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Supporting Information

For

Efficient synthesis of methanol and ethylene glycol via the hydrogenation of CO₂derived ethylene carbonate on Cu/SiO₂ catalysts with balanced Cu⁺-Cu⁰ sites

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Fig. S1 N₂O titration profiles of various Cu/SiO₂ catalysts.

The N₂O titration process includes the following steps [1-3]: CuO+H₂ \rightarrow Cu+H₂O (1); 2Cu+N₂O \rightarrow Cu₂O+N₂ (2); Cu₂O+H₂ \rightarrow 2Cu+H₂O (3).

According to the XRD results, the as-calcined Cu/SiO₂-MHT, Cu/SiO₂-AEH and Cu/SiO₂-AE catalysts mainly showed the characteristic diffractions of copper phyllosilicate and no obvious CuO diffraction was observed. After reduction, the three Cu/SiO₂ catalysts (MHT, AEH and AE) contained Cu₂O species and a little Cu⁰ species. As well known, the Cu⁺ from reduction of copper phyllosilicate is very stable, and it is difficult to be further reduced to Cu⁰. If we use N₂O titration to calculate the Cu dispersion, the hydrogen consumption for the three Cu/SiO₂ catalysts (MHT, AEH and AE) catalysts will decrease a lot in the first step, resulting in Cu dispersion increased unreasonably. Hence, the Cu dispersion calculated by N₂O titration only represents the dispersion of a small amount of copper on Cu/SiO₂ catalysts (MHT, AEH and AE) catalysts. On the contrary, as-calcined Cu/SiO₂-PG contained large amount of CuO. The Cu dispersion from the N₂O titration is in good agreement with that from the XRD and TEM results. Therefore, we adopted the Cu dispersion from TEM results to calculate the TOF values.



Fig. S2 *In situ* FTIR spectra of MeOH adsorbed on the Cu/SiO₂-MHT catalyst at 180 °C. Besides the IR bands of the gaseous MeOH, one band centered at about 2125 cm⁻¹ was also detected, which is assigned to Cu⁺-CO.



Fig. S3 XRD patterns of the fresh and the spent Cu/SiO₂-MHT catalyst after 10 cycles.



Fig. S4 TEM image of the spent Cu/SiO₂-MHT catalyst after 10 cycles.



Fig. S5 The correlation of acid amount and the sum copper surface areas for Cu-based catalysts.



Fig. S6 Charge distribution of EC molecule calculated by DFT.

References

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