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

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Direct hydrogenolysis of highly concentrated cellulose (up to 15 wt%) into 1,2-propanediol and ethylene glycol without the formation of coke-like precipitates could be performed over CuCr catalysts. Addition of $Ca(OH)_2$ results in a significant increase in the EG yield.

Concerns about the depletion of fossil fuel reserves, the impact of anthropogenic CO_2 emissions, and the increasing energy demands have encouraged the exploration of new catalytic procedures for converting renewable biomass resources into valuable platform chemicals and renewable fuel components.¹ In comparison with starch or corn, lignocellulosic biomass may not compete with production of edible crops. And its valorisation can provide an environmentally friendly alternative for fossil energy. For the lignocellulosic biomass, cellulose becomes the first and foremost choice, since it is the world's largest organic raw material resource.² Therefore, the catalytic conversion of cellulose plays a principal role in the production of a variety of valuable chemicals for further biorefinery procedures.

Due to the insolubility of cellulose, it needs to be hydrolyzed into water-soluble saccharides including oligomers and glucose in the first step, and subsequently converted to sugar alcohols and other chemicals through hydrogenation and/or hydrogenolysis (Scheme 1). In previous work, cellulose has been reported to be transformed into polyols in the presence of hydrogen over various noble metal catalysts, such as Pt/Al_2O_3 (Route B),³ Ru/C,⁴ Ru/CNT,⁵ Pt/Na(H)-ZSM-5,⁶ Pt/carbon black.⁷ Besides, transition metal catalysts, Ni-W₂C/activated carbon, Ni-W/SBA-15, Ni-W_xC/CMK-3, M(Ni,Cu,Co,Fe)/W/SiO₂-Al₂O₃ were reported to be active for the production of ethylene glycol (Route A).⁸ Nickel nano-particles



Scheme 1 Catalytic conversion of cellulose into polyols.

supported on a variety of supports, Al_2O_3 , Kieselguhr, TiO₂, SiO₂, activated carbon, ZnO, ZrO₂, MgO, and carbon nanofibers, were also used for the hydrogenolysis of cellulose to polyols.⁹ Among them, high yield of 1,2-propanediol (30.7%)⁴ and ethylene glycol (75.4%)⁸ could be obtained, in spite of the active sites of the catalysts and the underlying mechanism of the C-C bond cleavage remains unclear. However, an actual and key problem of the previously reported processes lies in a low starting concentration of cellulose in solution (about 1–3 wt%), which led to an increase in the energy and water consumption and difficulty of products separation and purification. Obviously, promoting the concentration of cellulose is highly demanded both from the perspective of enhancing production capacity and reducing the water and energy consumption.

1,2-Propanediol (1,2-PD) and ethylene glycol (EG) are important renewable chemicals due to their extensive application. One of the promising routes for their production is the catalytic conversion of cellulose. Based on these above-mentioned facts, we conducted the direct hydrogenolysis of highly

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Fig. 1 XRD patterns of calcined CuCr catalysts with various molar ratios; *e.g.* CuCr(0.25) denoted the Cu/Cr molar ratio is 0.25.

concentrated cellulose in the liquid phase with CuCr catalysts [Routes C and D] for the first time. Interestingly, the CuCr catalyst exhibited an excellent catalytic performance and good resistance against coking. Though employed in high concentrations, cellulose can be converted completely with a high yield of 1,2-PD as the main product. Upon adding Ca(OH)₂ as a co-catalyst, the yield of EG was significantly increased, *i.e.* 42.6% of 1,2-PD and 31.6% of EG can be obtained in our case.

Wherein, a copper chromium catalyst (CuCr catalyst) was prepared by an epoxide-assisted sol–gel route following our previous report.¹⁰ Its crystalline phases were determined by X-ray diffraction measurement, as shown in Fig. 1. Cr_2O_3 as the main crystalline phase was observed for CuCr(0.25) and nevertheless almost pure CuCr₂O₄ phase was observed for CuCr(0.5). With increase in the Cu/Cr molar ratio, the characteristic peaks of CuCr₂O₄ decreased, and simultaneously CuO as a new phase appeared and gradually increased. It was noteworthy that the CuCr₂O₄ phase with low intensity was also detected, even though the Cu/Cr molar ratio increased up to 4.

Typically, the crystalline phases of CuCr(0.5) and CuCr(4) catalysts were further identified by their lattice spacing, measured from HRTEM images (Fig. S1[†]). The sizes ranging from 20 to 40 nm were also obtained. As seen in the HRTEM results (the structure of the CuCr₂O₄/CuO present in the CuCr(4) catalyst), a strong interaction between CuO and CuCr₂O₄ was confirmed by the H₂-TPR results (Fig. S2[†]). After H₂ treatment at 573 K, well-crystallized Cu was formed, while the diffraction peaks of CuCr₂O₄ and Cr₂O₃ with low intensity were also detected (Fig. S3[†]). Significantly, no obvious changes in crystalline phases were observed after the reaction, indicating that the catalysts exhibited good stability.

