Supporting information

Cu Supported on Thin Carbon Layer Coated Porous SiO$_2$ for Efficient Ethanol Dehydrogenation

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TEM images of C/SiO\textsubscript{2} and Cu/C/SiO\textsubscript{2}

Fig. S1 (a) and (b) TEM images of C/SiO\textsubscript{2} support, (c) and (d) TEM images recorded at different magnifications of the reduced Cu/C/SiO\textsubscript{2} catalysts. In panel d, the Cu particles were highlighted by white arrows.

It is difficult to distinguish the carbon layer from the SiO\textsubscript{2} matrix in the above images due to their similar atomic number (near Z-contrast) and the thin thickness of carbon layer (~0.5 nm).
TEM images of Cu/SiO$_2$ and Cu/C

Fig. S2 TEM images for the reduced Cu/SiO$_2$ (a and b) and Cu/C (c and d).
3 XRD patterns of the catalysts

![XRD patterns of the catalysts.](image)

From the HS-LEIS results, ca. 7% Cu particles located at the outside of the pores on Cu/C/SiO$_2$. In the high reduction temperature, these Cu species may more easily agglomerate, and show a larger metal size than those in the mesopores. So the mean size of Cu NPs may be overestimated by using a Scherrer equation based on the XRD patterns. This phenomenon was also reported by K. P. de Jong et al.,$^1$ who suggested that there is a small amount of relatively large Cu nanoparticles on the Cu-based catalysts. In this case, the mean diameter of Cu particles was calculated by using N$_2$O-H$_2$ titration method based on the consumption amount of H$_2$, which will provide more reliable particle size information.

In the case of Cu/SiO$_2$, although there are 15% Cu species outside the pores, they easily interact with the SiO$_2$ surface due to the direct contact. Hence, the distribution of Cu particles on SiO$_2$ is uniform. As Cu nanoparticles on oxide tend to be oxidized to a higher valence and monolayer dispersion$^2$ as soon as exposing to the air atmosphere (including O$_2$ and moisture) during analysis. So to Cu/SiO$_2$ catalyst, N$_2$O-H$_2$ titration method to analyze Cu particle size is also well-adopted.
4  **N₂ adsorption–desorption isotherms of the supports**

**Fig. S4** N₂ adsorption–desorption isotherms of SiO₂, C/SiO₂, and C supports. The isotherm of SiO₂ is vertically offset by +450 cm³ g⁻¹, STP.
5  XRD patterns of the supports

<table>
<thead>
<tr>
<th>Samples</th>
<th>d (100) or d(110)/nm</th>
<th>Wall Thickness/nm</th>
</tr>
</thead>
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<tr>
<td>SiO₂</td>
<td>9.526</td>
<td>3.4</td>
</tr>
<tr>
<td>C/SiO₂</td>
<td>9.526</td>
<td>4.5</td>
</tr>
<tr>
<td>C</td>
<td>9.370</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Wall thickness: 2×d_{100}/3/2-pore size for SiO₂ and C/SiO₂; 2×d_{110}/3/2-pore size for C.

Fig. S5 Low angle XRD patterns of the supports and corresponding calculated results.
6 The calculation of carbon consumption

![Diagram](image)

**Fig. S6** The model of Cu/C/SiO$_2$ catalysts after a methanation process of the carbon layer under a hydrogen atmosphere.

We assumed that the Cu NPs are rigid hemisphere, i.e., the morphology and diameter remain unchanged before and after the methanation of carbon. The carbon consumption $m_C$ etched by Cu nanoparticles was calculated as the following:

1) The density $\rho$ of carbon layer:

$$\rho = \frac{Q}{S_{BET} \times h} = \frac{86 \times 1000 \text{g}}{417 \text{m}^2 / \text{g} \times (7.6 - 6.5) \times 10^{-2} \pm 2 \text{m}} \approx 0.37 \text{g/cm}^3$$

$Q$: the carbon content of C/SiO$_2$; $S_{BET}$: the surface area of C/SiO$_2$; $h$: the thickness of carbon layer.

