

# Supporting Information For

## **One-pot Synthesized Core/Shell Structured Zeolite@Copper Catalysts for Selective Hydrogenation of Ethylene Carbonate to Methanol and Ethylene Glycol**

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## **Experimental**

### **Synthesis of the Si-rich Beta-D and MOR-D**

The high silica beta zeolite was obtained by dealumination of a commercial H-Beta aluminosilicate with a Si/Al molar ratio of 11, which was purchased from Shanghai Xinnian Petrochemical Additives Co., Ltd. The dealumination treatment was according to previous reported method.<sup>1</sup> The H-Beta zeolite was refluxed in 13 M HNO<sub>3</sub> solution with a liquid-to-solid mass ratio of 50 at 140 °C for 24 h. The product was recovered by centrifugation, washed with deionized water, dried at 100 °C overnight, and further calcined at 550 °C for 6 h, giving rise to Si-rich Beta (Si/Al ratio of 545) denoted as Beta-D. The high silica MOR was obtained by dealumination of a commercial mordenite with a Si/Al molar ratio of 7.8, which was purchased from Shanghai Fine Chemical Co., China. After refluxed in 6 M HNO<sub>3</sub> solution with a liquid-to-solid mass ratio of 50 for 24 h, the treated zeolite was subsequently filtrated and washed with deionized water several times. The zeolite was then dried at 100 °C overnight, and then calcined in air at 550 °C for 6 h. This zeolite was subjected to acid refluxing again, resulting in a Si-rich MOR (Si/Al ratio of 201) denoted as MOR-D.

### **Synthesis of Silicalite-1 Zeolites with Larger Crystal Sizes**

For control experiment, Silicalite-1 samples with larger crystal sizes were also hydrothermally synthesized.

S-1-340 with average size of 340 nm was hydrothermally synthesized from TEOS using TPAOH as OSDA. The synthetic gel was prepared with molar compositions of 1.0 SiO<sub>2</sub> : 0.18 TPAOH: 18 H<sub>2</sub>O. After stirring for 1 h at room temperature, the gel

was crystallized in a Teflon-lined steel autoclave at 170 °C for 2 days. The S-1-340 products were collected by filtration followed by washing with distilled water several times, dried at 100 °C overnight, and then calcined in air at 550 °C for 6 h to remove the organic template.

Silicalite-1-4800 with average size of 4800 nm was hydrothermally synthesized from fumed silica and using TPAOH as OSDA. The synthetic gel was prepared with molar compositions of 1.0 SiO<sub>2</sub> : 0.18 TPAOH : 18 H<sub>2</sub>O. After stirring for 1 hours at room temperature, the gel was crystallized in a Teflon-lined steel autoclave at 170 °C for 2 days. The S-1-4800 products were collected by filtration followed by washing with distilled water several times, dried at 100 °C overnight, and then calcined in air at 550 °C for 6 h to remove the organic template.

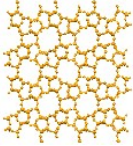
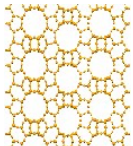
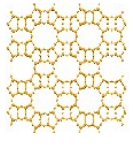
S-1-30000 with size of average 30000 nm was hydrothermally synthesized from colloidal silica (30 wt.%) using TPAOH and TPABr as co-structure-directing agents. The synthetic gels were prepared with molar compositions of 1.0 SiO<sub>2</sub>: 0.02 TPAOH : 0.01 TPABr : 12 H<sub>2</sub>O. After stirring for 12 hours at room temperature, the gel were crystallized in a Teflon-lined steel autoclave at 170 °C for 3 days. The S-1-30000 products were collected by filtration followed by washing with distilled water several times, dried at 100 °C overnight, and then calcined in air at 550 °C for 6 h to remove the organic template.

### **Catalytic performance**

The MeOH balance was calculated as follows:

$$\text{MeOH balance (\%)} = \frac{\text{Sel}_{\text{MeOH}} + \text{Sel}_{\text{CO}} + \text{Sel}_{\text{CO}_2}}{\text{Sel}_{\text{EG}}} \times 100\%$$

**Table S1.** Reaction results obtained for the selective hydrogenation of EC with different zeolite@Cu catalysts. <sup>a</sup>

Catalyst	Topology	Channel dimension Pore window	Cu loading (wt.%)	EC conv. (%)	Sel. <sup>b</sup> (%)	
					MeOH	EG
S-1@Cu	MFI	3D, 10-R	21.4	99	93	99
						
Beta-D@Cu	*BEA	3D, 12-R	22.3	97	71	99
						
MOR-D@Cu	MOR	2D, 12*8-R	21.8	99	8	45
						

<sup>a</sup> Reduction conditions: 250 °C, 4 h, H<sub>2</sub> (60 mL min<sup>-1</sup>); reaction conditions: 1 g catalyst, 180 °C, 4 h, 4 MPa H<sub>2</sub>, GHSV<sub>H<sub>2</sub></sub> = 2400, WHSV<sub>EC</sub> = 0.13.

<sup>b</sup> Main by-products: ethanol, CO or CO<sub>2</sub>.

