<sup>[24]</sup> This further indicated that some TEOS still remained in the dried Cu-SiO<sub>2</sub> precursor. Similarly, the band at ~ 1664  $\text{cm}^{-1}$  corresponds to the bending mode of OH groups of adsorbed H<sub>2</sub>O.<sup>[21]</sup> There were no frequencies of the  $\delta_{OH}$  bands at 694 cm<sup>-1</sup> for Cu(OH)<sub>2</sub> and 670 cm<sup>-1</sup> for

Cu<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>2</sub>, thus indicating the absence of copper hydroxide and copper phyllosilicate in calcined xCD-Cu-SiO<sub>2</sub> catalysts <sup>[25]</sup>. Notwithstanding, copper phyllosilicate was often formed in the Cu-Si catalysts prepared by ion-exchanged and ammonia evaporation methods.<sup>[16b, 26]</sup> In addition, the relative amount of Cu-O-Si units in calcined samples could be calculated by the ratio of band intensities at 962 and 800 cm<sup>-1</sup>. Figure 6D clearly shows that the relative amount of Cu-O-Si units largely increased with the β-CD doping. Therefore, the dominating copper species were Cu-O-Si layers in the calcined catalysts.

### **TGA** analysis

More detailed information on copper species could be further investigated by TGA analysis in the N<sub>2</sub> atmosphere given in Figure 7. It was clear that the decomposition temperature of pure  $\beta$ -CD was ~ 300 °C in N<sub>2</sub> or air conditions (Figure 7A and Figure S4), in keeping with the reported results <sup>[27]</sup>. As the EA analysis showed that C contents were less than 0.3 wt% in the calcined xCD-Cu-SiO<sub>2</sub> (x≤ 0.2) samples,  $\beta$ -CD doping in catalyst was nearly decomposed before 300 °C. As shown in Figure 7B, all the samples continuously lost weight

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from RT to 300 °C, which was probably attributed to the evaporation of the absorbed water (< 120 °C) and the loss of crystal water, as well as well dispersed  $\beta$ -CD (120-300 °C). With a further elevating the temperature, the following weight loss was mainly due to the transformation of bulk CuO to into

 $Cu_2O$  or the collapse of silica skeleton <sup>[3, 5a]</sup>. The inset picture of Figure 7B indicated that Cu-SiO<sub>2</sub> catalyst exhibited the least weight loss before 300 °C and continued to slightly loss weight, while the 0.1CD-Cu-SiO<sub>2</sub> sample was more stable in high temperature.



**Figure 7.** TGA analysis of (A) pure  $\beta$ -CD and (B) the dried xCD-Cu-SiO<sub>2</sub> catalysts in N<sub>2</sub> atmosphere (inset picture was enlargement from 250-350 °C): (a) Cu-SiO<sub>2</sub>; (b) 0.05CD-Cu-SiO<sub>2</sub>; (c) 0.1CD-Cu-SiO<sub>2</sub>; (d) 0.2CD-Cu-SiO<sub>2</sub>; (e) 0.3CD-Cu-SiO<sub>2</sub>.



**Figure 8.** XPS spectra of the xCD-Cu-SiO<sub>2</sub> catalysts. (A) Cu 2p photoelectron spectra of the calcined samples, (B) Cu 2p photoelectron spectra of the reduced samples, (C) Cu LMM XAES spectra of the reduced samples: (a) Cu-SiO<sub>2</sub>; (b) 0.05CD-Cu-SiO<sub>2</sub>; (c) 0.1CD-Cu-SiO<sub>2</sub>; (d) 0.2CD-Cu-SiO<sub>2</sub>; (e) 0.3CD-Cu-SiO<sub>2</sub>.

### Surface chemical states of the catalysts

In DMO hydrogenation reaction, it is significant to investigate the surface chemical states of the catalysts due to a synergetic effect between  $Cu^0$  and  $Cu^+$ .<sup>[18]</sup> As can be seen from part (A) of Figure 8, the Cu  $2p_{3/2}$  peak centered at ~

935.4 eV along with the shakeup satellite peaks indicated that in calcined xCD-Cu-SiO<sub>2</sub> (x $\leq$  0.2) samples copper existed in the oxidation state of Cu<sup>2+</sup>. Meanwhile, the surface of calcined 0.3CD-Cu-SiO<sub>2</sub> catalyst also possessed some Cu<sup>2+</sup> species and the major copper species were Cu<sub>2</sub>O, as evidenced by XRD analysis. Generally, the Cu 2p<sub>3/2</sub> BE of

