Supporting Information

Conversion of highly concentrated cellulose to 1, 2-propanediol and ethylene glycol over high efficient CuCr catalysts

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Experimental

The catalyst preparation and characterization have been reported in detail previously [10]. The CuCr catalyst was prepared by an epoxide-assisted sol-gel route. XRD patterns of the samples were measured in a D/MAX-2400 diffractometer with a Cu Kα monochromatized radiation source (λ=1.5418 Å), operated at 40 KV and 100 mA. TEM and High-resolution TEM (HRTEM) were performed by using a Philips CM200 FEG transmission electron microscope, operated at 200 kV. Hydrogen-temperature programmed reduction (H_2-TPR) of the samples was carried out in a stream of 90 % argon and 10 % hydrogen with a flowing rate of 50 mL·min-1. The sample was heated at 10 K·min-1 from room temperature to 1073 K. The amount of the hydrogen consumption during the reduction was estimated with a thermal conductivity detector. XPS data were obtained using an ESCALAB250 Surface Science instrument. Monochromatic Al Ka (1486.6 eV) x-ray source was used as incident radiation. The base pressure in the measurement chamber was 2×10^{-10} mbar. The analyzer slit was set to 0.4 mm and a pass energy of 200 eV was chosen, resulting in an overall energy resolution better than 0.5 eV. Charging effects were compensated by the usage of a flood gun. The binding energies were calibrated based on the C1s peak at 284.5 eV as a reference. The XPS peaks are analyzed using a Shirley-type background and a nonlinear least-squares fitting of the experimental data based on a mixed Gaussian/Lorentzian peak shape.

Cellulose conversion was performed in a 50 mL stainless steel autoclave with mechanical stirrer and an electric temperature controller, operated under H2 pressure of 6.0 MPa at 518 K for 5 h. The cellulose (Avicel pH-101, CAS: 9004-34-6) was directly used without any treatment. Prior to the reaction, the prepared catalysts were reduced by 10 % H2 in Ar at 573 K for 2 h. The liquid products were analyzed with a Waters 1525 HPLC equipped with a Refractive Index Detector (CAPCELL PAK NH2 UG80S5 column: 4.6 mm×250 mm), and a Bruker 450-GC gas chromatograph equipped with a flame ionization detector (FFAP GC column: 30 m×0.32 mm×0.5 μm). While the gas products were analyzed with a 7890F gas chromatograph equipped with thermal conductivity detector (TDX-01 column: 4 mm×2 m). The conversion of the cellulose was determined by the change of cellulose weight before and after the reaction as reported in in the literature [1]. The yield of liquid product was calculated from the equation: yield (%) = (weight of target product)/(weight of cellulose put into the reactor)×100%.

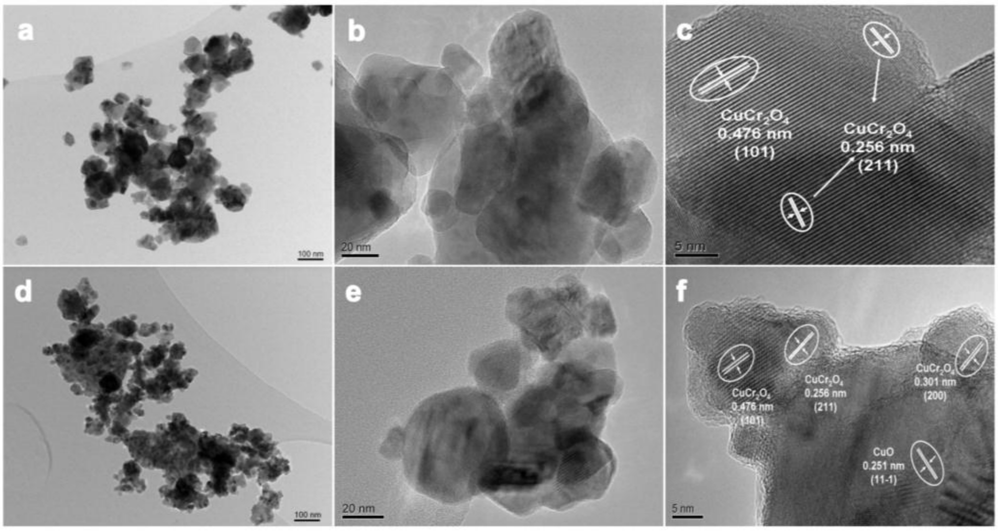

Fig. S1 TEM and HRTEM images of CuCr(0.5) catalyst (a, b, c), and CuCr(4) catalyst (d, e, f).