*At comparable Cu loadings, MFI-type silicate is obviously superior to \*BEA and MOR as the support of Cu NPs for the selective EC hydrogenation, in particular in terms of MeOH selectivity.*

**Table S2.** The MeOH balance and selectivity of gaseous products in the selective hydrogenation of EC with different reduction temperature on S-1-210@Cu-21.4.<sup>a</sup>

Catalyst	Reduction temperature	MeOH balance (%)	Sel. (%)		
			MeOH	CO	CO <sub>2</sub>
S-1-210@Cu-21.4	150	97	88	2.6	6.4
S-1-210@Cu-21.4	250	97	93	1.1	2.9
S-1-210@Cu-21.4	350	97	87	2.2	7.8
S-1-210@Cu-21.4	450	96	67	4.3	24.7

<sup>a</sup> Reduction conditions: 4 h, H<sub>2</sub> (60 mL min<sup>-1</sup>); reaction conditions: 1 g catalyst, 180

°C, 4 h, 4 MPa H<sub>2</sub>, GHSV<sub>H2</sub> = 2400, WHSV<sub>EC</sub> = 0.13.

**Table S3.** The batch-wise reaction results obtained for the selective hydrogenation of EC with different solvents over S-1@Cu catalysts.<sup>a</sup>

Catalyst	Solvent	Cu (wt.%)	EC conv. (%)	Sel. (%)	
				MeOH	EG
S-1@Cu	1, 4-dioxane	21.4	98	74	99
S-1@Cu	ethanol	21.4	97	9	60
S-1@Cu	gamma valerolactone	21.4	34	1	57

<sup>a</sup> Reduction conditions: 250 °C, 4 h, H<sub>2</sub> (60 mL min<sup>-1</sup>); reaction conditions: 0.176 g catalyst, 10 mL of 10 wt.% EC in 1,4-dioxane, 180 °C, 4 h, 4 MPa H<sub>2</sub>.

**Table S4.** Representative Cu-Silica-based catalysts and their catalytic properties for the selective hydrogenation of EC.

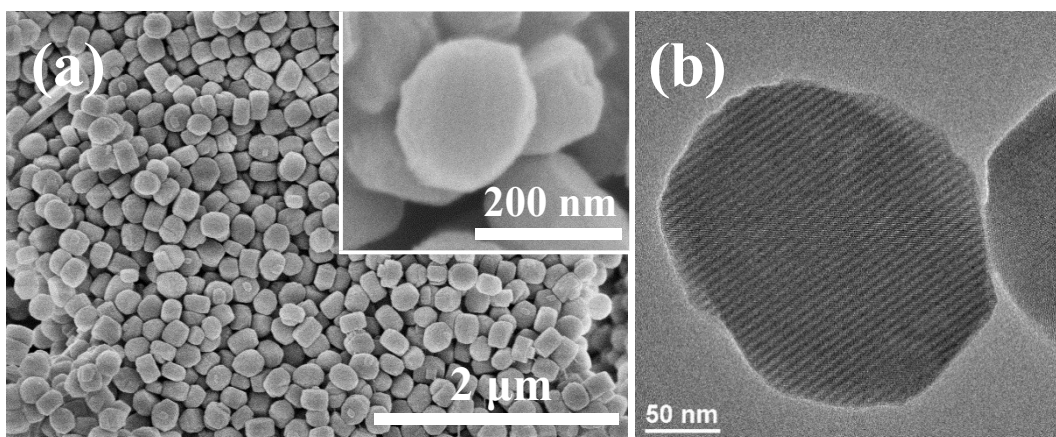
No.	Catalyst	T (°C)	P <sub>H<sub>2</sub></sub> (MPa)	Cu (wt.%)	EC conv. (%)	Sel. (%)		Lifetime (h)	Ref.
						MeOH	EG		
1	50Cu/HMS <sup>a</sup>	180	3	44.6	100.0	74.0	99.0	>100	2
2	70%Cu-SiO <sub>2</sub> -PG <sup>b</sup>	160	6	56.0	99.0	97.0	98.0	>80	3
3	Cu/SBA-15	200	5	10.0	100.0	62.3	94.7	-	4
4	10%Cu/SiO <sub>2</sub> -AE <sup>c</sup>	180	5	9.5	100.0	70.8	98.0	-	5
5	0.7Cu/MCM-41	180	3	33.3	97.0	70.0	98.0	<100	6
6	3.0-CuSi-NAM <sup>d</sup>	180	3	3.1	99.0	60.0	97.0	-	7
7	Cu-Mg-Zr/SiO <sub>2</sub>	180	4	60.0	99.0	82.0	99.0	208	8
8	S-1@Cu	180	4	21.4	99.0	93.0	99.0	>350	This work

<sup>a</sup> The Cu nanoparticles were supported on HMS-type mesoporous silica.