CuO is detected at 933.5 eV<sup>[16b, 28]</sup> and copper phyllosilicate is 934.9 eV,<sup>[16b, 26]</sup> which are relatively lower than 935.4 eV. It was maybe a charge transfer from copper ions toward the silica matrix that lead to the big positive Cu  $2p_{3/2}$  BE shift, namely, a strong interaction between the Cu<sup>2+</sup> and SiO<sub>2</sub> <sup>[21]</sup>. Thus the XPS results explained that in the calcined precursors exhibited highly dispersed Cu-O-Si units, which were comparable to copper phyllosilicate.<sup>[16b, 29]</sup>

The XPS spectra and X-ray induced Auger spectra (XAES) of the reduced xCD-Cu-SiO<sub>2</sub> catalysts were also illustrated in Figure 8B-C. The BE of Cu 2p3/2 in reduced samples were changed to 933.1 eV and showed no any corresponding satellite peaks, which was responsible for complete reduction of Cu<sup>2+</sup> to Cu<sup>+</sup> or / and Cu<sup>0,[19]</sup> The Cu LMM spectra were further used to discriminate between Cu<sup>+</sup> and Cu<sup>0</sup> species,<sup>[30]</sup> as shown in Figure 8C and Table S1. All the Cu LMM spectra displayed a broad and asymmetrical peak, declaring clearly that Cu<sup>+</sup> and Cu<sup>0</sup> species were stable coexistence on the surface of the reduced xCD-Cu-SiO<sub>2</sub> catalysts. Furthermore, the original Cu LMM peaks were deconvoluted to two symmetrical peaks centered at ~ 913.0 and 916.5 eV, corresponding to  $Cu^+$  and  $Cu^0$  species, respectively.<sup>[31]</sup> The results listed in Table S1 showed that the ratio of  $Cu^+$  / ( $Cu^+$  +  $Cu^0$ ) did not change much with the β-CD doping mass fraction lower than 0.1. However, the ratio was decreased from 62.1% to 57.5% when the  $\beta$ -CD loading was 0.3, which was probably because that the main copper species were already Cu<sub>2</sub>O and its weekly interaction with support. Hence, the high ratio of Cu<sup>+</sup> for the reduced catalysts implies the strong interaction between copper and support.

## Structure-performance relationship of the catalysts

## Formation mechanism and structure evolution during the synthesis process

It is commonly known that the synthesis processes of heterogeneous catalysts are comprised of multi steps, and the compositions would go through complicated changes.<sup>[32]</sup> In this work, the xCD-Cu-SiO<sub>2</sub> catalysts prepared by sol-gel method, containing three steps: sol-gel generation, calcination and reduction. The whole structure evolution processes with a possible mechanism for formation of  $\beta$ -CD doped Cu-SiO<sub>2</sub> catalysts were systemically discussed below.

For the purpose of investigating the role of  $\beta$ -CD during nucleation and growth of solid gel, different mass fraction (x= 0-0.3) of  $\beta$ -CD were doped to Cu-SiO<sub>2</sub> catalyst. Many articles proves that there is interaction between various metal ions such as Cu<sup>2+,[10b, 27]</sup> Ca<sup>2+,[33]</sup> Fe<sup>3+,[34]</sup> and  $\beta$ -CD or its derivatives. It is attributed to the special structure of  $\beta$ -CD that possesses a segment of a hollow cone with an interior

