Sorbitol-derived carbon overlayers encapsulated Cu nanoparticles on SiO₂: Stable and efficient for the continuous hydrogenation of ethylene carbonate

Highlights

Cu@C/SiO₂ was fabricated by an in situ sacrificial coating encapsulation strategy

The interaction of Cu with carbon altered the electronic properties of Cu species

Cu@C/SiO₂ exhibited a stable 91% MeOH yield without deactivation during 736 h

Carbon overlayers suppress Cu particles sintering and stabilize the Cu²⁺/Cu⁺ ratio
Sorbitol-derived carbon overlayers encapsulated Cu nanoparticles on SiO₂: Stable and efficient for the continuous hydrogenation of ethylene carbonate

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SUMMARY
An ultrastable and efficient Cu@C/SiO₂ nanocatalyst was fabricated for the hydrogenation of ethylene carbonate, in which Cu nanoparticles are encapsulated by sorbitol-derived graphitized carbon overlayers. During the calcination of Cu-sorbitol/SiO₂ precursors under N₂ atmosphere, sorbitol decomposed to CO and CO₂. The in situ generated CO not only reduced Cu²⁺ to Cu⁰/Cu⁺, but also formed graphitized carbon overlayers on the Cu surface via the disproportionation of CO. The Cu@C/SiO₂ catalyst exhibited superior catalytic performance (91% MeOH yield and 43.6 h⁻¹ TOF) at a H₂/EC molar ratio of 20. Of particular note, the Cu@C/SiO₂ catalyst showed remarkable long-term stability during 736 h time-on-stream test without any deactivation. The graphitized carbon overlayers on the surface of Cu nanoparticles not only functioned synergistically with the surface Cu⁰/Cu⁺ sites to promote the EC hydrogenation but also suppressed the sintering of Cu nanoparticles. Furthermore, the interaction of Cu nanoparticles and graphitized carbon overlayers stabilized the surface Cu⁺/(Cu⁰+Cu⁺) ratio.

INTRODUCTION
As well known, CO₂ is one of the typical greenhouse gases. Global warming and climate changes caused by massive anthropogenic CO₂ emissions have become a worldwide concern (Baker et al., 2018; Smith and Myers, 2018). China has committed to realize peak CO₂ emissions by 2030 and to achieve the goal of carbon neutrality by 2060. Undoubtedly, the transformation and utilization of CO₂ have become an urgent issue in sustainable chemistry. Converting CO₂ to value-added fuels or chemicals, such as methanol (MeOH), has attracted extensive attention (Aresta et al., 2014). However, the inert nature of CO₂ hinders its efficient utilization.

MeOH can be produced from CO₂ hydrogenation at relatively higher temperatures (250–350 °C) with higher hydrogen pressures (5–10 MPa) (Meng et al., 2021; Han et al., 2021; Rui et al., 2020; Wang et al., 2017). Alternatively, CO₂ can also be indirectly converted to MeOH via the hydrogenation of “relay molecules” such as carbonates, carbamates, and formates under mild conditions, which was first developed by Milstein and co-workers using PNN pincer-type Ru(II) complexes (Balaraman et al., 2011). Amongst the relay molecules, the hydrogenation of ethylene carbonate (EC) to MeOH and ethylene glycol (EG) is of particular interest and has been regarded as a highly promising route (Scheme 1). As well known, EC is available industrially from the well-established “Omega process”, in which the cycloaddition of CO₂ with ethylene oxide is involved (Zubar et al., 2018; Decortes et al., 2010). More importantly, this indirect conversion process can be considered an example of a green carbon cycle that generates no carbon waste. Therefore, the development of effective catalysts for the hydrogenation of EC is the key issue in this process.

Recently, notable contributions to the hydrogenation of EC using homogeneous Ru, Mn, or Fe pincer-type complexes have been reported by the groups of Ding, Rueping, Leitner, and Werner (Zubar et al., 2018; Han et al., 2012; Kaithal et al., 2018; Liu et al., 2019). Nevertheless, difficult separation, recovery, and high costs of the homogeneous catalysts restrain industrial applications. In contrast, heterogeneous catalysts have attracted much more attention owing to easy separation and recovery from the reaction systems.

Among the heterogeneous catalysts, Cu-based catalysts are very active in the EC hydrogenation because of their unique ability for C=O/C–O bond hydrogenolysis (Prašnikar et al., 2021; Pavlišić et al., 2020; Huš...
et al., 2017). A wide scope of Cu-based catalysts has been developed (Lian et al., 2015; Chen et al., 2015, 2021b; Liu et al., 2015; Deng et al., 2018; Zhou et al., 2018; Ding et al., 2019; Song et al., 2020; Zhang et al., 2020). However, poor on-stream stability resulting from easy sintering of Cu nanoparticles owing to the low Tammann temperature of Cu nanoparticles still hinders the practical application. To enhance the catalytic performance and catalyst stability, modification of Cu-based catalysts with different additives or dopants (such as transition metals like Mg-Zr, Al, and Mo, and organic compounds like glucose and β-cyclodextrin) has been attempted (Tian et al., 2018; Shu et al., 2021; Yang et al., 2021; Song et al., 2021b; Chen et al., 2019; Zhang et al., 2018). Nonetheless, the on-stream stability or the catalytic performance is still unsatisfactory. In addition, it is worth noting that most Cu-based catalysts need pre-reduction in H₂ prior to the hydrogenation of EC in order to behave better. Therefore, the design of an effective and ultrastable Cu-based catalyst using a low-cost synthetic strategy is still challenging for the hydrogenation of EC to MeOH and EG.

Herein, we developed an efficient Cu@C/SiO₂ catalyst via a facile approach for the hydrogenation of EC, in which Cu nanoparticles were encapsulated by sorbitol-derived graphitized carbon overlayers. The Cu@C/SiO₂ catalyst afforded superior catalytic performance, showing 91% MeOH yield and 98% EG yield at a H₂/EC ratio of 20. Remarkably, the turnover frequency (TOF) of MeOH formation reached up to 43.6 h⁻¹ based on an EC conversion below 15%, higher than those reported in the literature. Of particular note, the Cu@C/SiO₂ catalyst was ultrastable during 736 h on-stream test without any deactivation.

RESULTS AND DISCUSSION

Evolution of sorbitol and Cu species

As described in the Experiment section, the Cu-sorbitol/SiO₂ catalyst precursor was prepared by a modified ammonia evaporation method using copper nitrate and silica sol as precursors, followed by calcination in N₂ at 350 °C for 4 h to obtain the resultant Cu@C/SiO₂ catalyst. To make clear what happened during the preparation of the Cu@C/SiO₂ catalyst and track the evolution of Cu species and sorbitol, the Cu@C/SiO₂ catalyst and related precursors were characterized thoroughly. Firstly, XRD was adopted to detect the crystalline phase of Cu species in as-calcined Cu@C/SiO₂ and as-calcined Cu/SiO₂. Clearly, typical metallic Cu (JCPDS No. 04–0836#) and Cu₂O phases (JCPDS No. 05–0667#) were detected for as-calcined Cu@C/SiO₂ (Figure 1A) (Deng et al., 2018; Song et al., 2021b), indicating that Cu²⁺ species have been already reduced to Cu and Cu₂O during calcination. A similar phenomenon was also observed in the case of mannitol-modified Cu/SiO₂ catalyst for the hydrogenation of diethyl oxalate, where Cu²⁺ species were also reduced to Cu and Cu₂O during calcination in nitrogen (Chen et al., 2020). By contrast, no Cu or Cu₂O phase, but copper phyllosilicate was detected for the as-calcined Cu/SiO₂ catalyst, suggesting that Cu²⁺ species have not been reduced during calcination yet, although the Cu/SiO₂ catalyst after reduction in hydrogen at 350 °C also showed the similar diffraction patterns of metallic Cu and Cu₂O. This big contrast aroused our interest to discover the inherent difference between these two samples. When we recalle the preparation procedures for these two samples, the only difference is that sorbitol was added during the preparation of Cu-sorbitol/SiO₂. Consequently, sorbitol in Cu-sorbitol/SiO₂ may play a key role during the calcination process in N₂.