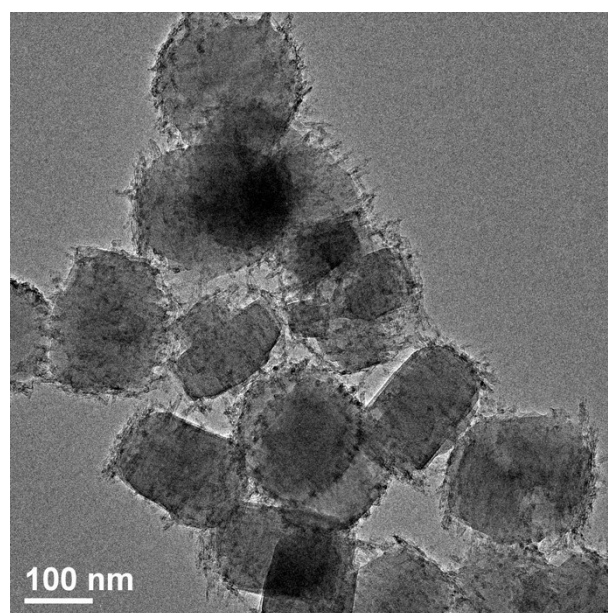
<sup>b</sup> Prepared by a precipitation-gel (PG) method.

<sup>c</sup> Prepared by ammonia evaporation (AE) method.

<sup>d</sup> CuSi-NAM is short for Cu/SiO<sub>2</sub> nanoarray monolithic catalyst.