Hydrogenolysis of highly concentrated cellulose into polyols was conducted in an aqueous medium. Due to the complexity of cellulose hydrogenolysis, as previous reports,⁸ the polyols, such as 1,2-PD, EG, propanol (PrOH), glycerol (GLY), erythritol (ERY), sorbitol (SOR), mannitol (MAN), and some unknown products, were observed (Fig. S4†). While only a little amount of CO and CO₂ as gas products, lower than 0.1%, could be detected. In addition, some water-soluble oligomers were formed, which could not be determined by the GC or HPLC under the present conditions. Based on these facts, the total yield of listed products obtained was low. Several typical hydrogenation catalysts including 2%Ni-30%W/AC, 3% Pt-1%Ru/C, NiCr, CuFe, and NiMg were tested in order to compare the CuCr catalysts in the reaction, the corresponding results are listed in Table 1. Apart from the CuCr and NiMg (0.25) catalysts, the other catalysts exhibited poor activity with serious coking or polymerization (black bulk solids) at high concentration. Under these conditions, the conversion could not be obtained accurately.

Cellulose could be converted in the hot water even in the absence of catalysts, since water at elevated temperatures (above 473 K) can generate H⁺ ions capable of performing acid-catalyzed reactions. However, coke-like precipitates apparently formed from the acid-catalyzed condensation reactions,¹³ and this process would be enhanced at high concentration of cellulose. Thus, a suitable catalyst should be used for preventing the coking or condensation reactions. In the case of Ni, Pt and Ru based catalysts with great hydrogen activation, the increase of dissociative proton in the solution led to the enhancement of condensation reactions and the formation of coke-like precipitates or polymers. Nevertheless, the catalysts with alkaline support could restrain these reactions, such as NiMg(0.25) catalysts. This is because of the increase of catalyst basicity leading to C-C cleavage and reducing the formation of coke-like precipitates.14 Besides, the CuFe catalyst was unsuited for hydrogenolysis of high concentration cellulose compared to the CuCr catalyst, which was related to the structure properties of catalysts. As suggested in the hydrogenolysis of glycerol,¹⁰ the formation of spinel CuCr₂O₄ greatly enhanced the hydrogenolysis performance. This is due to the fact that the characteristic of the reduction mechanism leads to formation of epitaxially bound phases of metallic copper. In addition, the hydrogen atoms are occluded as bulk hydrogen in the CuCr₂O₄ spinel structure, which are able to be released onto the catalyst surface during the reaction to hydrogenate,¹⁵ while the CuFe catalysts gave low activity due to the absence of spinel CuFe₂O₄ in the reduced catalysts. The underlying reason needs to be further clarified. Indeed, there is a balance between hydrogenolysis and condensation in the conversion of cellulose. Relatively rapid hydrogenolysis over the CuCr catalyst did not result in formation of coke-like precipitates. Thus, the CuCr catalyst, which could restrain the formation of coke-like precipitates and polymers in the conversion of highly concentrated cellulose, is a highly efficient catalyst.

Cellulose could be completely converted without the formation of coke-like precipitates, irrespective of the Cu/Cr molar ratio, as listed in Table 1. Meanwhile, the yield of 1,2-PD increased almost linearly from 21.8% to 36.3%. This increase was related to the structure of CuCr catalysts as well as to the difference in the effective contact of cellulose with active sites. An increase in active copper could lead to the increase of 1,2-PD yield. Such phenomenon was in good agreement with the selectivity of 1,2-PD in glycerol hydrogenolysis over CuCr catalysts in our present study.¹⁰ A similar trend in PrOH yield was also observed, it gradually increased from 8.9% to 13.5%. As suggested, the CuCr(4) catalyst was used in the later