To understand the role of sorbitol and to uncover the truth why Cu species can be reduced during the calcination of Cu-sorbitol/SiO₂ in N₂, the calcination processes of pure sorbitol and Cu-sorbitol/SiO₂...
were monitored by TPD-MS. As displayed in Figure S1A, sorbitol decomposed to CO and CO₂ during heating in nitrogen. Accordingly, Cu-sorbitol/SiO₂ also gave CO (weak) and CO₂ (strong) signals (Figure 1B), confirming that CO and CO₂ were in situ produced from the decomposition of sorbitol during the calcination process in nitrogen. Notably, no hydrogen signal was detected during the calcination of Cu-sorbitol/SiO₂ or pure sorbitol (Figure S1B). In contrast, no CO or CO₂ signals were detected for the reference Cu/SiO₂ catalyst (Figure 1B). In addition, according to the TPD-MS profiles in Figures 1B and S1A, the CO signal was much stronger than that of CO₂ for pure sorbitol, while it became weaker for Cu-sorbitol/SiO₂. This implies that CO in situ generated from sorbitol decomposition during the calcination of Cu-sorbitol/SiO₂ was partly consumed.

Moreover, the thermogravimetric analysis (TGA) of sorbitol in N₂ was also made to get some insights into the decomposition of sorbitol. Obviously, 100% weight loss was detected during the temperature rising from 240 to 350 °C, indicating that sorbitol completely decomposed to gaseous products without any solid residue (Figure 1C). For the TGA profile of Cu-sorbitol/SiO₂, the weight loss (160–350 °C) is also attributed to the decomposition of sorbitol. No obvious weight loss was detected when the temperature further rose to 350–600 °C in nitrogen (Figure 1D), indicating that sorbitol completely decomposed below 350 °C without any solid residue. Therefore, we deduce that in situ generated CO, via decomposition of sorbitol, acted as a reducing agent to reduce the Cu²⁺ species to Cu⁰ or Cu⁺ during the calcination in N₂ because there was no hydrogen released from the decomposition of sorbitol, just as observed in mannitol-modified Cu/SiO₂ catalyst (Chen et al., 2020).

Subsequently, to deeply understand the dispersion and morphology, the related samples were characterized using TEM (Figures 1E and 1F). According to the statistical results, the Cu/SiO₂ and Cu@C/SiO₂ catalysts have comparable Cu nanoparticle sizes of 3.9 and 3.3 nm, with the Cu particles dispersion of 25.6 and 30.3%, respectively (Table 1). Moreover, the HRTEM images of the Cu@C/SiO₂ catalyst in Figures 1G and 1H clearly show that Cu nanoparticles are encapsulated within thin layers of other substances. To specify the substance surrounding the Cu nanoparticles, the related samples were further characterized using XPS. As displayed in Figure 2A, the peak intensity of C1s for Cu@C/SiO₂ is much stronger than that of
adventitious carbon contamination. After deconvolution, there are three C1s peaks at 284.8, 286.5, and 288.2 eV, attributable to the C-C, C-O, and O-C=O species, respectively (Mou et al., 2019; Wang et al., 2016), suggesting that carbon overlayers with oxygen-containing carbonaceous functional groups surround the Cu nanoparticles. In contrast, the reference Cu/SiO2 catalyst only showed a weak and broad C1s peak attributable to the adventitious carbon contamination.

Furthermore, in order to distinguish the type of carbon overlayers deposited on the outer surface of Cu nanoparticles, Raman spectroscopy was applied. As shown in Figure 2B, there are two bands at 1369 and 1600 cm\(^{-1}\), the characteristic D band and G band of sp2 carbon species, respectively, for as-calcined Cu@C/SiO2 (Huang et al., 2019; Johnson and Thomas, 1984). The band area ratio ID/IG of 0.45 implies a high degree of graphitization in the carbon overlayers. Additionally, the G band was obviously blue-shifted by ~20 cm\(^{-1}\) (compared with 1580 cm\(^{-1}\)), which might be ascribed to an interaction between Cu and carbon overlayers (He et al., 2019; Calizo et al., 2009). However, the as-reduced Cu/SiO2 catalyst does not show any Raman information.

As for the origin of carbon overlayers, it was possibly derived from the disproportionation of CO (2CO (g) → C (s) + CO\(_2\) (g)) (Kim et al., 2021), rather than from the direct decomposition of sorbitol because the TG analysis results confirmed that sorbitol totally decomposed to gaseous compounds without any solid residue (Figure 1C). Then, C (s) formed graphitized carbon overlayers with the possible promotion of Cu nanoparticles. With regards to the formation mechanism of carbon overlayers, it might be similar to that of graphene film growth on Cu substrates (Li et al., 2009) or the quasi-graphic C shell-coated Cu catalyst (Kim et al., 2021). According to the literature (Kim et al., 2021), the C shell epitaxially grew on Cu with quasi-graphitic bonding via a gas-solid reaction governed by the CO (g) - CO\(_2\) (g) - C (s) equilibrium. Gaseous CO dissociated and was then adsorbed on the Cu surface to form graphene nuclei. As CO was continuously supplied, an atomically thin graphene layer grew, and a second layer formed through self-regulated epitaxial growth. Therefore, based on the above characterization results and the literature, CO, in situ generated from sorbitol decomposition, not only reduced Cu\(^2+\) to Cu\(^0\)/Cu\(^+\) but also formed graphitized carbon overlayers via the disproportionation. In order to visually display the preparation process, the synthetic route for the Cu@C/SiO2 catalyst is schematically illustrated in Figure 3A.

Furthermore, we also tracked the evolution of Cu species using the FT-IR spectroscopy. As displayed in Figure 2C, there is no typical \(\delta_{\text{OH}}\) band at 670 cm\(^{-1}\) or \(v_{\text{SiO}}\) shoulder peak at 1040 cm\(^{-1}\) for Cu@C/SiO2 and Cu-sorbitol/SiO\(_2\), indicating that no copper phyllosilicate existed on Cu@C/SiO\(_2\) and Cu@sorbitol/SiO\(_2\) (Song et al., 2020; Gong et al., 2012; Yuez et al., 2013), which is in good agreement with the XRD results. However, the relative content of copper phyllosilicates, in terms of the peak area ratio of \(I_{\text{2400}}\)/\(I_{\text{800}}\) at 670 cm\(^{-1}\) and 800 cm\(^{-1}\) (the \(v_{\text{SiO}}\) band of SiO\(_2\)) (Toupance et al., 2002; Chen et al., 2008), was 0.22 and 0.20, respectively, for the as-dried and as-calcined Cu/SiO\(_2\) catalyst (Figure 2D). The XRD results of as-dried and as-calcined Cu/SiO\(_2\) also confirmed the formation of copper phyllosilicates (JPCDS No. 027-01883) (Figures 1A and S2) (Song et al., 2021b; Yuez et al., 2013). This indicates that the introduction of sorbitol during the catalyst preparation process changed the evolution of Cu species. Nevertheless, a new band appeared at approximately 970 cm\(^{-1}\) for Cu-sorbitol/SiO\(_2\), suggesting the possible formation of Cu-O-Si species (Figure 2C) (Song et al., 2021b; Ye et al., 2017). After calcination under N\(_2\) atmosphere, the Cu@C/SiO\(_2\) catalyst showed an obvious shoulder peak at 965 cm\(^{-1}\), a hint of the presence of Cu\(^+\)-O-Si (Song et al., 2021b; Ye et al., 2017), which was also detected in the as-reduced Cu/SiO\(_2\) catalyst. Moreover,
the $\delta_{346}$ vibration of copper phyllosilicates at 670 cm$^{-1}$ for Cu/SiO$_2$ disappeared after reduction in hydrogen (Figure 2D), demonstrating that copper phyllosilicates were completely reduced to Cu species with lower valences.