2) The number of Cu nanoparticles per 100 mg catalyst:

$$N = \frac{m_{Cu}}{V_{Cu} \times \rho_{Cu}} = \frac{8.8 \times 1000 \text{g}}{0.5 \times \frac{4}{3} \pi (1.1 \times 10^{-9} \text{m})^3 \times 8.96 \times 10^6 \text{g} / \text{m}^3} \approx 0.35 \times 10^{18}$$

$m_{Cu}$: the Cu loading on C/SiO$_2$; $V_{Cu}$: the volume of a single Cu particle, the diameter is based on the dispersion data; $\rho_{Cu}$: the density of Cu metal, 8.96 g/cm$^3$.

3) The carbon consumption $m_C$ per 100 mg catalyst:

$$m_C = \pi R^2 \times N \times h \times \rho = \pi \times (1.1 \times 10^{-9} \text{m})^2 \times 0.35 \times 10^{18} \times 0.5 \times 10^{-9} \text{m} \times 0.37 \times 10^{6} \text{g} / \text{m}^3 \approx 0.24 \text{mg}$$
7  Raman spectra

Fig. S7 Raman spectra of the supports and catalysts.

In general, D and G bands are used to indicate the graphitization degree of carbon materials. As reflected by Raman spectroscopy, the intensity ratio of the D to G bands ($I_D/I_G$) of C/SiO$_2$ and SiO$_2$ is 0.96 and 0.94. This amorphous feature of the carbon layer is favorable for the dispersion of Cu species during an impregnation process.$^3$ Because the intensity ratio of $I_D/I_G$ of Cu/C/SiO$_2$ is nearly equal to that of the C/SiO$_2$ (0.97 vs. 0.96), the effect of methanation on the nature of the carbon layer is negligible.
**Fig. S8** (a) XPS survey spectra of Cu/C/SiO$_2$ and Cu/SiO$_2$ catalysts. High-resolution (b) Si 2p, (c) C 1s, and (d) O 1s spectra of these catalysts.
9 CO-DRIFTS spectra

Fig. S9 In situ DRIFTS spectra of CO adsorption at room temperature after purging He 20 min.
10 Stability test

Fig. S10 (a) Stability test of ethanol dehydrogenation over Cu/Carbon catalysts. (b) The acetaldehyde formation rates on Cu/C/SiO$_2$, Cu/SiO$_2$, and Cu/C. Reaction conditions: 260 °C, weight hourly space velocity (WHSV) of $C_2H_5OH = 2.4 \frac{g_{C_2H_5OH}}{g_{cat} \cdot h^{-1}}$, and $N_2$ 40 mL/min. Reduction: 450 °C for 2 h.
Dependence of product selectivity and ethanol conversion on W/F

**Fig. S11** Dependence of C₂H₅OH conversion and CH₃CHO selectivity in the ethanol dehydrogenation reaction over the reduced catalysts.
12 CH$_3$CHO-TPD profiles

![CH$_3$CHO-TPD profiles of C/SiO$_2$ and SiO$_2$ at m/z = 15.](image)

The main desorption peaks of the C/SiO$_2$ and SiO$_2$ supports are at 125 and 163 °C, respectively. This m/z=15 signal attributes to -CH$_3$ groups. Compared with the C/SiO$_2$ support, there is an apparent desorption peak at ~440 °C on SiO$_2$. The m/z = 29 ion fragmentation may come from CH$_3$CHO, C$_2$H$_3$CHO, CH$_3$COOC$_2$H$_5$, CH$_3$COC$_2$H$_5$, etc. By combining these results, one can conclude that by-products are produced from CH$_3$CHO molecules on the Si-OH groups.
## 13 Summary of the catalytic data of Cu-based catalysts

