1   *Supporting information:*

2 The highly dispersed Cu nanoparticles as an efficient catalyst

3 for the synthesis of biofuel 2-methylfuran

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1. Catalysts characterization

Dissociative N_2O adsorption measurement:

Copper dispersion and the specific surface area of metallic copper of catalyst are measured by dissociative N_2O adsorption. The N_2O chemisorption process consists of three sequential processes:

$$CuO + H_2 \rightarrow Cu + H_2O \qquad (1)$$
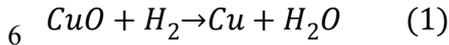
$$Hydrogen\ consumption = A_1$$

$$2Cu + N_2O = Cu_2O + N_2 \qquad (2)$$

$$Cu_2O + H_2 = 2Cu + H_2O \qquad (3)$$
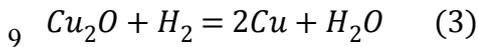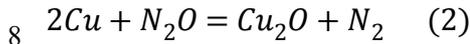
$$Hydrogen\ consumption = A_2$$

Process (1) represents reduction of CuO in the sample. In this process, a flow of 5 vol. % H_2/He (30mL/min) is used as the reducing agent, and the temperature increased from the room temperature to 400°C with a heating rate of 5 °C/min. Process (2) represents the oxidation of surface Cu to Cu_2O by 10 vol. % N_2O/Ar at 60 °C, which is a well-known method to evaluate the dispersion and crystallite size of Cu catalysts. After that, the reduced catalyst is swept with pure He (30mL/min) for 0.5 h. Subsequently, the sample is purged with pure He (30mL/min) for 0.5 h to remove the residual N_2O. Finally, process (3) was performed to reduce the Cu_2O species of catalyst surface. In this process, a flow of 5 vol. % H_2/He (30mL/min) is also used as the reducing agent, and the temperature increased from room temperature to 400 °C with a heating rate of 5 °C/min. The dispersion (D_{Cu}) of Cu was calculated as follows:

$$D_{Cu} = \frac{2A_2}{A_1} \times 100\%$$

It has extensively been used in literature. The specific area of metallic copper was calculated from the amount of H_2 consumption (A_2) with 1.46×10^{19} copper atoms per m^2:

$$S_{Cu} = \frac{1353W_{Cu}A_2}{A_1} \times 100\%$$

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11   **Fig S1** The photos of two CuO/SiO$_2$ catalysts after calcination at 450 °C:

12   A) CP-CuO/SiO$_2$ catalyst, B) AE-CuO/SiO$_2$ catalyst

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3 **NH$_3$-TPD analysis:**
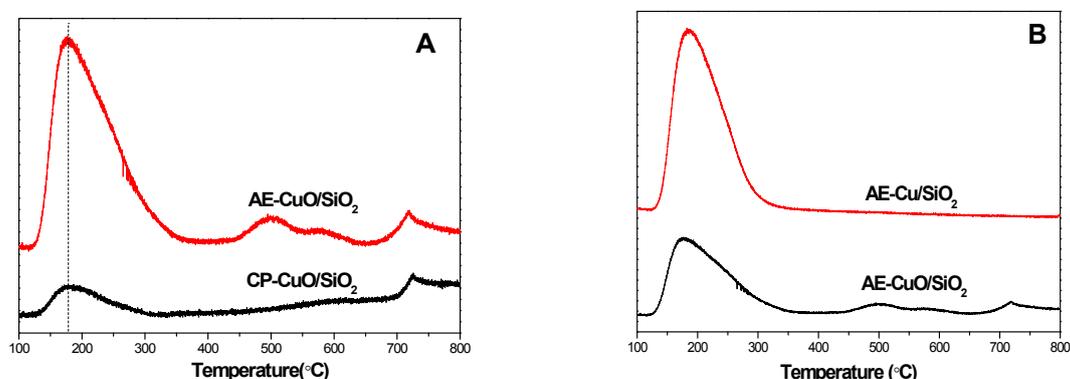
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5 **Fig S2** NH$_3$-TPD of A) the calcined CP-CuO/SiO$_2$ and AE-CuO/SiO$_2$ samples, B) the reduced AE-Cu/SiO$_2$ and
6 the calcined AE-CuO/SiO$_2$ samples

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8   In order to investigate the surface acidity, NH$_3$-TPD was performed on the calcined samples
9 (Fig S2A). Generally, the strength of acid sites, which is determined by the NH$_3$ desorption
10 temperature is classified as three types, weak acid (150-300 °C), medium acid (300-500 °C), and
11 strong acid (500-650 °C) [1]. In this work, CP-CuO/SiO$_2$ and AE-CuO/SiO$_2$ samples both showed
12 a main peak at 190 °C, which could be attributed to NH$_3$ desorption from the weak acid sites.
13 Besides, there was a minor peak at 500 °C related to the medium acid of AE-CuO/SiO$_2$ surface
14 due to the formation of copper phyllosilicate phase. Obviously, AE-CuO/SiO$_2$ catalyst showed the
15 largest peak at around 190 °C, indicating that it had much more the weak acid sites than CP-
16 CuO/SiO$_2$ sample. An obvious increase of acid acidity of AE-CuO/SiO$_2$ sample might result from
17 the formation of the special lamellar structure, which was in accord with that of the reduced
18 samples (Fig. 6). Interestingly, the weak acid sites of the reduced AE-Cu/SiO$_2$ sample were much
19 more than that of the calcined AE-CuO/SiO$_2$ sample in Fig. S2B. The reason might be related to
20 the production of Cu$^+$ species during the reduction process, which could improve the activity and
21 promote the hydrogenolysis of intermediate FOL.

