Electronic Supplementary Material (ESI) for RSC Advances.

Continuous heterogeneous hydrogenation of CO_2-derived dimethyl carbonate to methanol over Cu-based catalyst

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Complementary reaction and catalyst characterization data.

The percentage conversion of DMC was as follows:

$$\text{DMC Conversion (\%)} = \frac{\text{mol of DMC charged - mol of DMC left}}{\text{mol of DMC charged}} \times 100\%$$

No gas product was observed when the reactant was methanol instead of DMC with catalyst, indicating that the decomposition of methanol on catalysts was negligible under our experimental condition. Hence, we presume here that two moles methanol will be produced from the two methoxy group of DMC when one mole DMC was converted. It can be assumed that these methanol produced from the two methoxy group had been added in the raw material, then exclude them in the final analysis by subtracting a constant. The STY_{MeOH} and the yield of methanol mentioned below represents that the methanol comes from the hydrogenation of C=O.

$$\text{Selectivity (\%)} = f_{is} \cdot \frac{A_1 - A_2}{A_s} \times 100\%$$

f_i: the absolute correction factor of MeOH

f_s: the absolute correction factor of internal standard substance

f_{is}: the relative correction factor of MeOH

A_1: the total peak area of MeOH in GC test

A_2/ A_s: the peak area of MeOH from two methoxyl groups of DMC in GC test / the peak area of internal standard substances in GC test

For the hydrogenation of DEC and DPC, the conversions of the DEC and DPC (denoted as M) were also controlled at 100%, and yields of EtOH and propanol (denoted as *i*) were calculated as follows:

$$\text{Conversion (\%)} = \frac{\text{mol of M charged} - \text{mol of M left}}{\text{mol of M charged}} \times 100\%$$

$$\text{Selectivity (\%)} = f_{is} \cdot \frac{A_i}{A_s} \times 100\%$$

f_i: the absolute correction factor of product *i*

f_s: the absolute correction factor of internal standard substance

f_{is}: the relative correction factor of product *i*

A_i: the total peak area of *i* in GC test

A_s: the peak area of internal standard substance in GC test

Table S1 Uptake of hydrogen in temperature-programmed reduction (TPR) experiments.

Entry	Catalyst	H_2 Consumption (mmol/g_{Cat})
1	20Cu/SiO_2	0.26
2	30Cu/SiO_2	0.33
3	40Cu/SiO_2	0.46
4	50Cu/SiO_2	0.88

Table S2 Hydrogenation of different carbonates in the presence of the 20Cu/SiO_2 catalyst calcined at 723 K and reduced at 573 K.

Entry	Catalyst	Conv. (%)	Sel. (%)	
			Methanol	Ethanol/Propanol
1	DEC	100	76.7	99.0
2	DPC	100	82.1	99.1

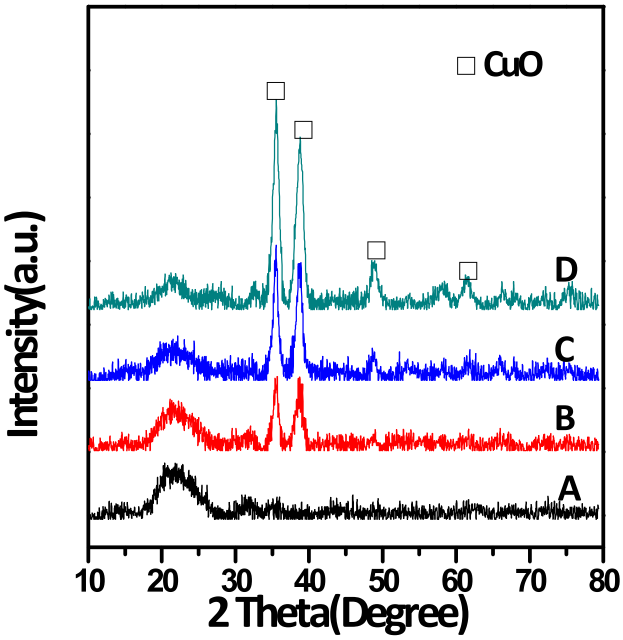

Figure S1 XRD patterns of xCu/SiO_2 calcinated at 723 K: A) 20Cu/SiO_2, B) 30Cu/SiO_2, C) 40Cu/SiO_2, D) 50Cu/SiO_2.

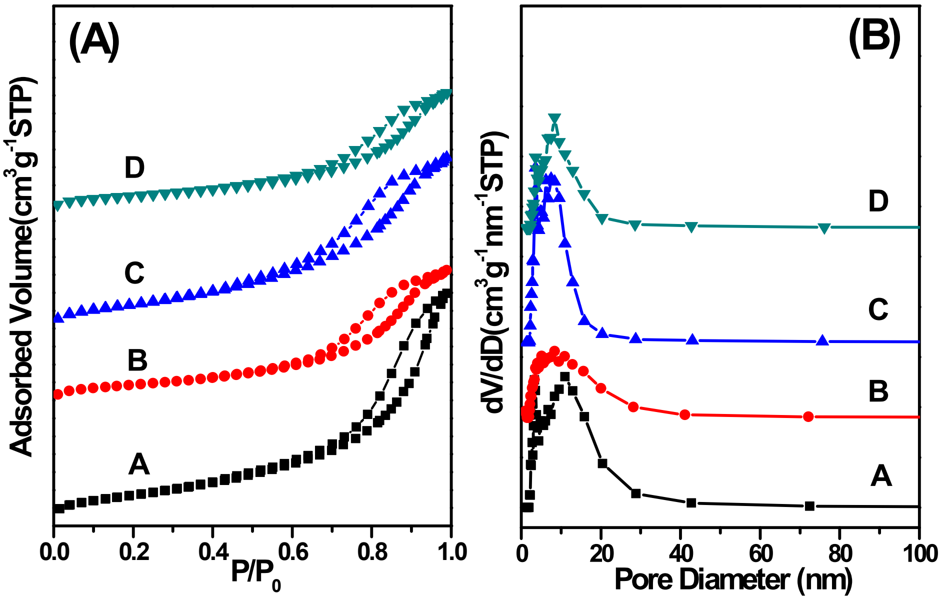

Figure S2. N_2 adsorption–desorption isotherms of (A) the calcined catalysts with different copper loadings and (B) BJH pore size distribution of the calcined catalysts with different copper loadings: A) 20Cu/SiO_2, B) 30Cu/SiO_2, C) 40Cu/SiO_2, D) 50Cu/SiO_2.