Additionally, N$_2$ adsorption-desorption isotherms of Cu-based catalysts reveal the mesoporous structure because of type IV isotherms with H3-type hysteresis loops at P/P$_0$ = 0.8–1.0 (Figure S3A). The average pore size of Cu/SiO$_2$ centered at 3.6 nm (Figure S3B), which was also a hint of copper phyllosilicates existing in the catalyst (Song et al., 2020; Chen et al., 2009). However, there was no similar pore size distribution for Cu@C/SiO$_2$. This was in good agreement with the XRD and FT-IR spectroscopic results. The BET-specific surface area of Cu@C/SiO$_2$ was 141 m$^2$ g$^{-1}$, much lower than that for Cu/SiO$_2$ with 340 m$^2$ g$^{-1}$, mainly owing to that Cu@C/SiO$_2$ did not experience the evolution of a copper phyllosilicate precursor with lamellar structures. Furthermore, mesopores with a diameter of about 20 nm existed in Cu@C/SiO$_2$, and probably originated from the removal of sorbitol. The ICP-AES results show that the Cu/SiO$_2$ and Cu@C/SiO$_2$ catalysts contain comparable Cu loadings of about 18 wt % in addition to comparable Cu particle sizes, although they experienced different evolutions of Cu species and thus had different surface properties. For clarity, the relevant physicochemical parameters for these two Cu-based catalysts are listed in Table 1.

Catalytic performance and stability of the Cu@C/SiO$_2$ catalyst

Before the discussion of the catalytic performance with different Cu-based catalysts, a phenomenon should be paid attention to with regards to the hydrogenation of EC to MeOH and EG, that the selectivity to MeOH is usually lower than that of EG (Chen et al., 2015; Zhou et al., 2018; Song et al., 2020, 2021b).
According to the reaction equation, the selectivity to MeOH should be equal to that to EG theoretically, if 3 mmol of hydrogen reacts with 1 mmol of EC. However, when EC reacts with equivalent hydrogen, EG and CO or CO₂ will be released via decarbonylation or decarboxylation. Besides, hydrolysis of EC with a trace amount of water cannot be avoided to produce EG and CO₂ (Chen et al., 2015; Zhou et al., 2018; Song et al., 2021b). In addition, MeOH can also decompose to CO in some cases (Song et al., 2020). All these side reactions would give rise to lower MeOH selectivity. Hence, MeOH selectivity is an important index to reflect the catalyst ability.

With the graphitized carbon overlayers deposited on the outside of Cu nanoparticles, we are eager to investigate the Cu@C/SiO₂ catalyst toward the hydrogenation of EC at 180 °C under 4 MPa of H₂ with a H₂/EC ratio of 20 in a fixed-bed reactor. For comparison, the reference Cu/SiO₂ catalyst, prepared by a similar method just without the addition of sorbitol but experienced calcination at 450 °C and pre-reduction in hydrogen at 350 °C, was also submitted to the EC hydrogenation under the same conditions. As summarized in Table 1, the reference catalyst Cu/SiO₂, even after pre-reduction in H₂ prior to the catalytic test, achieved a MeOH selectivity of 72.0% at an EC conversion of 99.6% at a weight liquid hourly space velocity (WLHSVₜ₝) of 0.26 h⁻¹. To our delight, the as-calcined Cu@C/SiO₂ catalyst, just after calcination in nitrogen without further pre-reduction in H₂, afforded a 91% MeOH selectivity at an EC conversion of 99.9% at the same WLHSVₜ₝ of 0.26 h⁻¹. Actually, the Cu-sorbitol/SiO₂ precursor was also calcined in air at 450 °C for 4 h, followed by a reduction in H₂ at 350 °C for 4 h, and then submitted to the hydrogenation of EC in a fixed-bed reactor. To our disappointment, the catalyst only afforded 68.5% MeOH selectivity, much lower than that obtained with the Cu@C/SiO₂ catalyst, indicating that the calcination atmosphere is the key factor to influence the decomposition of sorbitol. Remarkably, the MeOH selectivity with the Cu@C/SiO₂ catalyst was obviously improved compared with those with the reference catalysts, confirming the importance of carbon overlayers on the outer surface of Cu nanoparticles.

In order to obtain the intrinsic catalytic activity, the hydrogenation of EC with the Cu/SiO₂ and Cu@C/SiO₂ catalysts was further investigated in the kinetic regime (<15% EC conversion). The turnover frequency of MeOH formation (TOFₘeOH) obtained from the two catalysts was calculated based on surface Cu atoms. As a result, the TOFₘeOH over the Cu@C/SiO₂ catalyst reached 43.6 h⁻¹, about 1.7 times higher than that of the Cu/SiO₂ catalyst (25.2 h⁻¹). Moreover, according to the Arrhenius plots displayed in Figure 4A, the apparent activation energy Eₐ with the Cu@C/SiO₂ catalyst (98.9 kJ·mol⁻¹) is much lower than that with the Cu/SiO₂ catalyst (142.2 kJ·mol⁻¹), indicating that the encapsulation of carbon overlayers on the outer surface of Cu nanoparticles might result in new hydrogenation active sites (Cu³⁺-O-C species) and thus improve the catalytic efficiency.

Based on the above results, the Cu@C/SiO₂ catalyst afforded superior catalytic performance, which might be the best candidate for EC hydrogenation at this stage. To discover the performance of the Cu@C/SiO₂
catalyst to the greatest extent, the reaction parameters were optimized subsequently. Figure S4A showed the effect of calcination temperature on EC conversion and product selectivity with the Cu@C/SiO2 catalyst after calcination at various temperatures from 350 °C to 450 °C. It is of particular note that the Cu@C/SiO2 catalyst has the self-reduction property, so the calcination temperature is the reduction temperature actually. With increasing the catalyst calcination/reduction temperature from 350 °C to 450 °C, the EC conversion decreased obviously, and the MeOH selectivity decreased slightly although the MG selectivity remained almost constant. Subsequently, the effect of the H2/EC ratios was also investigated. As shown in Figure S4B, the EG selectivity remained almost constant in the range of 10–40. However, EC conversion and MeOH selectivity increased at first and then reached a plateau at a H2/EC molar ratio of 20, then remained almost constant with the further increase of the H2/EC molar ratio to 40. A similar conclusion was also drawn in the case of the nanoflower-like Cu/SiO2 catalyst (Zhang et al., 2020).

