

Fig. S1. Changes in BDO conversion and selectivity to GBL with reaction time over 0.15g of Cu(80)-SiO<sub>2</sub> and 1.0g of Cu(12)/SiO<sub>2</sub> at 250°C and 1 atm. Reaction conditions: BDO feed rate, 2.0 cm<sup>3</sup>/hr; N<sub>2</sub> carrier gas flow rate, 45 cm<sup>3</sup>/min.

Catalyst	Cu Surface Area	
	Cu m <sup>2</sup> /g catalyst	Cu m <sup>2</sup> /g Cu
Cu(12)/SiO <sub>2</sub> (Fresh)	3.9	32.5
Cu(12)/SiO <sub>2</sub> (used)	0.9	7.5
Cu(80)-SiO <sub>2</sub> (Fresh)	5.9	7.4
Cu(80)-SiO <sub>2</sub> (used)	3.1	3.9

## Table S1. Cu Surface Area of Copper-Silica Catalyst

The metallic copper surface area was determined by the nitrous oxide (N<sub>2</sub>O) titration method for all the samples. The samples were reduced at 300 °C using 10% H<sub>2</sub> in inert gas. And then Pure 10% N<sub>2</sub>O with a flow rate of 60 ml/min was allowed to pass over the sample at 60°C for 2 h. It was assumed that only the surface copper was oxidized to Cu<sub>2</sub>O under these conditions by the surface reaction, N<sub>2</sub>O(g) + 2Cu<sup>0</sup> (s)  $\rightarrow$  (Cu–O–Cu) (s) + N<sub>2</sub>(g). The copper surface area of the catalyst was determined from the amount of N<sub>2</sub>O consumed, which was analyzed with a thermal conductivity detector (TCD). The experimental error in Cu surface areas was about 5% using this technique.