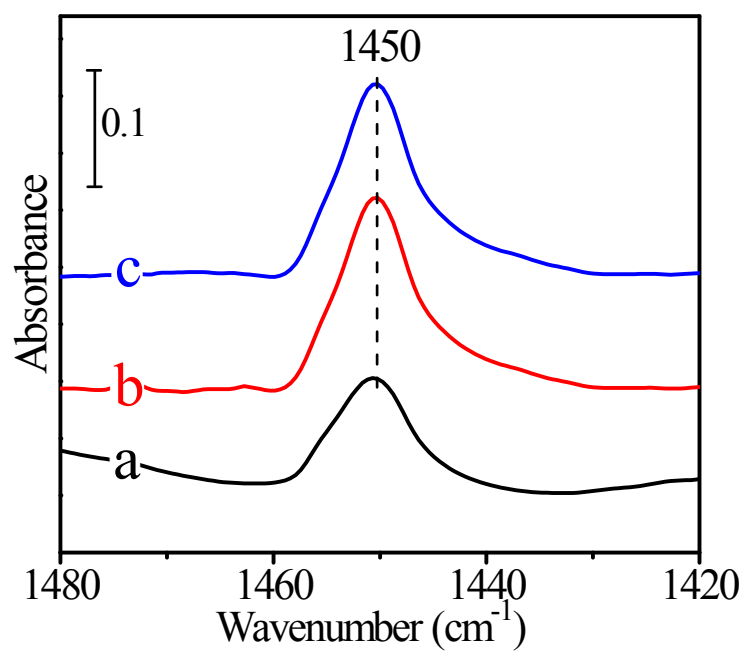


**Fig. S1** SEM images (a) and TEM image (b) of S-1-210.

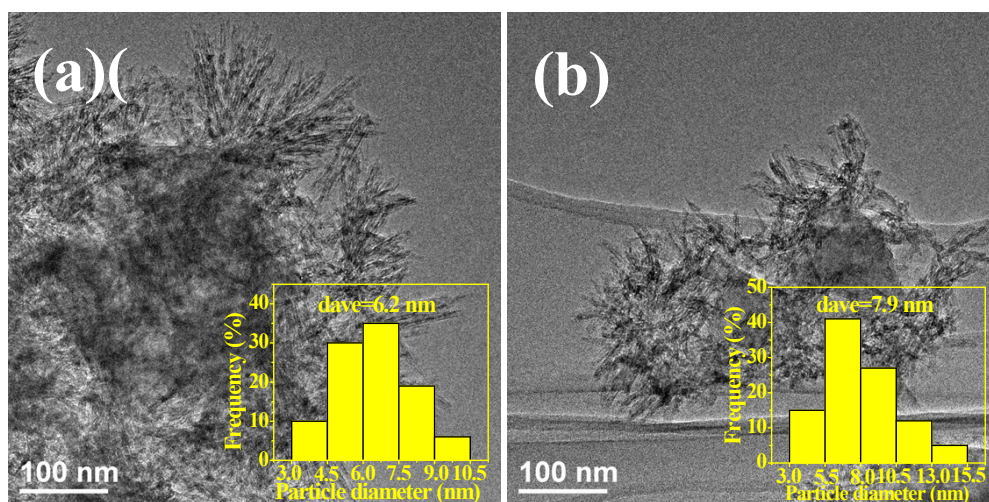


**Fig. S2** TEM images of S-1@Cu with 21.4 wt.% Cu loading.

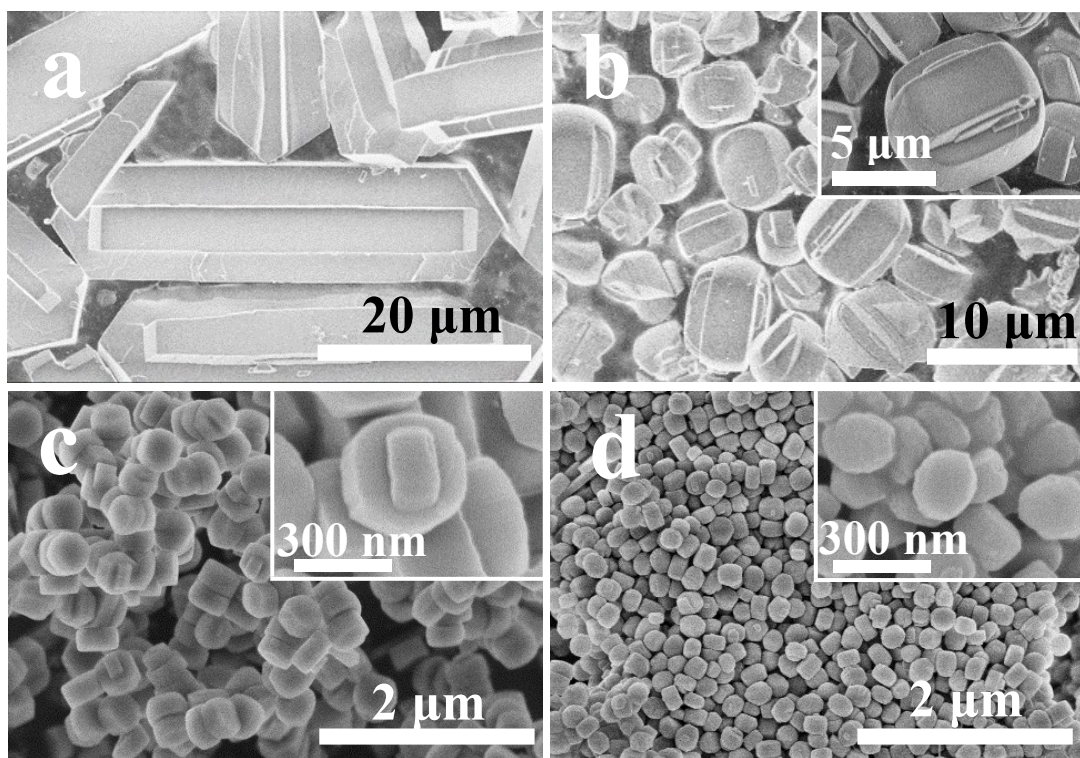




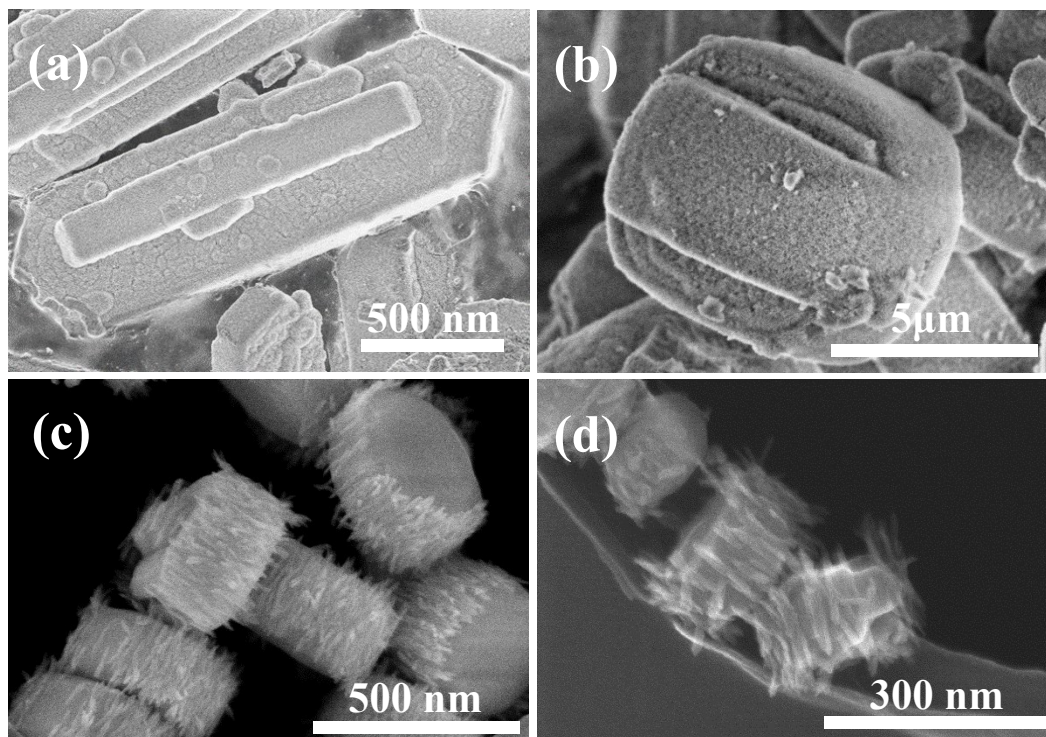
**Fig. S3** Pyridine-adsorbed FTIR spectra of S-1@Cu (a), Beta-D@Cu (b) and MOR-D@Cu (c). The pyridine desorption was carried out by evacuation at 150 °C for 30 min.