Additionally, the long-term stability of the Cu@C/SiO2 catalyst was also investigated. As displayed in Figure 4B, stable 99.9% EC conversion, 98.2% EG selectivity, and 91% MeOH selectivity, respectively, were afforded by the Cu@C/SiO2 catalyst during the whole 736 h on-stream test. However, the stability of the Cu@C/SiO2 catalyst cannot be guaranteed only from the long-term performance because the total conversion of EC was obtained during the whole process under the tested conditions, where the active sites for the reaction under the tested conditions might be much more than the reaction actually needed. Nevertheless, the unchanged average Cu particle size of the used Cu@C/SiO2 catalyst after 736 h on-stream test compared with that of the fresh Cu@C/SiO2 catalyst (Figure S4C) surely confirmed the excellent stability of the Cu@C/SiO2 catalyst. By contrast, obvious deactivation within 200 h for the Cu/SiO2 catalyst in the continuous hydrogenation of EC was observed under the same conditions (Figure 4B). Obviously, the carbon overlayers on the outer surface of Cu nanoparticles played a vital role in stabilizing Cu nanoparticles. This also confirms that the Cu@C/SiO2 catalyst is robust for the hydrogenation of EC to MeOH and EG even at a H2/EC ratio of 20, exhibiting great potential for the industrial application.

Of particular note, the Cu@C/SiO2 catalyst in this case notably surpasses most of those Cu-based catalysts reported in the literature, in terms of the catalyst activity, selectivity, and stability. As clearly shown in Table S1, most of the Cu-based catalysts in the literature exhibited 56.1–85.8% MeOH selectivity at a higher H2/EC molar ratio of 100–300 (Chen et al., 2015, 2019, 2021b; Deng et al., 2018; Zhou et al., 2018; Tian et al., 2018; Shu et al., 2021; Yang et al., 2021), which will definitely bring huge waste of hydrogen resources. The S-1@Cu catalyst in our previous studies exhibited a higher MeOH yield of 92% at a H2/EC molar ratio of 100. However, an obvious deactivation of S-1@Cu catalyst was observed after 350 h (Ding et al., 2019). The gradual deactivation was also encountered with the highly selective B-70%CuSiO2-PG catalyst at a H2/EC molar ratio of 60 (Liu et al., 2015). In this case, the Cu@C/SiO2 catalyst afforded a MeOH yield of 91% at an extremely low H2/EC ratio of 20. Moreover, the Cu@C/SiO2 catalyst showed an excellent lifetime for at least 736 h without any deactivation.

Figure 4. Catalytic performance and stability of the Cu@C/SiO2 and Cu/SiO2 catalyst
(A and B) Arrhenius plots of the hydrogenation of EC over the Cu@C/SiO2 and Cu/SiO2 catalysts (A), stability test of the Cu@C/SiO2 and Cu/SiO2 catalysts in the EC hydrogenation at T = 180 °C, P(H2) = 4.0 MPa, H2/EC = 20 (mol·mol⁻¹) and WHSVEC = 0.26 g·gcat⁻¹·h⁻¹ (B).

Table S1. Performance of Cu-based catalysts in the hydrogenation of EC to MeOH, EG, and MG.
We also compared the Cu@C/SiO₂ catalyst with those Cu-based catalysts modified by other organic compounds such as glucose and β-cyclodextrin. Although the CuG₁/SiO₂-ACE catalyst (glucose-modified Cu/SiO₂ catalyst prepared by an ammonia evaporation method) in our previous studies showed enhanced catalytic performance in terms of MeOH selectivity and catalyst lifetime compared with the unmodified Cu/SiO₂ catalyst, the aggregation of Cu nanoparticles cannot be avoided at all. As a result, the average Cu particle size increased from 4.8 nm for the fresh CuG₁/SiO₂-ACE catalyst to 12 nm for the used one after 500 h time-on-stream test even at a WLHSV of 0.13 g·g_{cat}^{-1}·h^{-1} (Chen et al., 2019). β-cyclodextrin modified Cu/SiO₂ catalyst was prepared by one-step hydrolysis precipitation (HP) method and applied to the hydrogenation of EC in a batch reactor after pre-reduction in H₂. In comparison with unmodified Cu/SiO₂ catalysts, the reusability of β-cyclodextrin modified Cu/SiO₂ catalyst was improved to some extent. The authors ascribed the improvement to the residual carbon derived from the decomposition of β-cyclodextrin, which likely retarded the aggregation of Cu nanoparticles (Zhang et al., 2018). Nevertheless, the improvement of MeOH selectivity was very limited because only about 64.6% selectivity to MeOH was afforded with β-cyclodextrin in MeOH selectivity was very limited because only about 64.6% selectivity to MeOH was afforded with β-cyclodextrin modified Cu/SiO₂ catalysts. Therefore, the enhancement of sorbitol to the Cu/SiO₂ catalyst for the hydrogenation of EC was superior to other organic compounds, perhaps the graphitized carbon overlayers, different from other residual carbon, play an important role to improve the catalytic activity of the Cu@C/SiO₂ catalyst.

To explore the catalytic performance of the Cu@C/SiO₂ catalyst to the greatest extent, the Cu@C/SiO₂ catalyst was also investigated under the H₂/EC ratio of 20 at higher WLHSV. Clearly, 99% EC conversion was still accomplished with 90% selectivity to MeOH even if the WLHSV increased from 0.26 to 0.91 g·g_{cat}^{-1}·h^{-1} (see Table S1). Furthermore, in order to deeply understand the Cu@C/SiO₂ catalyst, the STY (space-time yield) and TOF of MeOH were calculated and summarized in Table S1 according to the raw data in the literature. In this work, the Cu@C/SiO₂ catalyst afforded the STY of 0.296 g·g_{cat}^{-1}·h^{-1} and TOF of 43.6 h⁻¹ at a H₂/EC ratio of 20 (Table S1). To the best of our knowledge, it is one of the highest STYs and TOF values obtained with the Cu-based catalysts up to now. We deduce that the interaction between Cu nanoparticles and graphitized carbon overlayers may inhibit the side reactions such as decarbonylation and decarboxylation of EC or MeOH decomposition, thus enhancing the selectivity to MeOH. This is also consistent with the Cu-Mo interface (Song et al., 2021b).

Further characterizations of Cu@C/SiO₂ and Cu/SiO₂

To deeply understand the origin of the superior catalytic performance and long-term stability of the Cu@C/SiO₂ catalyst, a series of characterizations were further applied. H₂-TPR was carried out to study the reducibility and the interaction of metal-support/dopant (Figure 5A). A reduction peak at 220 °C was detected for as-calcined Cu/SiO₂, which can be attributed to the reduction of highly dispersed CuO to Cu⁰ and copper phyllosilicates to Cu⁺ (Song et al., 2021b; Chen et al., 2008). By comparison, the reduction for as-calcined Cu@C/SiO₂, which can be attributed to the reduction of highly dispersed CuO to Cu⁰ and copper phyllosilicates to Cu⁺ (Song et al., 2021b). This is also consistent with the Cu-Mo interface (Song et al., 2021b).