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electron-rich hydrophobic cavity and exterior hydrophilic surface (Scheme 2A).<sup>[27]</sup> Above all, β-CD molecules would cross-link with each other through the hydroxyls under ultrasonication (Scheme 2B).<sup>[27, 33]</sup> Figure S5 showed that only 0.2CD could not be well dissolved in 21.6 g water, while adding with 10.6 g Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O could obtain a homogeneous and blue transparent solution, even for the 0.3CD. We first assumed that the acid condition would be favorable for β-CD dissolution and then added 3 mL 1M HNO<sub>3</sub>, but it had no effect on β-CD dissolution. The UV-vis spectra of these examples indicated that the absorbance of NO3<sup>-</sup> and d-d transfer have been decreased with an increase in β-CD concentration (Figure S5). These results indicated that there was interaction between  $Cu^{2+}$  and  $\beta$ -CD, giving rise to well dispersed β-CD and copper species. Moreover, the characteristic peaks of β-CD disappeared in both XRD (Figure 4B) and FT-IR files (Figure 6B) after drying, as well as decomposed earlier in TGA curves (< 300 °C, Figure 7B). On the contrary, the dried pure Cu-SiO<sub>2</sub> catalyst without doing with any amount of β-CD displayed obvious copper species of Cu<sub>2</sub>(OH)<sub>3</sub>NO<sub>3</sub> instead of Cu-O-Si units, as evidenced by EA analysis (Table 1), XRD (Figure 4B) and FT-IR files (Figure 6B). Huang et al. reported that the main copper species of CuO-SiO<sub>2</sub> catalyst prepared by the impregnation method was Cu<sub>2</sub>(OH)<sub>3</sub>NO<sub>3</sub>, which were easily transformed into bulk CuO after calcination. As a result, it showed a much poor activity and short stability in glycerol reaction.<sup>[22]</sup> Meanwhile, the higher mass fraction of  $\beta$ -CD (x> 0.1) would obviously led to bigger spheres (Figure S3C-D), thus the S<sub>BET</sub> decreased from 324.5 to 227.8 cm<sup>3</sup> g<sup>-1</sup> and copper dispersion also decreased from 16.5 to 8.6% (Table 1).

After calcination, the doing  $\beta$ -CD molecules were removed and left some stacking fault, as supported by EA analysis (Table 1) and TEM images (Figure 3B-C). Yao's group recently has reported similar defect mechanism for enhancing oxygen reduction reaction activity by using metalorganic frameworks as hard templates or precursors.<sup>[35]</sup> As we know, some loosely and well dispersed CuO were easily aggregated to form large CuO particles as identified by XRD (Figure 4C) and H<sub>2</sub>-TPR (Figure 5A) results. Fortunately, these results further showed that CuO particle sizes became smaller and fewer when increasing β-CD introduction. Furthermore, it was surprised that a auto-reduction reaction was happened to 0.3CD-Cu-SiO2 catalysts as illustrated by XRD (Figure 4C) and XPS analysis (Figure 8A). Regrettably, it displayed a poor DMO hydrogenation activity. From the FT-IR result (Figure 7C-D), we concluded that the main copper species were Cu-O-Si units rather than copper phyllosilicate formed during sol-gel process. Owing to the strong interaction between silica and copper species, the copper oxidation state of most metallic copper was +1 in reduced

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xCD-Cu-SiO<sub>2</sub> catalysts, as well as some  $Cu^0$  species (Table S1 and Figure 8C).

Given our results and the literature,<sup>[27, 33, 36]</sup> a possible schematic mechanism for formation of  $\beta$ -CD doped Cu-SiO<sub>2</sub> catalysts is proposed and shown in Scheme 2. The Cu<sup>2+</sup> would be absorbed on  $\beta$ -CD to form a homogenous complex spheres. Then the presence of ordered Cu- $\beta$ -CD structure

ensured the uniform distribution of the copper precursor in silica channels. After calcination, the generated defects promoted the dispersion of copper species and exposed more active sites to enhance its catalytic performance. Therefore, doping proper amount of  $\beta$ -CD is an efficient strategy to synthesize Cu-SiO<sub>2</sub> catalyst with small particle size and high dispersion.



### Silica surface of the assemblies

Scheme 2. A possible schematic mechanism for formation of  $\beta$ -CD doped Cu-SiO<sub>2</sub> catalysts.