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3 **XPS analysis:**
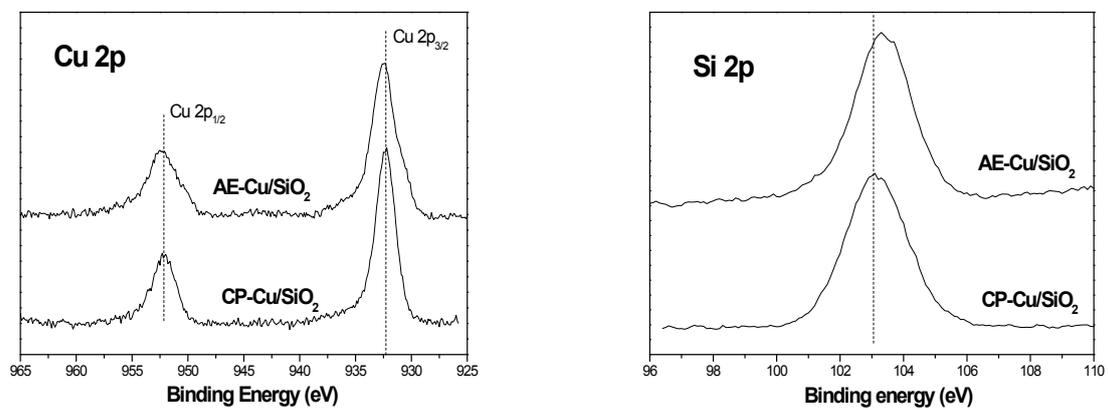
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5   **Fig S3** XPS spectra of the reduced Cu/SiO_2 catalysts

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CO-FTIR analysis:
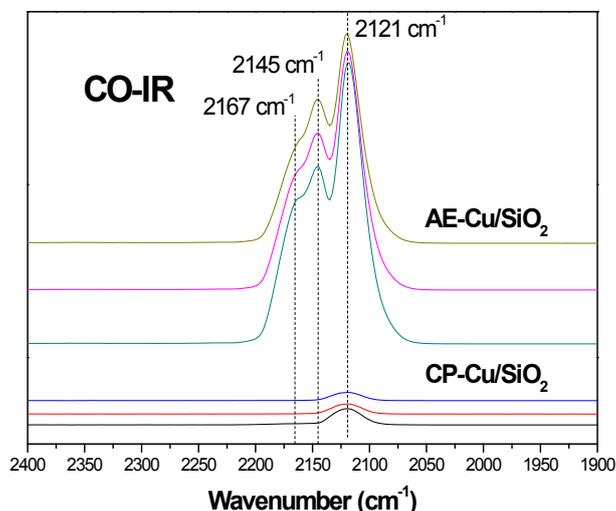
Fig S4 CO-IR spectra of the calcined Cu/SiO_2 catalysts: at 20 °C and purged with He for 1, 5, 10 min (the peak intensity is decreased with 1, 5, 10 min)

The copper species of catalysts surface was probed further using Fourier transform infrared spectroscopy of adsorbed CO (CO-IR) at 20 °C. Intense bands in the range of 2200 cm^{-1} and 2050 cm^{-1} were detected for $AE-Cu/SiO_2$ catalyst, while $CP-Cu/SiO_2$ catalyst showed only a very weak adsorption with a maximum at 2121 cm^{-1}. The former literatures [2, 3, 4] also reported that only CO adsorption on Cu^+ forms is stable, while CO adsorption on Cu^{2+} species is not stable at RT. The difference between the CO spectra of the two samples further verified the presence of Cu^+ sites on $AE-Cu/SiO_2$ catalyst, while on $CP-Cu/SiO_2$ catalyst Cu(I) sites were almost totally absent, indicating that $AE-Cu/SiO_2$ catalyst exhibited the formation of Cu^+ species due to the enhanced interaction of copper-silicon and the results were consistent with XPS results.

On the other hand, it is reasonable that copper particles are highly dispersed in $AE-Cu/SiO_2$ catalyst with attributing the intensity of the band as the semi-quantity method for the amounts of copper species [3]. The peak area of CO adsorption over $AE-Cu/SiO_2$ catalyst is much higher than that of $CP-Cu/SiO_2$ catalyst, indicating that copper dispersion of $AE-Cu/SiO_2$ catalyst are much higher than $CP-Cu/SiO_2$ catalyst. In line with the higher copper dispersion, $AE-Cu/SiO_2$ catalyst is superior to $CP-Cu/SiO_2$ catalyst in its catalytic activity for furfural hydrogenation [4]. Copper

1 dispersion derived from CO-IR is consistent with the results of N_2O titration.