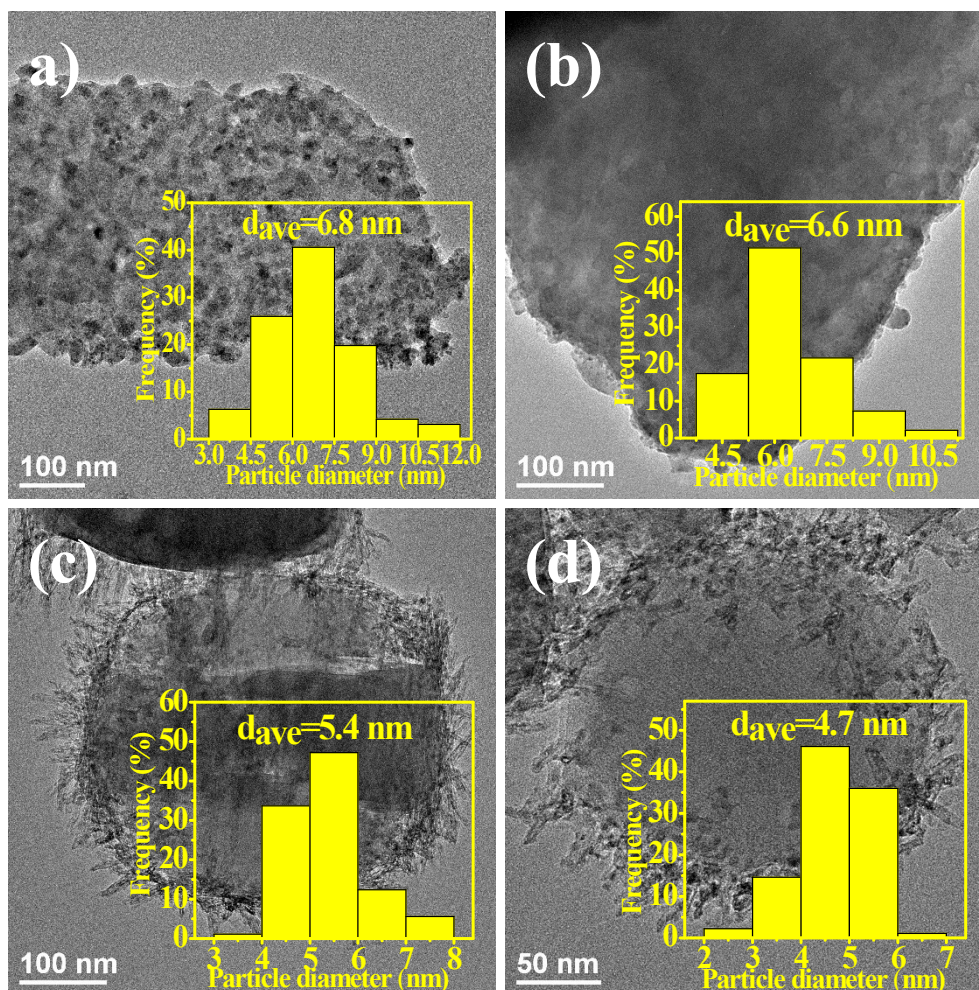
**Fig. S4** TEM images of Beta-D@Cu (a) and MOR-D@Cu (b) reduced at 250 °C. The insets show the distribution of Cu NPs sizes



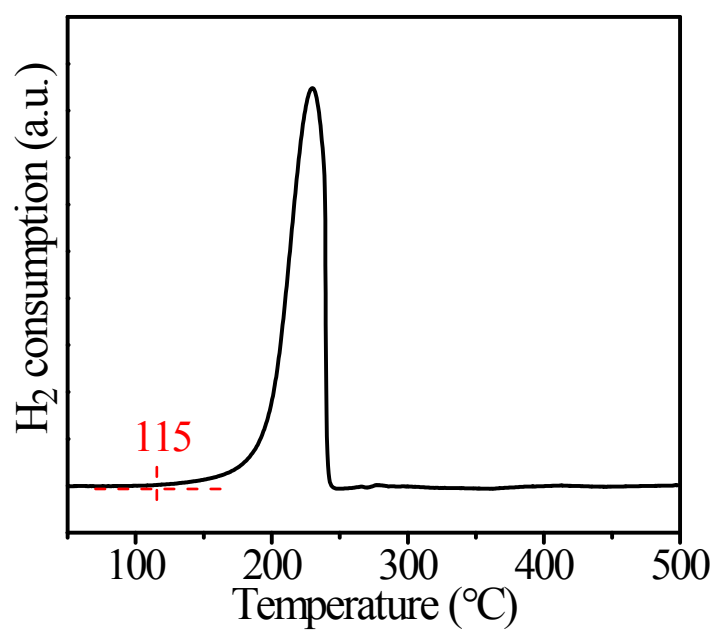
**Fig. S5** SEM images of S-1-30000 (a), S-1-4800 (b), S-1-340 (c) and S-1-210 (d) samples.