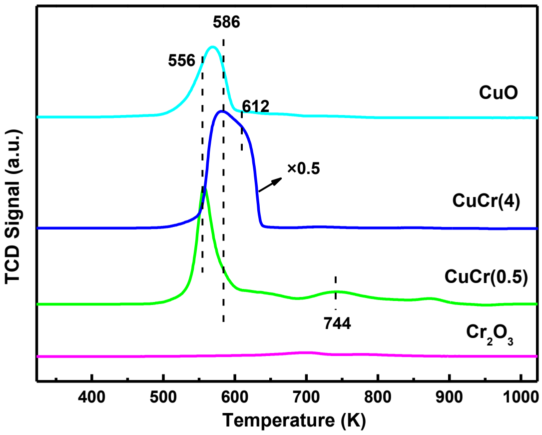

Fig. S2 H_2-TPR profiles of CuCr catalysts with different molar ratios.

The H_2-TPR behavior of CuCr catalysts with different molar ratios was investigated as shown in Figure S2. In the case of CuO catalyst, one hydrogen consumption peak positioned at 569 K was observed, which was attributed to the reduction of copper oxide crystallites to metallic copper. As known, the Cr_2O_3 was hardly reduced under given condition due to the very high and negative free energy of formation, which was in good agreement with the observed in Cr_2O_3 profile. After deconvolution of the peaks contained in the envelope of the TPR pattern, the H_2 consumption peak of the CuCr(0.5) catalyst exhibited two main peaks corresponding to T_{max} of 556 and 744 K. Wherein, the reduction of Cu^{2+} on the surface of $CuCr_2O_4$ occurred at the low temperature, indicating that such species with small particle size were more readily reduced compared to copper oxide. At higher temperature, the H_2 consumption peak could be attributed to the gradual reduction of $CuCr_2O_4$ with larger size in the bulk. In the case of CuCr(4) catalyst, the wide reduction peak could be deconvoluted into peaks positioned at 586 and 612 K, which were associated with CuO and $CuCr_2O_4$, respectively. This result suggested that the $CuCr_2O_4$ in CuCr(4) catalyst gave the higher reduction temperature compared to that in CuCr(0.5) catalyst. Based on these facts, it was reasonable to believe that there was a significant interaction between CuO and $CuCr_2O_4$ in the CuCr(4) catalyst.

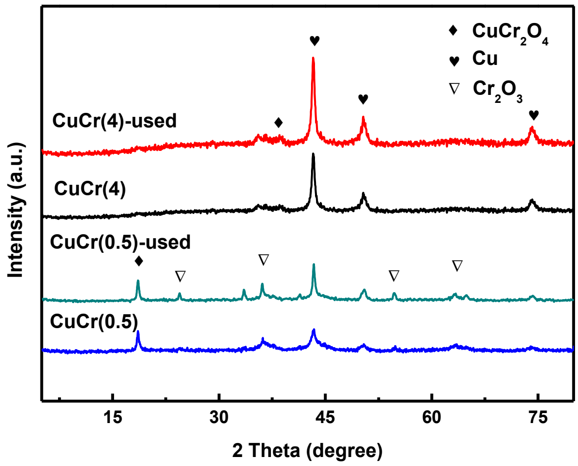

Fig. S3 XRD patterns of the reduced catalysts with different Cu/Cr molar ratios.

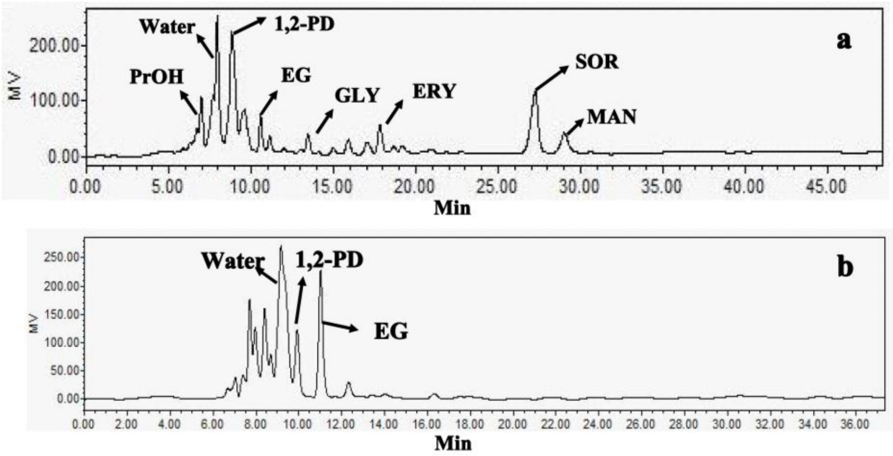

Fig. S4 HPLC analysis spectra of cellulose hydrogenolysis products over (a) CuCr(4) catalysts, (b) CuCr(4) 0.06 g Ca: 3 g cellulose, 30 g water, 0.3 g CuCr(4) catalyst, 518 K,6.0 MPa H_2, 900 rpm, 5 h.