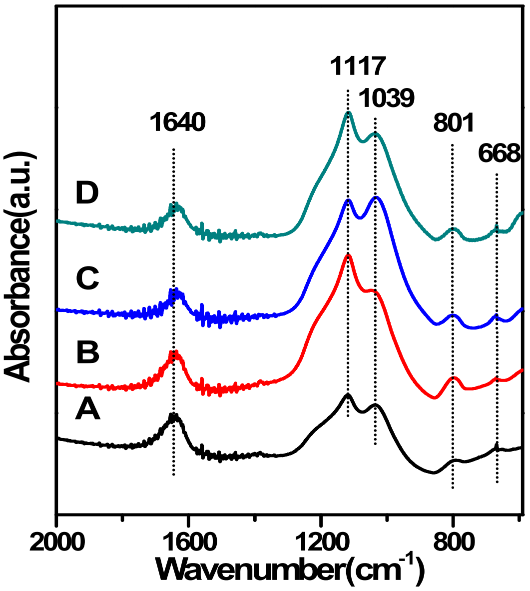

Figure S3. FT-IR spectra of: A) 20Cu/SiO_2,B) 30Cu/SiO_2, C) 40Cu/SiO_2, D) 50Cu/SiO_2.

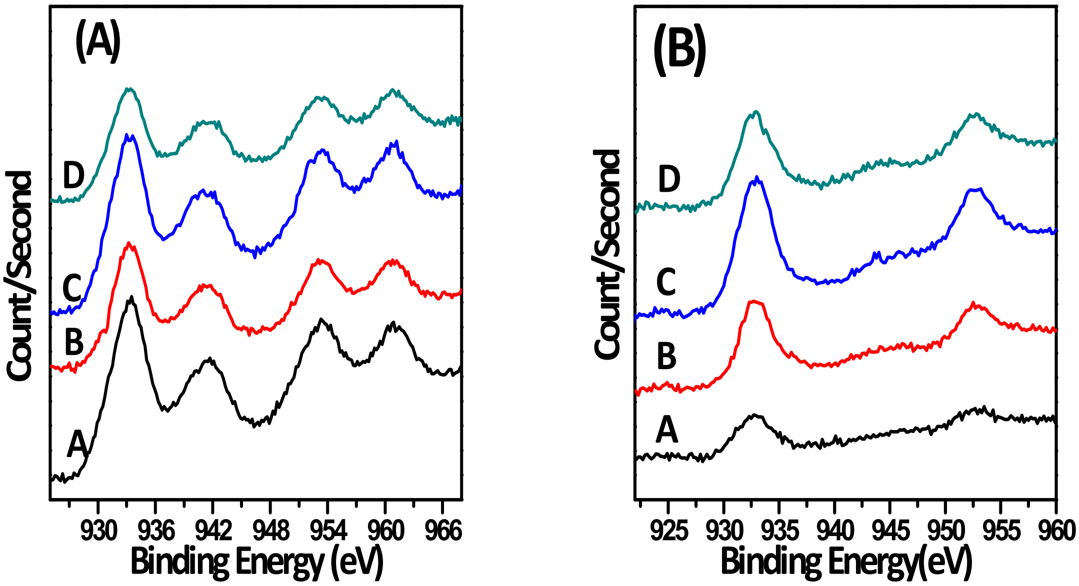

Figure S4. (A) Cu 2p photoelectron spectra of catalysts calcinated at 723 K and (B) reduced at 573 K with different copper loadings: A)20Cu/SiO_2, B) 30Cu/SiO_2, C) 40Cu/SiO_2, D) 50Cu/SiO_2.

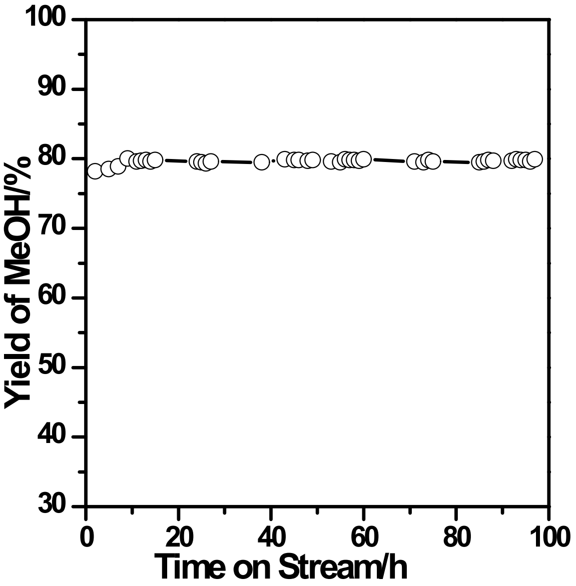

Figure S5. MeOH yield vs time on stream at 503 K. Reaction Conditions: liquid hour space velocity (LHSV) =0.2 h^{-1}, H_2/DMC = 260 (mol/mol), 503 K, 2.5 MPa.