## Insight into correlation between copper species and catalytic performance

As mentioned above, three kinds of copper species in the calcined precursors, namely Cu-O-Si units, high dispersed CuO and bulk CuO clusters. The amount of different kind of copper species and Cu dispersion varied much with increasing  $\beta$ -CD loading. To clearly show the effect of  $\beta$ -CD loading on the EG yield and the metallic specific area, Figure 9 was illustrated their relations. The 0.1CD-Cu-SiO<sub>2</sub> catalyst exhibited the highest copper surface area and thus showed a perfect DMO hydrogenation activity with a TOF value of 11.4  $h^{-1}$ , which was much higher than pure Cu-SiO<sub>2</sub> catalyst (4.8  $h^{-1}$ , Table S2). But excessive  $\beta$ -CD loading would lead to bigger spheres and agglomeration. Consequently, the EG yield was decreased from 0.36 to 0.12 g g<sub>-catal</sub><sup>-1</sup> h<sup>-1</sup>. This finding suggests that the copper surface was mainly responsible for the catalytic activity of Cu-SiO<sub>2</sub> in the DMO hydrogenation, which is consistent with Yin's conclusion in Cu-HMS catalysts with variation in copper loading <sup>[21]</sup>. Without doubt, other factors, such as Cu particle sizes, S<sub>BET</sub>, ratio of Cu<sup>+</sup> / (Cu<sup>+</sup> + Cu<sup>0</sup>), pore structural properties, metalsupport interaction and stacking fault, all influence the catalytic activity over Cu-SiO<sub>2</sub> catalysts.<sup>[21, 36-37]</sup> For example, the copper species were not well dispersed and hence more difficult to be reduced before calcination (Figure S6). The dried 0.1CD-Cu-SiO<sub>2</sub> catalyst produced a very small  $S_{BET}$  of 86.2 m<sup>2</sup> g<sup>-1</sup> and a low  $V_p$  of 0.03 cm<sup>3</sup> g<sup>-1</sup>(Figure S7). Thus EG yield at 210 °C over dried 0.1CD-Cu-SiO<sub>2</sub> catalyst was much poor, namely 0.05 g g-catal<sup>-1</sup> h<sup>-1</sup>. As shown in Figure S4, β-CD was nearly decomposed at 550 °C. Thus the dried 0.3CD-Cu-SiO<sub>2</sub> sample was further calcined at 550 °C for 5 h. As listed in Table S3, after removing the carbon- and nitrogen-containing residue species to expose more active sites, the 0.3CD-Cu-SiO<sub>2</sub>-550 catalyst delivered a much better performance. However, it was still lower than the 0.1CD-Cu-SiO<sub>2</sub> sample. The reason that why the 0.3CD-Cu-SiO<sub>2</sub> sample achieved a lower catalytic performance was complicated. First, from the XRD and H<sub>2</sub>-TPR results, we know that the auto-reduction behaviours was happened to the 0.3CD-Cu-SiO<sub>2</sub> sample alone. Then, the NH<sub>3</sub>-TPD result indicated that its moderate acid site decreased much while the strong acid site improved. Ai et al. reported that suitable surface acidity could promote the hydrogenation of DMO.<sup>[38]</sup> Furthermore, as mentioned above, it possessed a large Cu NPs, a low dispersion and a low copper surface area, as well as a low ratio of  $Cu^+$  /  $(Cu^+ + Cu^0)$ . Taken together, the 0.3CD-Cu-SiO<sub>2</sub> sample did not deliver a comparable performance. Therefore, a proper mass fraction of β-CD (x= 0.1) with highly dispersed Cu-O-Si units and copper surface

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area were needed to achieve optimum performance in DMO hydrogenation to EG.



**Figure 9.** EG yield and copper metal surface area as a function of  $\beta$ -CD loading. Reaction conditions: P(H<sub>2</sub>)= 2.0 MPa, T= 210 °C, WHSV<sub>DMO</sub>= 0.72 g g<sub>-catal</sub><sup>-1</sup> h<sup>-1</sup>, H<sub>2</sub>/DMO= 50.

### Explanation on the long-term stability

Figure 2 indicated that 0.1CD-Cu-SiO<sub>2</sub> catalyst showed much higher activity and remarkable stability than pure Cu-SiO<sub>2</sub> catalyst in time on-stream. Besides the same solvent deactivation effect on the Cu-based catalysts,<sup>[39]</sup> we need to discuss many other reasons. Firstly, carbon deposition was excluded since both of the used catalysts exhibited carbon content of 3.92% and 4.77% in Cu-SiO<sub>2</sub>-Used and 0.1CD-Cu-SiO<sub>2</sub>-Used catalysts, respectively. Zheng et al. also did not consider carbon deposition as the main reason for Cu-SiO<sub>2</sub> catalyst deactivation.<sup>[30]</sup> Then S<sub>BET</sub> decreasing and Cu sintering were believed to be the main cause of Cu-SiO<sub>2</sub> catalyst deactivation. As shown in Figure S8, the S<sub>BET</sub> of Cu-SiO<sub>2</sub>-used catalyst was reduced from 319.0 to 245.1 cm<sup>3</sup> g<sup>-1</sup> (23.2%), while the 0.1CD-Cu-SiO<sub>2</sub>-used catalyst had only a 8.4% loss of the initial value of specific surface area. Popa et al. prepared a new kind of stable Cu-SiO<sub>2</sub> catalyst by using (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> as precipitant, showing a smaller loss of S<sub>BET</sub> as well.<sup>[16a]</sup> Both the XRD patterns and TEM images indicated that Cu nanoparticles of the used Cu-SiO<sub>2</sub> catalyst aggregated more seriously (Figure S9-10). Third, the deactivation was related to hydrogenation product. As Cu-SiO<sub>2</sub> catalyst showed a MG selectivity of ~ 35.0%, the selectivity of EG was decreased much. Generally, once MG was generated more than 10%, we should increase the reaction temperature to prevent the deactivation owing to MG would accelerate copper species sintering.<sup>[31]</sup> Yin et al. presumed that MG adsorbed via the carbonyl oxygen atoms on the catalyst surfaces under reaction conditions.<sup>[40]</sup> Furthermore, the 0.1CD-Cu-SiO<sub>2</sub> catalyst possessed more Cu-O-Si units and defects, which could stabilize the active copper species during DMO hydrogenation. As shown in Figure S11, Ding et al. reported that Cu<sub>2</sub>O reduced from Cu-