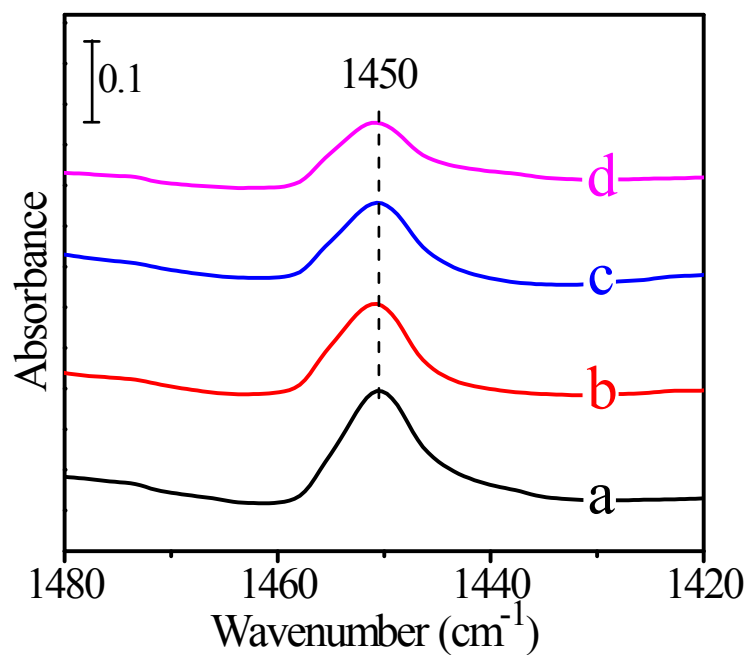
**Fig. S6** SEM images of S-1-30000@CuSiO<sub>3</sub> (a), S-1-4800@CuSiO<sub>3</sub> (b), S-1-340@CuSiO<sub>3</sub> (c) and S-1-210@CuSiO<sub>3</sub> (d).



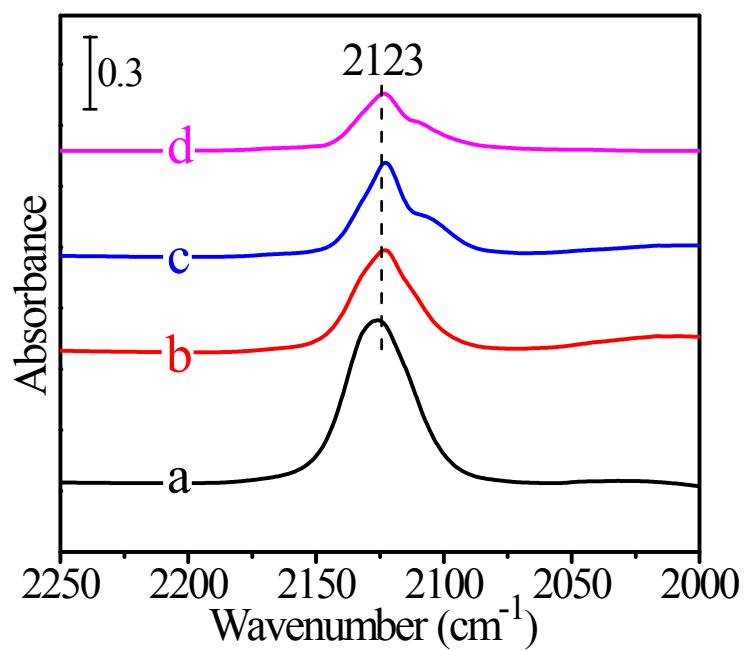
**Fig. S7** TEM images of S-1-30000@Cu (a), S-1-4800@Cu (b), S-1-340@Cu (c) and S-1-210@Cu (d). The insets show the distribution of Cu NPs sizes.