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2. *The catalytic performance of catalysts*

4 **Table S1** The catalytic performance of CP-Cu/SiO$_2$ catalyst at the different reaction temperature [a]

T(ºC)	Conversion (%)	Selectivity (%)[b]			
		2-MF	FOL	RO	Others
140	63.2	1.8	98.2	0	0
160	76.8	17.5	82.1	0.2	0.2
180	95.7	27.1	72.3	0.3	0.3
200	96.7	49.4	49.7	0.5	0.5

5 [a] Atmospheric pressure, H_2/furfural=17, WHSV=2.0 h^{-1}

6 [b] 2-MF=2-methylfuran, FOL=furfuryl alcohol, RO=the ring open products(i.e. 2-pentanone, 1-pentanol, 2-

7 pentanol), Others = furan, 2-methyltetrahydrofuran, tetrahydrofurfuryl alcohol, furfural polymers

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3. Catalyst deactivation

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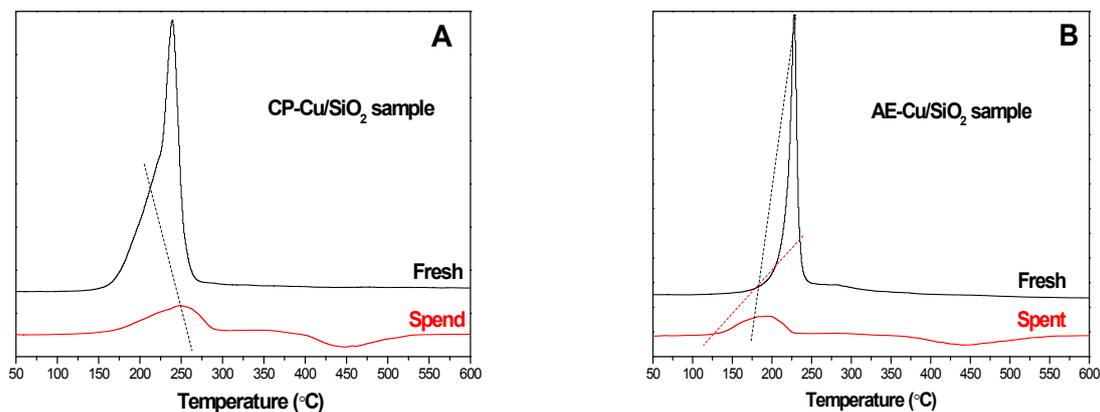
Fig S5 H_2-TPR of the fresh and spent samples

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We performed H_2-TPR of the spent CP-Cu/SiO$_2$ and AE-Cu/SiO$_2$ samples (Fig S5), which has performed the long-term performance of 215 h. The stability of samples was performed at 200 °C, therefore the spent samples after the stability test 215 h were purged with the pure N_2 at 200 °C for 12h. After that, the spent samples were cooled to room temperature in pure N_2. Afterward, the spent samples were passivated with 0.5 vol. % O_2/N_2 for 2 h. Finally, the H_2-TPR analysis was performed on the spent samples.

Obviously, the reduction temperature of spent CP-Cu/SiO$_2$ sample increased and widened to the higher temperature than the fresh sample (Fig S5A), while the reduction temperature of spent AE-Cu/SiO$_2$ sample dramatically decreased from 210 °C to 170 °C (Fig S5B). The reasons were attributed to the loss of copper species and the aggregation of copper particles on the spent CP-Cu/SiO$_2$ sample according to ICP-OES analysis and TEM results. However, copper loading of spent AE-Cu/SiO$_2$ sample is 23.4% according to ICP-OES in Table 1, indicating that the spent AE-Cu/SiO$_2$ sample almost had not the loss of copper species. According to Fig S5B, the reduction temperature of spent AE-Cu/SiO$_2$ sample was lower than the fresh AE-Cu/SiO$_2$ sample, and the peak area of spent AE-Cu/SiO$_2$ sample was much smaller than the fresh AE-Cu/SiO$_2$ sample. The minor peak of spent AE-Cu/SiO$_2$ sample at 170 °C was related to the reduction of

passivation layer (0.5 vol. % O_2/N_2). The spent samples at 450°C both exhibited an inverted peak, which was related to the desorption of H_2 chemisorption.

Reference

[1] H. Atia, U. Armbrusterb, A. Martinb, J. Catal. 258 (2008) 71–82.

[2] K. Hadjiivanov, H. Knözinger, J. Catal. 191, (2000) 480–485.

[3] J. Xue, X. Wang, G. Qi, J. Wang, M. Shen, W. Li, J. Catal. 297 (2013) 56–64.

[4] K. Hadjiivanov, T. Tsoncheva, M. Dimitrov, C. Minchev, H. Knözinger, Appl. Catal. A: General 241, (2003) 331-340.