O-Si units was more stable than the Cu<sup>+</sup> species reduced from copper phyllosilicate in the Cu-SiO<sub>2</sub> catalyst <sup>[5a]</sup>. Therefore, we can speculate that the stable catalytic behavior of 0.1CD-Cu-SiO<sub>2</sub> catalyst was attributed to the highly dispersed copper species immobilized by the support. In addition, it was surprised to find that the ratio of Cu<sup>+</sup> / (Cu<sup>+</sup> + Cu<sup>0</sup>) clearly increased in both Cu-SiO<sub>2</sub>-Used and 0.1CD-Cu-SiO<sub>2</sub>-Used catalysts under H<sub>2</sub> atmosphere (Figure S12), which was opposite to the results of La-Cu-SiO<sub>2</sub> catalysts.<sup>[30]</sup> Similar phenomenon was happened to the spent Cu-SiO<sub>2</sub> catalyst used for hydrogenation of methyl acetate and the authors attributed this finding to the surface oxidation of copper species at Cu-SiO<sub>2</sub> interface by methyl acetate.<sup>[41]</sup> In fact, the stable surface chemical environment plays important roles in maintaining catalytic stability.<sup>[40]</sup> From this point, there is room for improvement in stability of 0.1CD-Cu-SiO<sub>2</sub> sample.

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### Conclusions

In this work, the effect of introduced  $\beta$ -CD on the structure and properties of Cu-SiO<sub>2</sub> catalysts was systematically investigated.  $\beta$ -CD doping first inhibited and then accelerated the coagulation of copper species and even reduced them as doping amount increased, and the optimized doping amount for the outstanding stability and activity was observed for the 0.1CD-Cu-SiO<sub>2</sub> catalyst. This was attributed to highly dispersed copper species with smaller particles sizes, more Cu-O-Si units, larger S<sub>Cu</sub> and S<sub>BET</sub>. However, the XPS analysis of the used catalysts indicated that the ratio of Cu<sup>+</sup> and Cu<sup>0</sup> was still slowly unbalanced. Therefore, it should take more hopeful techniques to immobilize copper species in our future work.

### **Experimental Section**

### Catalyst preparations

The  $\beta$ -CD doped catalysts were synthesized by the sol-gel method, as reported in our previous paper.<sup>[8]</sup> A typical preparation procedure of these catalysts is illustrated in Scheme 3 and described as follows: 10.6 g Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O and a certain amount of  $\beta$ -CD (Mass fraction x= 0-0.3) were dissolved with 21.6 g distilled water under ultrasonication (25 kHz, 40 °C) for 15 min in a beaker. A homogeneous and blue transparent solution was obtained. Then other regents including 31.8 g tetraethylorthosilicate (TEOS) and 41.4 g ethanol (EtOH) were added into the prepared solutions under vigorous stirring. The mixed solution was then stirred at 65 °C for 1~2 h until generating solid gel. After being aged at room temperature (RT) for 24 h, the obtained xerogel was dried at 65 °C for 7 h, 70 °C for 7 h, 100 °C for 40 h and 120 °C for 4 h. Finally, the  $\beta$ -CD doped Cu-SiO<sub>2</sub> composite catalyst precursors were calcined at 300 °C for 5 h in air and noted as xCD-Cu-SiO<sub>2</sub> catalysts, where x represents mass fraction of  $\beta$ -CD.

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Scheme 3. Schematic illustration of the  $xCD-Cu-SiO_2$  catalyst preparation.