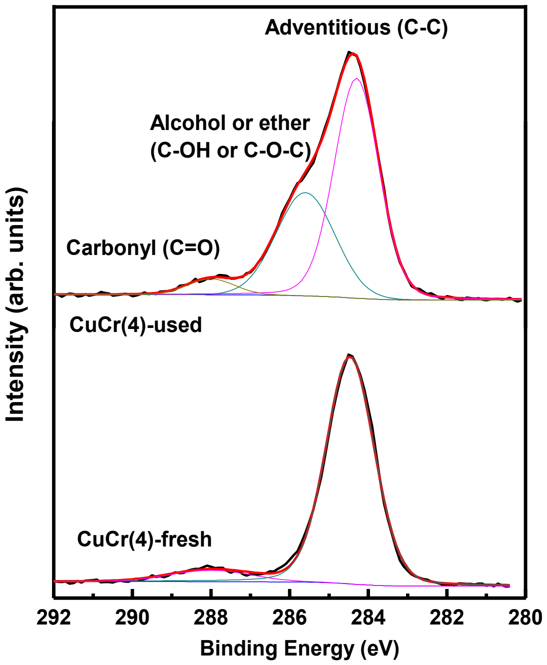

Fig. S5 Carbon 1s electron spectra from fresh and used catalysts

Fig. S5 shows the carbon 1s electron spectra from fresh and used catalysts. In the fresh catalyst, the C 1s spectrum was curve-fitted with two individual components that represent adventitious carbon (C=O, 288.1 eV) and carbonyl group (C-C, 284.5 eV).[2] Spectral contribution from alcohol or ether groups (C-OH or C-O-C, 285.7 eV)[2] in the used catalyst was observed, which can be explained by the deposition of both the reaction product and oligomers on the surface of CuCr(4) catalyst.

References

1. N. Ji, T. Zhang, M. Zheng, A. Wang, H. Wang, X. Wang and J. G. Chen, *Angew. Chem. Int. Ed.*, 2008, **47**, 8510; M. Y. Zheng, A. Q. Wang, N. Ji, J. F. Pang, X. D. Wang and T. Zhang, *ChemSusChem*, 2010, **3**, 63; Y. Zhang, A. Wang and T. Zhang, *Chem. Commun.*, 2010, **46**, 862; I. G. Baek, S. J. You and E. D. Park, *Bioresour. Technol.*, 2012, **114**, 684.

2. M. Cinar, L. M. Castanier and A. R. Kovscek, *Energy & Fuels*, 2011, **25**, 4438.

Table S1 Effect of reaction temperature on conversion and products [a] over CuCr catalysts

Reaction temperature (K)	Yield (%)								Conversion (%)
	PrOH	1,2-PD	EG	GLY	ERY	SOR	MAN	Total	
488	4.6	18.8	2.9	2.6	1.3	22.5	7.3	60.0	75.1
493	8.7	26.2	3.8	1.9	1.5	15.7	3.7	61.5	82.3
503	14.0	23.5	6.5	3.0	2.0	12.5	4.9	66.4	100
518	13.5	36.3	7.6	3.4	2.9	6.5	2.3	72.5	100
533	13.7	16.2	5.1	1.6	1.7	1.0	0.2	39.5	100

[a] Reaction condition: 3 g cellulose, 30 g water, 0.3 g CuCr(4) catalyst, 6.0 MPa H_2, 900 rpm, 5 h.

Table S2 Effect of reaction pressure on conversion and products [a] over CuCr catalysts

Reaction pressure (MPa)	Yield (%)								Conversion (%)
	PrOH	1,2-PD	EG	GLY	ERY	SOR	MAN	Total	
4.0	11.5	10.1	4.7	1.5	0.9	0.8	0.4	29.9	100
5.0	12.6	19.1	5.5	2.2	2.3	2.4	1.1	45.2	100
6.0	13.5	36.3	7.6	3.4	2.9	6.5	2.3	72.5	100
7.0	13.9	32.8	5.0	2.2	3.4	9.9	3.5	70.7	100
8.0	13.0	31.0	5.5	2.7	2.7	9.6	2.7	67.2	100

[a] Reaction condition: 3 g cellulose, 30 g water, 0.3 g CuCr(4) catalyst, 518 K, 900 rpm, 5 h.

Table S3 Effect of reaction time on conversion and products [a] over CuCr catalysts

Reaction time (h)	Yield (%)								Conversion (%)
	PrOH	1,2-PD	EG	GLY	ERY	SOR	MAN	Total	
0.5	7.5	26.0	5.4	3.0	2.0	15.0	4.0	62.9	89.6
1	9.9	29.3	5.8	2.4	2.1	13.1	4.5	67.1	95.1
2	12.3	34.8	6.0	2.3	1.5	9.8	3.6	70.3	100
5	13.5	36.3	7.6	3.4	2.9	6.5	2.3	72.5	100
10	16.4	27.3	5.5	2.0	1.8	2.6	0.6	56.2	100

[a] Reaction condition: 3 g cellulose, 30 g water, 0.3 g CuCr(4) catalyst, 518 K , 6.0 MPa H_2, 900 rpm.