**Fig. S8** H<sub>2</sub>-TPR profile of S-1-210@CuSiO<sub>3</sub> catalyst.

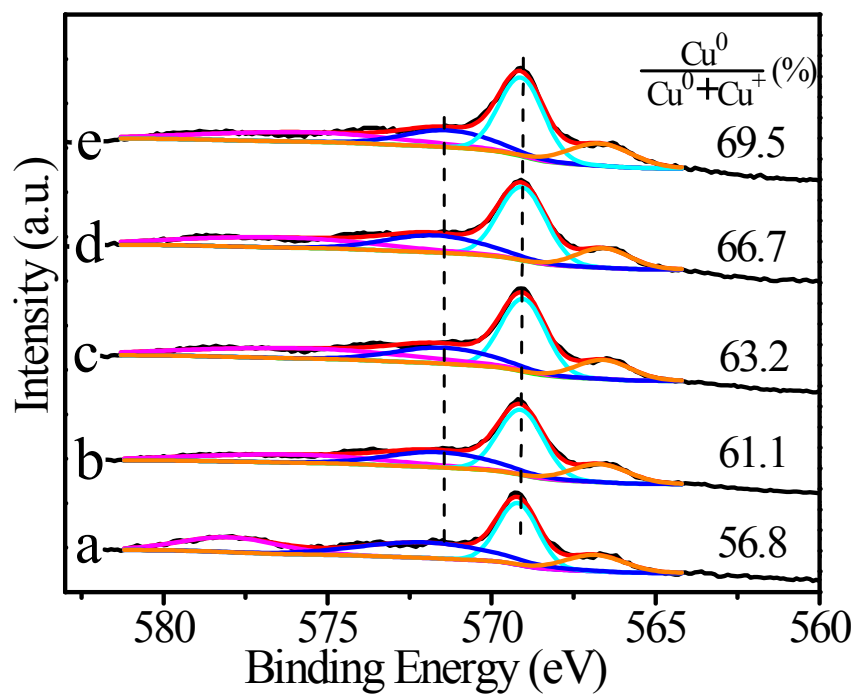


**Fig. S9** Pyridine-adsorbed FTIR spectra of the S-1-210@Cu catalysts after reduced at 150 °C (a), 250 °C (b), 350 °C (c) and 450 °C (d), respectively. The pyridine desorption was carried out by evacuation at 150 °C for 30 min.

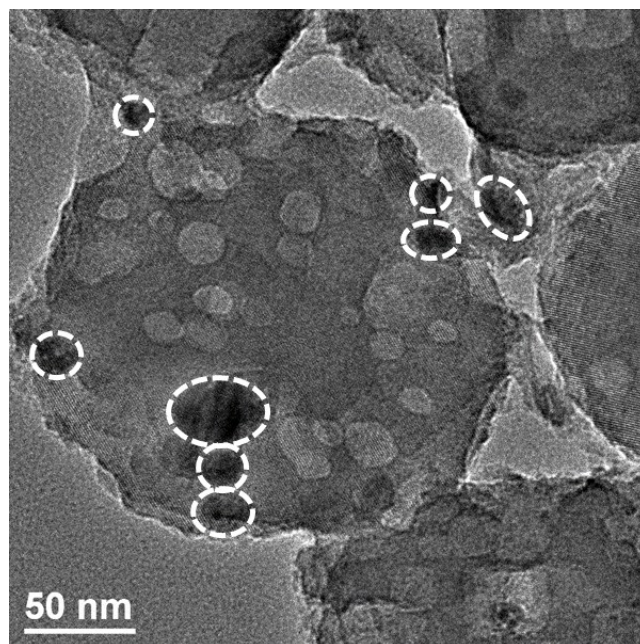


**Fig. S10** FTIR spectra of CO adsorbed on the S-1-210@Cu catalysts after reduced at 150 °C (a), 250 °C (b), 350 °C (c) and 450 °C (d), respectively.

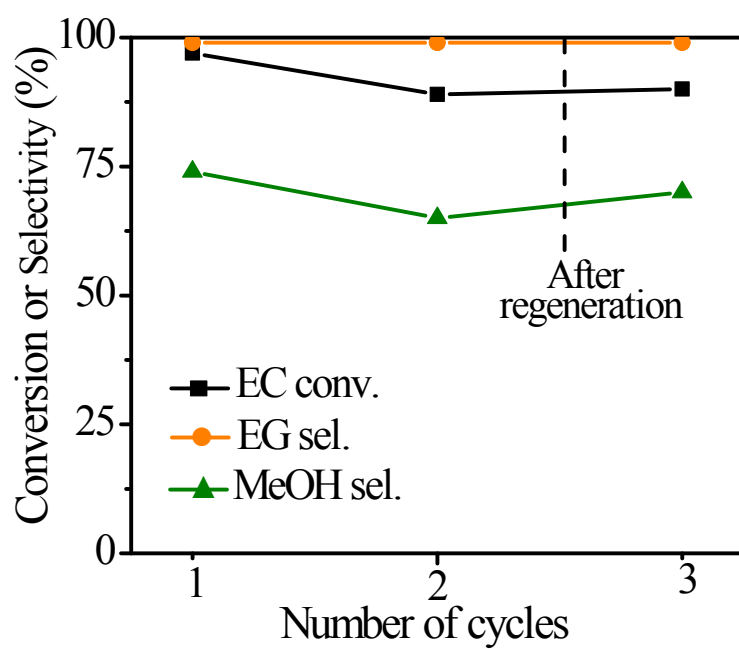




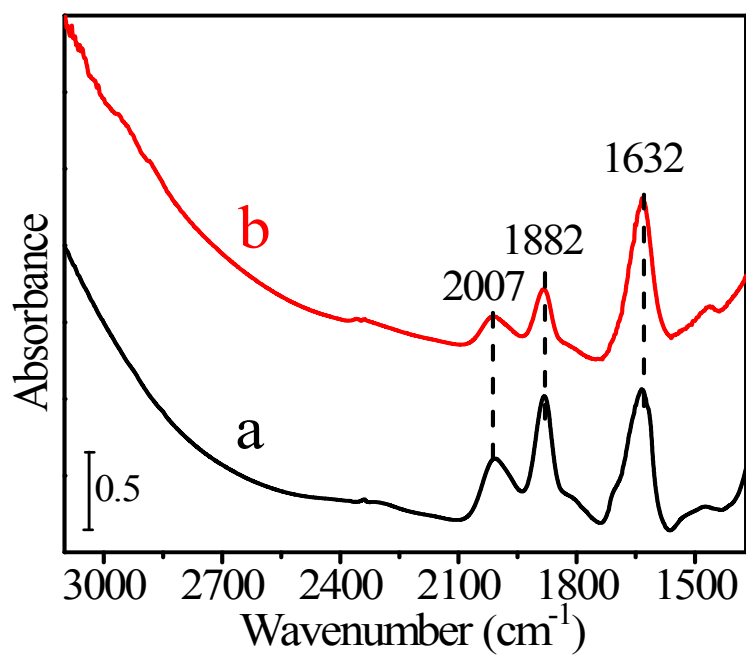
**Fig. S11** Cu LMM Auger electron spectra of S-1-210@Cu-13.6 (a), S-1-210@Cu-17.4 (b), S-1-210@Cu-21.4 (c), S-1-210@Cu-25.2 (d) and S-1-210@Cu-31.7 (e) after reduced at 250 °C for 4 h.