Next, the surface chemical states of Cu species of Cu@C/SiO₂ and Cu/SiO₂ were further probed by XPS. As shown in Figure 5B, the BEs at around 932 and 952 eV are assigned to Cu 2p3/2 and Cu 2p1/2 of Cu⁰/Cu⁺ species, respectively (Wang et al., 2015). It seems that Cu⁺/Cu⁰ species on as-calcined Cu@C/SiO₂ and as-reduced Cu/SiO₂ were re-oxidized to Cu²⁺ by exposure to air during the preparation of XPS samples because Cu²⁺ satellite peak (943.8 eV) was detected for both samples. Nevertheless, the Cu²⁺ satellite peak of the as-calcined Cu@C/SiO₂ catalyst was much weaker than that of as-reduced Cu/SiO₂, which strongly implies that Cu nanoparticles for the as-calcined Cu@C/SiO₂ catalyst are covered by carbon overlayers and not easily re-oxidized to Cu²⁺. Furthermore, to precisely distinguish Cu⁰ from Cu⁺ species, Cu LMM spectra were also measured (Figure 5C). The asymmetric peak can be deconvoluted into two peaks centered at about 569.9 and 573.0 eV corresponding to Cu⁰ and Cu⁺, respectively (Wang et al., 2015; Yao et al., 2018). As a result, the Cu⁺/(Cu⁰ + Cu⁺) molar ratio increased from 35% in as-reduced Cu/SiO₂ to 51% in as-calcined Cu@C/SiO₂ catalyst, suggesting that an interaction between Cu and carbon overlayers might...
be derived from the formation of a distinct chemical bond (Cu\textsuperscript{+}-O-C) located at the Cu-carbon overlayers interfaces (Yao et al., 2020). In addition, the interaction between carbon overlayers and Cu was also reflected by the BE of the Cu\textsuperscript{+} species in Cu@C/SiO\textsubscript{2} (573.2 eV), which is lower than that of Cu/SiO\textsubscript{2} (574.0 eV). This interaction via carbon overlayers may not only increase the surface Cu\textsuperscript{+}/(Cu\textsuperscript{2+}+Cu\textsuperscript{0}) molar ratio but also benefit the catalyst stability. Furthermore, in situ FT-IR spectroscopy of CO adsorbed on Cu@C/SiO\textsubscript{2} and Cu/SiO\textsubscript{2} was also applied to distinguish various surface cupreous species. As displayed in Figure 5D, a main CO peak at 2119 cm\textsuperscript{-1} along with a weak shoulder peak of 2112 cm\textsuperscript{-1} was detected for the Cu@C/SiO\textsubscript{2} catalyst. However, one asymmetric and intense CO vibration band centered at 2100-2160 cm\textsuperscript{-1} was observed for the Cu/SiO\textsubscript{2} catalyst. Obviously, the asymmetric CO band can be deconvoluted to two peaks at around 2124 and 2112 cm\textsuperscript{-1}. Considering that CO chemisorbed on Cu\textsuperscript{0} sites is weak and can be swept off by flushing with nitrogen, the bands at 2124, 2119, and 2112 cm\textsuperscript{-1} should be assigned to the Cu\textsuperscript{+}-CO species (Song et al., 2021b; Zheng et al., 2013). Nevertheless, that the IR bands of Cu\textsuperscript{+}-CO species centered at different positions also imply the formation of new Cu species on the Cu@C/SiO\textsubscript{2} catalyst. In combination with FT-IR and H\textsubscript{2}-TPR results, we speculate that the CO bands at 2112, 2119, and 2124 cm\textsuperscript{-1} may be attributed to CO adsorbed on Cu\textsuperscript{+}-O-Si units, Cu\textsuperscript{+}-O-C, and copper phyllosilicate-derived Cu\textsuperscript{+}, respectively. Besides, the intensity of CO vibration band adsorbed on Cu@C/SiO\textsubscript{2} was quite weaker than that on Cu/SiO\textsubscript{2}. Considering that the Cu/SiO\textsubscript{2} and Cu@C/SiO\textsubscript{2} catalysts have comparable Cu nanoparticle sizes (3.3–3.9 nm, Figures 1E and 1F), the dramatically decreased intensity of CO vibration bands can be reasonably ascribed to the lower CO coverage, caused by the encapsulation of Cu nanoparticles by carbon overlayers. Similar phenomena were commonly observed after the introduction of overlayers (Chen et al., 2021a; Tang et al., 2016; Song et al., 2021a).

In addition, the acidity of Cu-based catalysts usually plays a significant role in ester hydrogenation, because Cu\textsuperscript{+} species can act as Lewis acid sites (LAS) to polarize the O=C-O group of esters (Gong et al., 2012; Yue et al., 2013). In order to understand the surface acidity and acid type of the Cu@C/SiO\textsubscript{2} and Cu/SiO\textsubscript{2}
catalysts, NH3-TPD and pyridine-FTIR spectroscopy were also applied (Figure S5). The NH3-TPD profiles verify the presence of weak acid sites (<200 °C) in Cu@C/SiO2 and Cu/SiO2. Besides, a weak NH3 desorption peak in the medium-strong acidity region (200–400 °C) was detected for the Cu@C/SiO2 catalyst (Song et al., 2018, 2021b). In addition, the surface acidity of Cu@C/SiO2 (0.14 mmol·g⁻¹) was comparatively higher than that of Cu/SiO2 (0.08 mmol·g⁻¹). The above results indicate that the introduction of carbon overlayers significantly enhances the strength and quantity of surface acid sites, which might be caused by the presence of the Cu⁺-O-C species. Furthermore, the IR spectroscopic investigations of pyridine adsorption indicated that only Lewis acid sites existed on the Cu/SiO2 and Cu@C/SiO2 catalyst surface (Song et al., 2020, 2021b).

To understand the difference in the catalytic performance of the Cu/SiO2 and Cu@C/SiO2 catalysts toward the hydrogenation of EC, the in situ FT-IR spectroscopy was adopted to investigate the EC adsorption and hydrogenation behaviors with flowing hydrogen. Figures 5E and 5F displays the FT-IR spectra of EC hydrogenation with different H2 flushing time. For both catalysts, two small bands at 1300-1500 cm⁻¹ assigned to scissoring and wagging vibrations of CH2 (δCH2 and δCH2as) and two C=O stretching vibration bands in the region of 1700-1850 cm⁻¹ were detected after EC adsorption (Ding et al., 2019; Song et al., 2020, 2021b). After switching on H2 flow, the intensities of the C=O stretching vibration band gradually decreased with reaction time, along with the disappearance of δCH2 and δCH2as. Meanwhile, some new bands appeared, highly consistent with the vibration bands of pure EG and pure MeOH (at 1416 and 1349 cm⁻¹). In addition, another band at 1605 cm⁻¹, appearing in MeOH stretching vibration region (1540-1740 cm⁻¹), was only observed for Cu@C/SiO2 (Figures 5F and S6). This implies that Cu@C/SiO2 is more favorable for MeOH formation. More importantly, the C=O vibration band totally disappeared on the Cu@C/SiO2 catalyst after 45 min, shorter than that (60 min) for the total conversion of EC on the Cu/SiO2 catalyst. This indicates that the hydrogenation of the C=O bond was faster on the Cu@C/SiO2 catalyst, in good agreement with the observed overall catalytic behaviors.

Based on the catalyst structure analysis, a possible synergistic catalysis for the hydrogenation of EC was proposed (Figure 3B). The surface Cu0 species are responsible for the adsorption and dissociation of H2, and Cu+ serves as surface Lewis acid sites, providing the adsorption sites for the C=O bond. The C=O group can chemisorb at the Cu-C interface via an interaction between the carbonyl oxygen and Cu+. The hydrogenation of EC starts with the nucleophilic attack of adsorbed H atoms to the electron-deficient carbon of the ester group. Furthermore, the promotion of H2 activation on the Cu surface by graphitized carbon can facilitate the activation of EC (Zheng et al., 2022), which is beneficial to the selectivity toward MeOH.