### **Catalytic performance**

The five catalysts were conducted on a stainless-steel fixed-bed reactor with a continuous flow unit to measure their catalytic activity and durability. Typically, 3.5 g of the catalyst precursor (10-20 meshes) was packed into the center of the reactor with the thermocouple inserted into the catalyst bed to better control of reaction temperature. The sample was first activated under pure H<sub>2</sub> (99.99% purity) flow (100 ml min<sup>-1</sup>) at 350 °C for 5h and then cooled to the desired reaction temperature (170-280 °C). A 20 wt% DMO (99% purity) in methanol was pumped into the reactor using a high pressure pump (Lab Alliance Series I pump). It should be pointed out that the system pressure was 2.0 MPa, H<sub>2</sub>/DMO molar ratio is 50, and the weight hour space velocity (WHSV<sub>DMO</sub>) was 0.72 g g<sub>-catal</sub><sup>-1</sup> h<sup>-1</sup>. The products were condensed and analyzed on a gas chromatograph (GC-900C, Shanghai TianPu analysis instrument Co., LTD) equipped with a flame ionization detector (FID) and a DB-WAX 60m capillary column. The conversion of DMO was calculated as the input mole amount of DMO subtracts the output mole amount of DMO and then divided by the input mole amount of DMO. The selectivity of a product was calculated as the mole amount of one product divided by the total mole amount of all products formed.

### **Catalyst characterization**

The copper loading was measured by inductively coupled plasma optical emission spectrometer (ICP-OES) on a Jobin Yvon Ultima2. Elemental analysis (EA) was obtained by Elementar Vario EL-Cube elemental analyzer. N2 adsorption-desorption isotherms were conducted on a Micromeritics ASAP 2020 at 77 K. Before measurement, the catalyst was degassed in vacuum at 250 °C for 5 h. Then the specific surface area (S<sub>BET</sub>) was estimated by the Brunauer-Emmett-Teller (BET) method. In the meantime, the specific surface area of metallic copper (S<sub>Cu</sub>) and copper dispersion were performed on the TP-5080 instrument by the adsorption and decomposition of N<sub>2</sub>O with the pulse titration method. Thermogravimetric analysis (TGA) data were collected on a NETSCHZ STA-449C thermal analyzer in the temperature range 30-900 °C with a heating rate of 10 °C min<sup>-1</sup> under N<sub>2</sub> or air atmosphere. X-ray diffraction patterns (XRD) were obtained from a Rigaku MiniFlex II diffractometer using Cu-Ka radiation source at a scan rate of 2° per min with a scanning angle (20) ranging from 10° to 85°. Transmission electron microscopy (TEM) images were obtained on a Tecnai F20 apparatus at an acceleration voltage of 200 kV. Temperature-programmed reduction (H<sub>2</sub>-TPR) was carried out on a Micromeritics Autochem II 2920 instrument connected with a Hidden Qic-20 mass spectrometry (MS). The H<sub>2</sub> consumption of calcined catalysts was calculated from H<sub>2</sub>-TPR results using CuO as reference material. It was first integrated by the software of Origin 9.0 (100~400 °C) and then divided by the sample mass (g). The temperature-programmed desorption profiles (NH<sub>3</sub>-TPD) were obtained on a TP-5080 instrument. Fourier-transform infrared (FT-IR) spectra were recorded on a Bruker Vertex 70 FT-IR with a spectral resolution of 2 cm<sup>-1</sup> in the range 4000-400 cm<sup>-1</sup>. The UV-vis spectra were obtained on PerkinElmer Lambda 365. The surface species were detected by X-ray photoelectron spectroscopy (XPS) using a ESCALAB 250Xi equipped with an Al K $\alpha$  X-ray radiation source (h $\nu$  = 1486.6 eV). The binding energy (BE) values were referenced to the Si 2p peak at 103.7 eV.

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Here we report a series of cyclodextrin doped Cu-SiO<sub>2</sub> catalysts prepared *via* a one-pot synthesis method, which largely enhance the selectivity of ethylene glycol and long-term durability.

Run-Ping Ye, Ling Lin, Chang-Qing Liu, Chong-Chong Chen, and Yuan-Gen Yao<sup>\*</sup>

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One-pot Synthesis of Cyclodextrin Doped Cu-SiO<sub>2</sub> Catalysts for Efficient Hydrogenation of Dimethyl Oxalate to Ethylene Glycol