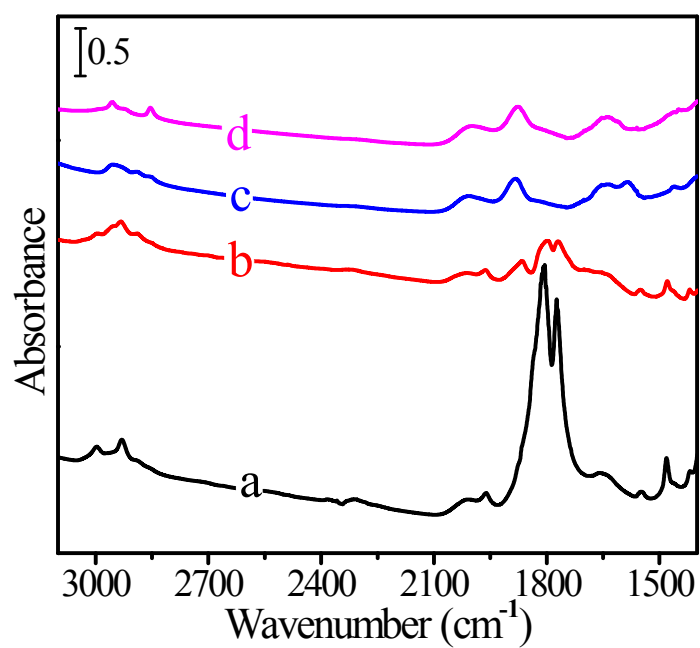
**Fig. S12** TEM image of the used S-1-210@Cu-21.4 catalyst in EC hydrogenation for 550 h.



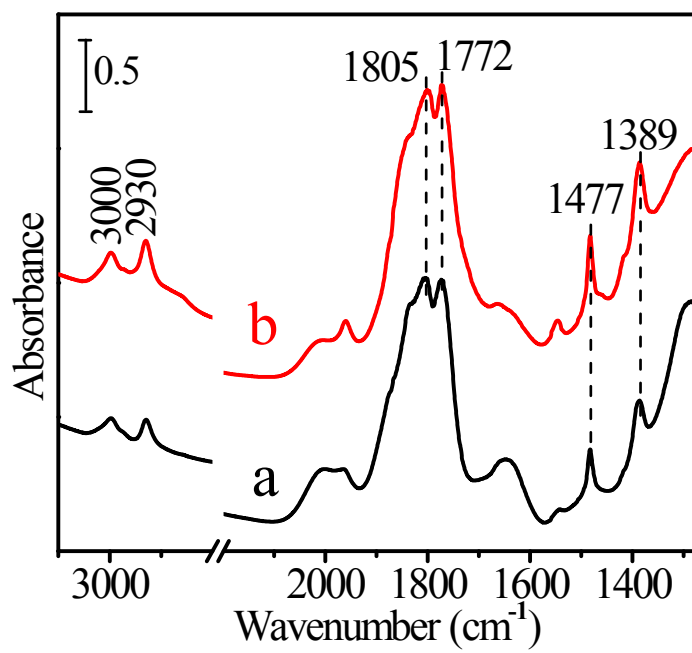
**Fig. S13** The recycling use of S-1-210@Cu-21.4 in a batch reactor for selective hydrogenation of EC to MeOH and EG. Reaction conditions: 0.176 g catalyst, 10 mL of 10 wt.% EC in 1,4-dioxane, 180 °C, 4 h, 4 MPa H<sub>2</sub>. Reduction conditions: 250 °C, 4 h, H<sub>2</sub> (60 mL min<sup>-1</sup>).



**Fig. S14** FTIR spectra of S-1-210 (a) and S-1-210@Cu-21.4.



**Fig. S15** FTIR spectra of EC (a), EG (c) and MeOH (d) adsorbed on S-1-210@Cu-21.4 under N<sub>2</sub> atmosphere at 180 °C and the spectrum for *in-situ* EC hydrogenation at 180 °C on S-1-210@Cu-21.4 under 5% H<sub>2</sub>/N<sub>2</sub> atmosphere (b).



**Fig. S16** FTIR spectra for the *in-situ* EC hydrogenation at 180 °C on S-1-210 (a) and S-1-210@CuSiO<sub>3</sub>-21.4 (b) under 5% H<sub>2</sub>/N<sub>2</sub> atmosphere.

## References

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