Further discussion

The enhanced MeOH selectivity and stability with this graphitized carbon overlayers-encapsulated Cu-based catalysts were attempted to interpret in several ways. First, according to the detailed characterization results discussed above, the introduction of carbon overlayers slightly enhanced the dispersion of Cu and increased S_{Cu,0} (Table 1). Meanwhile, carbon overlayers on the outer surface of Cu nanoparticles not only altered the physicochemical properties of the Cu@C/SiO2 catalysts but also influenced the electronic properties of Cu nanoparticles owing to the interaction between Cu and carbon overlayers. According to the literature, the suitable Cu⁺/(Cu⁺+Cu0) ratios on the surface led to the optimal MeOH selectivity (Deng et al., 2018; Ding et al., 2019; Tian et al., 2018; Song et al., 2021b). In addition, it is generally accepted that Cu0 species activate H2, while Cu+ species activate the carbonyl group (Gong et al., 2012; Yue et al., 2013; Wang et al., 2015). The Cu⁺/(Cu⁺+Cu0) ratio calculated from Figure 5C is ca. 0.51 for the fresh Cu@C/SiO2 catalyst, which is close to the optimal ratio for the EC hydrogenation obtained in our previous work (Song et al., 2020, 2021b). The higher ratio of Cu⁺ sites and the interaction of Cu nanoparticles with graphitized carbon overlayers were favorable to activate the O-C=O group of EC, thus accelerating the reaction as confirmed by the markedly reduced Ea value.

Second, catalytic efficiency and stability can be improved by the encapsulation strategy and adjustment of the electronic properties of the metal center surface by interaction with overlayers (Chen et al., 2021a). When recalling the MeOH selectivity and catalyst stability, a 72% yield of MeOH was obtained over Cu/SiO2, while significantly improved catalytic efficiency of Cu@C/SiO2 was obtained, resulting in a 91% yield of MeOH. Most importantly, the yield of MeOH kept stable at 91% during the 736 h on-stream test without any deactivation, reflecting astonishing stability. Meanwhile, the Cu⁺/(Cu⁺+Cu0) ratio (50.8%, Figure S7) and the average Cu particle size of the used Cu@C/SiO2 catalyst are almost unchanged compared to those
for the fresh catalyst, suggesting that the balanced Cu species can be stabilized by the interaction of Cu nanoparticles with graphitized carbon overlayers in addition to the inhibition of Cu nanoparticles aggregation under the reaction conditions. The stabilization of Cu nanoparticles by graphitized carbon overlayers, in this case, is very similar to the case of the C\textsubscript{60}-buffered Cu/SiO\textsubscript{2} catalyst. With the d-π interaction between Cu and C\textsubscript{60}, the C\textsubscript{60}-buffered Cu/SiO\textsubscript{2} catalyst had a stable Cu\textsuperscript{0}/Cu\textsuperscript{+} ratio to realize the hydrogenation of diethyl oxalate at ambient pressure with higher selectivity to ethyl glycol and longer lifetime (Zheng et al., 2022).

Conclusions
In this work, we fabricated an ultrastable and efficient Cu@C/SiO\textsubscript{2} catalyst for the continuous hydrogenation of EC to yield MeOH and EG by a facile approach. Simple calcination of sorbitol-coated Cu nanoparticles under N\textsubscript{2} atmosphere not only realized the reduction of Cu\textsuperscript{2+} to Cu\textsuperscript{0}/Cu\textsuperscript{+} but also led to the encapsulation of graphitized carbon overlayers on Cu nanoparticles. Such encapsulation created interfacial sites via the strong interaction between Cu and graphitized carbon overlayer species. Meanwhile, the graphitized carbon overlayers effectively prevent Cu nanoparticles from aggregation and stabilize the surface Cu\textsuperscript{+}/Cu\textsuperscript{0} ratio. As a result, the Cu@C/SiO\textsubscript{2} catalyst exhibited superior catalytic performance and stability, affording 91% MeOH yield and 98% EG yield within 736 h time-on-stream test without any deactivation. The characterization results and kinetic studies revealed that the graphitized carbon overlayers worked synergistically with surface Cu\textsuperscript{0} and Cu\textsuperscript{+} sites to promote EC hydrogenation rather than block the surface reactions. In addition, medium-strong Lewis acid sites on the Cu@C/SiO\textsubscript{2} catalyst surface were also favorable for MeOH formation. The graphitized carbon overlayers encapsulated Cu@C/SiO\textsubscript{2} catalyst showed potential in industrial application owing to economical preparation.

Limitations of the study
In this work, we designed and prepared a graphitized carbon encapsulated Cu@C/SiO\textsubscript{2} catalyst, which not only achieved comparable MeOH selectivity and better stability with the second metal-modified Cu/SiO\textsubscript{2} catalysts but also showed potential in industrial application owing to economical preparation. However, sorbitol-derived graphitized carbon overlayers on the outer surface of Cu nanoparticles may not be very uniform and the thickness of carbon overlayers was not successfully characterized although we attempted to get some insights.

STAR METHODS
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SUPPLEMENTAL INFORMATION
Supplemental information can be found online at https://doi.org/10.1016/j.isci.2022.105239.

ACKNOWLEDGMENTS
This work was financially supported by the Science and Technology Commission of Shanghai Municipality (No.22ZR1420100), the National Natural Science Foundation of China (No. 21872054), and “the Research Funds of Happiness Flower ECNU (2019ST2101).”

AUTHOR CONTRIBUTIONS
X. L. supervised this project. T. S. and X. L. conceived the ideas for the project and designed the experiments. T. S. conducted the material synthesis, characterizations, and catalytic tests. Y. Q. assisted with
the sample characterizations. T. S. prepared the original draft. X. L., C. Z., and P. W. reviewed and revised the article. All authors participated in the discussion of this project.

DECLARATION OF INTERESTS
X. L., T. S., and W. P. applied for a China patent based on the technology described in this work at East China Normal University (Application number: 202110835258.3). The other authors declare no competing interests.

Received: July 8, 2022
Revised: September 15, 2022
Accepted: September 26, 2022
Published: October 21, 2022

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STAR METHODS

KEY RESOURCES TABLE

| REAGENT or RESOURCE | SOURCE | IDENTIFIER |
|---------------------|--------|------------|
| Chemicals, Peptides, and Recombinant Proteins | | |
| Cu(NO$_3$)$_2$·3H$_2$O | Sinopharm | CAS: 10031-43-3 |
| Sorbitol | Aladdin | CAS: 50-70-4 |
| Ammonia solution | Sinopharm | CAS: 1336-21-6 |
| Ethylene carbonate | Aladdin | CAS: 96-49-1 |
| 1,4-dioxane | Richjoint | CAS: 123-91-1 |
| Colloidal silica | Sigma-Aldrich | CAS: 7631-86-9 |
| Software and algorithms | | |
| Origin 2018 | OriginLab | https://www.originlab.com/ |
| ICP-AES (IRIS Intrepid II XSP) | Thermo Fisher Scientific | https://www.thermofisher.com/ |
| XRD (D8 ADVANCE) | Bruker | https://www.bruker.com/ |
| N$_2$ physisorption (Autosorb-3B system) | Quantachrome | https://www.anton-paar.com/ |
| TEM (FEI Tecnai G2-TF30) | FEI | https://www.fei.com |
| AutoChem II Chemisorption Analyzer | Micromeritics | https://www.micromeritics.com/ |
| XPS (ESCALAB 250Xi) | Thermo Fisher Scientific | https://www.thermofisher.com/ |
| Raman (InVia) | Renishaw | https://www.renishaw.com.cn/ |
| TGA (TGA/SDTA851e) | METTLER TOLEDO | https://www.mt.com/cn/ |
| FT-IR | Thermo Nicolet | https://www.thermofisher.com/ |

RESOURCES AVAILABILITY

Lead contact

Further information and requests for resources should be directed to and will be fulfilled by the lead contact, Xiaohong Li (xhli@chem.ecnu.edu.cn).

Materials availability

This study did not generate new unique reagents.