<table>
<thead>
<tr>
<th>No.</th>
<th>Catalysts</th>
<th>T (°C)</th>
<th>WHSV (h⁻¹)</th>
<th>Feed composition</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
<th>Yield (%)</th>
<th>TOF (s⁻¹)</th>
<th>T (h)</th>
<th>k (h⁻¹)</th>
<th>τ (h)</th>
<th>Ref.</th>
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<td>4.3</td>
<td>C₂H₅OH = 7.6, N₂ = 92.4</td>
<td>90-45</td>
<td>~99</td>
<td>89-44</td>
<td>-</td>
<td>8</td>
<td>0.125</td>
<td>8</td>
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<td>C₂H₅OH = 5, N₂ = 95</td>
<td>74.8-32.7</td>
<td>~95</td>
<td>71.6</td>
<td>-</td>
<td>8</td>
<td>0.44</td>
<td>6.2</td>
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<td>66.8-64.3</td>
<td>-</td>
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<td>77</td>
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<td>42-36</td>
<td>-</td>
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<td>~32.7</td>
<td>-</td>
<td>10</td>
<td>0.018</td>
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<td>C₂H₅OH = 20.5, N₂ = 79.5</td>
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<td>58.0</td>
<td>32.0</td>
<td>-</td>
<td>N.D.</td>
<td>-</td>
<td>-</td>
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<tr>
<td>Ref</td>
<td>Catalyst</td>
<td>Reaction Temperature</td>
<td>Conversion (C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;OH)</td>
<td>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;OH, C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;3&lt;/sub&gt;N&lt;sub&gt;2&lt;/sub&gt;</td>
<td>76.1</td>
<td>21.0</td>
<td>16.0</td>
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<tr>
<td>[10]</td>
<td>30 wt% Cu/SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>220</td>
<td>0.36</td>
<td>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;OH = 20.5, N&lt;sub&gt;2&lt;/sub&gt; = 79.5</td>
<td>76.1</td>
<td>21.0</td>
<td>16.0</td>
<td>N.D.</td>
<td>N.D.</td>
<td>N.D.</td>
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<tr>
<td>7</td>
<td>10 wt% Cu/ZrO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>200</td>
<td>0.83</td>
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<td>45.0</td>
<td>23.0</td>
<td>10.3</td>
<td>N.D.</td>
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<td>N.D.</td>
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<td>8</td>
<td>30 wt% Cu/SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>220</td>
<td>0.44</td>
<td>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;OH = 20.5, N&lt;sub&gt;2&lt;/sub&gt; = 79.5</td>
<td>~50.0</td>
<td>77.9</td>
<td>39.0</td>
<td>N.D.</td>
<td>N.D.</td>
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<tr>
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<td>30 wt% Cu/Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>220</td>
<td>0.44</td>
<td>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;OH = 20.5, N&lt;sub&gt;2&lt;/sub&gt; = 79.5</td>
<td>~50.0</td>
<td>54.1</td>
<td>27.1</td>
<td>N.D.</td>
<td>N.D.</td>
<td>N.D.</td>
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<td>[11]</td>
<td>30 wt% Cu/Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>220</td>
<td>0.44</td>
<td>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;OH = 20.5, N&lt;sub&gt;2&lt;/sub&gt; = 79.5</td>
<td>~50.0</td>
<td>54.1</td>
<td>27.1</td>
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<td>N.D.</td>
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<tr>
<td>9</td>
<td>15 wt% Cu/Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>300</td>
<td>31.6</td>
<td>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;OH = 46, N&lt;sub&gt;2&lt;/sub&gt; = 54</td>
<td>~80</td>
<td>~86</td>
<td>~68.8</td>
<td>N.D.</td>
<td>N.D.</td>
<td>N.D.</td>
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<tr>
<td>10</td>
<td>10 wt% Cu/SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>280</td>
<td>2.4</td>
<td>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;OH = 15, N&lt;sub&gt;2&lt;/sub&gt; = 85</td>
<td>~83</td>
<td>~68</td>
<td>56.4</td>
<td>N.D.</td>
<td>N.D.</td>
<td>N.D.</td>
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</table>

* t, Reaction time. * k<sub>D</sub>, second-order deactivation rate constant acquired by fitting the deactivation profile with a second-order deactivation law: \( \frac{da}{dt} = -k_D a^2 \), where “a” denotes the normalized yield. * Time required for rates to decrease by \( e^{-1} \), \( \tau = 1/k_D \). * Due to the fast deactivation of Cu/Carbon, the initial conversion value was used by extrapolating the conversion to 0 min. * N.D., no detected.
References