Data and code availability

- All data reported in this paper will be shared by the lead contact upon request.
- This paper does not report original code.
- Any additional information required to analyze the data reported in this paper is available from the lead contact upon request.

METHOD DETAILS

Catalyst preparation

Chemical reagents including Cu(NO$_3$)$_2$·3H$_2$O (Sinopharm, 99%), sorbitol (Aladdin, 98%), ammonia solution (Sinopharm, 25%–28%), and colloidal silica (Sigma-Aldrich, Ludox-HS, 40 wt.%) were purchased from commercial suppliers and used as received.

The Cu@C/SiO$_2$ catalyst precursor, Cu-sorbitol/SiO$_2$, was prepared by a modified ammonia evaporation method. Firstly, 11 g of Cu(NO$_3$)$_2$·3H$_2$O and 0.35 g of sorbitol were dissolved in 140 mL of deionized water. After stirring for 30 min, 25 wt% ammonia solution was slowly added to the above solution under stirring to keep the initial pH of the suspension at 12–13. Then, colloidal silica with required amount was
added to the above solution and followed by stirring at RT for 4 h. After that, the mixture was heated to 90 °C to evaporate ammonia until the pH value of the suspension decreased to 6–7. Finally, the resultant solid was filtered, washed with plenty of water, and dried at 120 °C for 24 h to obtain Cu-sorbitol/SiO2.

For reference, Cu/SiO2 catalyst precursor was also prepared using the same synthesis procedures as for Cu@sorbitol/SiO2 except that no sorbitol was added. Subsequently, the obtained precipitate was calcined in air at 450 °C for 4 h. Before the catalytic test, the Cu/SiO2 catalyst precursor was reduced in H2 at 350 °C for 4 h.

**Catalyst characterization**

ICP-AES was applied to detect the actual Cu content in the Cu/SiO2 and Cu@C/SiO2 catalysts on Thermo IRIS Intrepid II XSP. A Bruker D8 ADVANCE powder diffractometer using Cu Kα radiation (λ = 0.15418 nm, 25 mA, 35 kV) was adopted to measure the X-ray diffraction (XRD) patterns of samples. N2 physisorption analysis was measured at 77 K using a Quantachrome Autosorb-3B system after the samples were degassed at 200°C for 3 h. The specific surface area was calculated by the BET (Brunauer-Emmett-Teller) equation from the adsorption branch. Transmission electron microscopy (TEM) images were taken by an FEI Tecnai G2-TF30 microscope at an acceleration voltage of 300 kV. Cu particle dispersion was obtained by D Cu(%) = 1.0/d Cu (nm) (according to d Cu (nm) = 0.26/SCu1/2, where d Cu represents the mean Cu particle size from TEM) (Song et al., 2020; Chen et al., 2019). Cu0 surface area (SCu0) was calculated according to $S_{Cu0} = \frac{D_{Cu} x N_a x Cu\, loading}{M_{Cu} x 1.6 x 10^{-23}} \approx 649 x D_{Cu} x Cu\, loading$ (Liu et al., 2015; Deng et al., 2018).

H2 temperature-programmed reduction (H2-TPR) measurements were conducted using a Micromeritics AutoChem II Chemisorption Analyzer equipped with a thermal conductivity detector (TCD). Typically, samples were pre-treated at 200 °C in He (30 mL min⁻¹) for 1 h and then cooled down to RT. After that, the samples were heated in 10% H2-Ar (30 mL min⁻¹) to 800 °C at a ramp rate of 10 °C min⁻¹. Temperature-programmed desorption of ammonia (NH3-TPD) of samples was also performed with a Micromeritics AutoChem II Chemisorption Analyzer. With regards to the NH3-TPD of Cu/SiO2, the as-calcined Cu/SiO2 was reduced at 350 °C in 10% H2-Ar (30 mL min⁻¹) for 4 h firstly, and then cooled down to 40 °C in He (30 mL min⁻¹). After that, the samples pre-adsorbed NH3 in 10% NH3-He (30 mL min⁻¹) for 30 min. Subsequently, the samples were purged by He (30 mL min⁻¹) at 100 °C for 40 min. Finally, the NH3-TPD profile was recorded in He by a TCD from 100 °C to 850 °C at a ramp rate of 10 °C min⁻¹. The NH3-TPD profile of the as-calcined Cu@C/SiO2 catalyst was also measured according to the same procedures as for the as-calcined Cu/SiO2 except that no reduction with H2 was adopted.

For the TPD-MS (temperature-programmed desorption-mass spectroscopy) analysis, about 60 mg of as-dried samples were heated from 30 °C to 700 °C with a heating rate of 10 °C min⁻¹ and the desorbed products (H2, CO or CO2) were monitored using MS (m/z = 2, 28 or 44). The X-ray photoelectron spectroscopy (XPS) analysis was conducted on a Thermo Fisher Scientific ESCALAB 250Xi spectrometer with an Al Kα radiation (1486.6 eV). All binding energies (BEs) were calibrated using Si 2p peak at 103.5 eV of SiO2 as reference. Raman spectra of the catalysts were obtained on a Renishaw InVia instrument with a 325 nm excitation wavelength. Thermogravimetric analyses (TGA) were measured on a Mettler Toledo TGA/SDTA851e thermal analyzer in the temperature range of 30–700 °C in N2.

Fourier transform infrared (FT-IR) spectra of the samples were obtained on a NEXUS 870 spectrometer with a spectral resolution of 4 cm⁻¹ and 64 scans. The in situ FT-IR spectroscopy was adopted to investigate the CO chemisorption and pyridine adsorption on samples with a Nicolet iS50 FTIR spectrometer. The as-calcined Cu/SiO2 catalyst was pressed into a self-supported wafer and placed into an in situ IR cell, followed by in situ reduction in H2 (30 mL min⁻¹) at 350 °C for 1 h, and then cooled down to 180 °C and kept at 180 °C in hydrogen (30 mL min⁻¹) for additional 30 min and finally cooled down to RT in N2 (30 mL min⁻¹). After that, the background spectrum was collected. The as-calcined Cu@C/SiO2 was pretreated in hydrogen (30 mL min⁻¹) at 180 °C for 30 min and cooled down to RT in N2 (30 mL min⁻¹) without adsorption at 350 °C in hydrogen for 1 h. After that, various adsorbates were introduced separately for adsorption under different conditions. For CO adsorption, the samples were exposed to CO (30 mL min⁻¹) at 30 °C for 10 min. Then, the samples were purged at 30 °C by N2.
(30 mL min\(^{-1}\)) for 30 min. Finally, the spectra were recorded. For pyridine adsorption, the samples were 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 taken in the range of 1400–1700 cm\(^{-1}\).

The FT-IR spectroscopy of EC desorption from the Cu/SiO\(_2\) and Cu@C/SiO\(_2\) catalysts and in situ EC hydrogenation on the Cu-based catalysts was also investigated using a Nicolet iS50 FT-IR spectrometer. Prior to the measurement, the Cu/SiO\(_2\) sample was pressed into a 30 mm self-supported wafer, then the wafer was cut into two 13 mm self-supported wafers (about 12–15 mg). Then, the one was placed into an in situ IR cell and pre-treated according to the procedures for the same sample before CO or pyridine adsorption, just for the purpose of taking the background spectrum. The other one was reduced in a specially designed quartz tube firstly. Subsequently, 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. After that, the sample with pre-adsorbed EC was placed into the in situ IR cell under N\(_2\) atmosphere, and heated to 180 °C in H\(_2\) (30 mL•min\(^{-1}\)). The spectra were collected every 10 min at 180 °C. The as-calcined Cu@C/SiO\(_2\) sample was also pretreated using the same procedures as for Cu/SiO\(_2\) except no reduction at 350 °C for 1 h.

**Catalytic test**

EC hydrogenation was performed in a stainless steel fixed-bed tubular reactor (with 550 mm length and 12 mm inner diameter). Specifically, 2.5 g of as-dried Cu-sorbitol/SiO\(_2\) catalyst precursor (20–40 mesh) was loaded in the middle position of the reactor and pretreated in N\(_2\) (60 mL•min\(^{-1}\)) at 350 °C for 4 h. After cooling down to 180 °C and switching N\(_2\) to H\(_2\) with 4.0 MPa, 10 wt% EC in 1,4-dioxane was pumped to the catalyst bed with WLHSV\(_{EC}\) of 0.26 g•g\(_{cat}\)\(^{-1}\)•h\(^{-1}\). The liquid effluent was collected by an online trap (6 °C) and analyzed by TECHCOMP GC-7900 Plus GC equipped with a flame ionization detector and a DM-5 capillary column (30 m × 0.32 mm × 1 μm). Experimental tests for the calculations of initial activity (in terms of turnover frequency, TOF) and activation energy (E\(_a\)) were carried out at an EC conversion below 15% by controlling the WLHSV\(_{EC}\). Furthermore, prior to the experiments for E\(_a\) and TOF calculations, limitations on catalytic performance due to internal and external diffusion and heat transfer were ruled out by the Weisz-Preter criterion and Mears’ criterion, respectively (see supplemental information for details).

EC conversion and product selectivity were defined as follows:

\[
\text{Conversion} (\%) = \frac{\text{mole of reactant charged} - \text{mole of reactant left}}{\text{mole of reactant charged}} \times 100\%
\]

\[
\text{Selectivity} (\%) = \frac{\text{mole of product generated}}{\text{mole of reactant charged} - \text{mole of reactant left}} \times 100\%
\]

TOF and STY (space time yield of MeOH) were calculated as follows:

\[
\text{TOF}_{\text{MeOH}} (\text{h}^{-1}) = \frac{\text{MeOH formation rate (mol•g}_{\text{cat}}^{-1}•\text{h}^{-1})}{\text{Number of Cu sites (mol•g}_{\text{cat}}^{-1})}
\]

\[
\text{EC conv.} \times \text{MeOH sel.} \times \frac{\text{WLHSV}}{\text{Molecular weight of EC (mol•g}_{\text{cat}}^{-1}•\text{h}^{-1})} = \frac{\text{Number of Cu sites (mol•g}_{\text{cat}}^{-1})}{\text{STY}_{\text{MeOH}}} = \frac{\text{WLHSV}_{\text{EC}} \times \text{EC Conv.} \times \text{MeOH Sel.} \times \text{M}_{\text{MeOH}}}{\text{M}_{\text{EC}}}
\]

where \(M_{\text{MeOH}}\) is the molecular weight of MeOH (g•mol\(^{-1}\)), \(M_{\text{EC}}\) is the molecular weight of EC (g•mol\(^{-1}\)).

Blank reactions were conducted under the same reaction conditions in order to make sure that the solvent 1,4-dioxane alone and SiO\(_2\) support alone did not have any catalytic activity. Additionally, carbon balances were close to 100 ± 3%. All data points were obtained in duplicate with an error of less than ±2%.
Absence of mass transport and heat transfer during kinetic measurements

The absence of mass transport resistances was checked by Weisz-Prater criterion (CWP) for internal diffusion and Mears’ criterion (CM) for external diffusion.

\[
C_{WP} = \frac{r_{obs}\rho_c R_p^2}{D_{eff} C_s} < 1
\]

\[
C_{M} = \frac{r_{obs}\rho_b R_p n}{k_c C_{Ab}} < 0.15
\]

Where \(r_{obs}\) = observed reaction rate, mol/kg\(_{cat}\)\cdot s

n = reaction order

R\(_p\) = catalyst particle radius, m

\(\rho_c\) = solid catalyst density, kg/m\(^3\)

\(\rho_b\) = bulk density of catalyst bed, kg/m\(^3\)

= (1-\(\Phi\)) \(\rho_c\) (\(\Phi\) = porosity)

D\(_{eff}\) = effective diffusivity, m\(^2\)/s

C\(_s\) = gas concentration of A at the external surface of the catalyst, mol/m\(^3\).

C\(_{Ab}\) = bulk gas concentration of A, mol/m\(^3\).

k\(_c\) = external mass transfer coefficient, m/s

For the kinetic measurements, the catalyst particles passed through a 20-mesh screen, which represents a 0.085 cm opening. The highest concentration of EC employed in the feed was 10 wt%.

For the Cu@C/SiO\(_2\) catalyst, the obtained highest reaction rate was 5.6 \(\times\) 10\(^{-3}\) mol\cdot kg\(_{cat}\)\(^{-1}\cdot s\(^{-1}\).

\[
C_{WP} = \frac{r_{obs}\rho_c R_p^2}{D_{eff} C_s} = \frac{[(5.6\times10^{-3}\text{ mol/kg}_{\text{cat}}\cdot s) \times (0.39\times10^{-3}\text{ kg/m}^3) \times (4.25\times10^{-4}\text{ m})^2]}{[(2.6\times10^{-6}\text{ m}^2/s) \times (2.7\times10^2\text{ mol/m}^3)]} = 5.62 \times 10^{-4} < 1
\]

\[
C_{M} = \frac{r_{obs}\rho_b R_p n}{k_c C_{Ab}} = \frac{[(5.6\times10^{-3}\text{ mol/kg}_{\text{cat}}\cdot s) \times (0.39\times10^{-3}\text{ kg/m}^3) \times (4.25\times10^{-4}\text{ m}) \times (1)]}{[(0.087\text{ m/s}) \times (2.7\times10^2\text{ mol/m}^3)]} = 3.95 \times 10^{-5} < 0.15
\]

Therefore, internal and external diffusion effects could be neglected during the kinetic experiments.

The absence of heat transfer was checked by Mears’ criterion.

\[
C_{M} = \left| \frac{-\Delta H_{\text{obs}} R_p E}{h R_g \rho_b} \right|
\]

where \(\Delta H\) = heat of reaction, kJ/mol

\(r_{obs}\) = observed reaction rate, mol/kg\(_{cat}\)\cdot s

\(\rho_b\) = bulk density of catalyst bed, kg/m\(^3\)

= (1-\(\Phi\)) \(\rho_c\) (\(\Phi\) = porosity)

R = catalyst particle radius, m

E = activation energy, kJ/mol

h = heat transfer coefficient between gas and pellet, kJ/m\(^2\cdot s\cdot K\)

R\(_g\) = gas constant, kJ/mol\cdot K

T = reaction temperature, K
For the Cu@C/SiO$_2$ catalyst, $\frac{-\Delta H_{\text{r, UT}}}{n \times F_0} = \left[ (77.23 \text{ kJ/mol}) \times (5.6 \times 10^{-3} \text{ mol/kgcat \cdot s}) \times (0.39 \times 10^3 \text{ kg/m}^3) \times (4.25 \times 10^{-6} \text{ m}) \times 98.9 \text{ kJ/mol} \right] / \left[ (6.5 \times 10^{-2} \text{ kJ/m}^2 \cdot \text{s} \cdot \text{K}) \times (453 \text{ K})^2 \times 8.314 \times 10^{-3} \text{ kJ/mol} \cdot \text{K} \right] = 6.4 \times 10^{-2} < 0.15.$

Therefore, heat transfer effect during the kinetic experiment could be neglected.