Table 1	Hydrogenolysis	of cellulose ^a	over various	catalysts
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	Yield (%)									
Catalysts	PrOH ^e	1,2-PD	EG	GLY	ERY	SOR	MAN	Total	Conversion (%)	Coking or Polymerization
2%Ni-30%W/AC ^b	5.3	4.6	21.1	2.1	1.2	2.1	0.9	37.3	_	Yes
3%Pt-1%Ru/C ^c	6.2	8.7	8.6	3.8	1.9	3.5	1.2	33.9	_	Yes
$NiCr(0.5)^d$	5.5	9.0	10.1	1.5	1.4	2.0	1.5	31.0	_	Yes
$CuFe(0.5)^d$	4.3	13.5	5.6	1.7	1.2	2.9	1.1	30.3	_	Yes
$NiMg(0.25)^{f}$	2.1	15.6	11.4	0.4	ND^{g}	ND	ND	29.5	100	No
CuCr(0.25)	8.9	21.8	4.5	2.0	1.4	4.2	4.3	47.1	100	No
CuCr(0.5)	10.8	27.7	5.4	1.9	1.8	5.6	1.8	55.0	100	No
CuCr(1)	11.6	29.9	5.7	2.0	2.1	5.7	2.1	59.1	100	No
CuCr(2)	12.6	31.4	6.2	2.4	2.5	5.7	2.8	63.6	100	No
CuCr(4)	13.5	36.3	7.6	3.4	2.9	6.5	2.3	72.5	100	No
$CuCr(4)-2^h$	14.2	27.4	4.9	2.2	3.4	5.8	3.4	61.3	100	No
$CuCr(4)-3^{i}$	14.5	25.3	4.3	2.5	3.6	5.7	2.8	58.7	100	No
$CuCr(4) 0.03 g Ca^{j}$	2.4	19.0	15.7	ND	ND	ND	ND	37.1	100	No
CuCr(4) 0.06 g Ca	2.3	42.6	31.6	ND	ND	ND	ND	76.5	100	No
CuCr(4) 0.12 g Ca	1.8	35.9	22.7	ND	ND	ND	ND	60.4	100	No
CuCr(4) 0.24 g Ca	1.4	25.7	22.0	ND	ND	ND	ND	49.1	100	No
$CuCr(4) 0.06 g Ca^k$	2.2	35.7	30.8	ND	ND	ND	ND	68.7	100	No

^{*a*} Reaction conditions: 3 g cellulose, 30 g water, 0.3 g catalyst, 518 K, 6.0 MPa H₂, 900 rpm, 5 h. ^{*b*} Prepared by a carbothermal hydrogen reduction (CHR) method.^{11 c} Prepared by a microwave-assisted method.^{12 d} Prepared by a sol–gel route.^{10 e} PrOH: 1-PrOH + 2-PrOH, amount of 1-PrOH is about six times as much as 2-PrOH for CuCr catalysts. ^{*f*} Prepared by a co-precipitation method. ^g ND = not detected. ^{*h*} CuCr(4) catalyst in the third run. ^{*j*} Ca(OH)₂ as a co-catalyst. ^{*k*} CuCr(4) 0.06 g Ca catalyst in the second run.

Table 2 Effect of cellulose concentration on conversion and products ^a over	CuCr catalysts
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Cellulose concentration ^b (wt%)	Yield (%)								
	PrOH	1,2-PD	EG	GLY	ERY	SOR	MAN	Total	Conversion (%)
6	12.2	30.3	4.9	2.3	2.3	6.1	4.7	62.8	100
8	12.9	35.8	4.1	2.3	1.9	6.7	3.8	67.5	100
10	13.5	36.3	7.6	3.4	2.9	6.5	2.3	72.5	100
12	15.1	24.3	6.5	2.3	2.8	3.2	2.5	56.7	100
15	10.2	11.1	4.7	1.6	1.7	2.2	0.9	32.4	100

^{*a*} Reaction conditions: 30 g water, 0.3 g CuCr(4) catalyst, 518 K, 6.0 MPa H_2 , 900 rpm, 5 h. ^{*b*} Concentration (wt%) = weight of cellulose × 100/ weight of water.

experiments because of the highest activity and the highest yield of polyols among all of CuCr catalysts.

Effects of the cellulose concentration on conversion and products were investigated. The corresponding results are shown in Table 2. Surprisingly, a very high conversion (100%) could be obtained even though the concentration increased up to 15 wt%. To the best of our knowledge, this starting concentration of cellulose is highest for the heterogeneous hydrogenolysis process. The yield of 1,2-PD increased with increase in the cellulose concentration at the beginning, it passed a maximum (36.3%) and gradually dropped to 11.1%. A similar trend in the total yield was observed. The reason was that the catalysts had enough active sites for hydrogenolysis of SOR and MAN, and for further hydrogenolysis of 1,2-PD at low cellulose concentration, otherwise, large amounts of watersoluble saccharides covered the active sites, and suppressed the desorption of products, resulting in low total polyols yield at high cellulose concentration. Accordingly, it is worthy of trust that superior results could be obtained by optimizing the reaction parameters under high concentration.

The reaction activities and product selectivities strongly depend on the reaction parameters of temperature and H₂ pressure in the aqueous reaction solutions. Table S1[†] shows the influence of reaction temperature on cellulose hydrogenolysis on the CuCr catalyst at 6.0 MPa H₂. Upon increasing the temperature, the cellulose conversion was increased. The maximum (100%) could be obtained at or above 503 K. This high conversion is related to the dissociation degree of hot water as reported by Liu et al., who found that the hydrolysis of cellulose was enhanced by a dissociative proton originating from water at high temperature.¹³ Below 518 K, the yield of SOR was successively decreased, and the opposite trend for 1,2-PD and PrOH yields was observed. These results demonstrated that converting SOR or MAN to lower polyols favored high temperature. While further increasing the reaction temperature to 533 K, the 1,2-PD and total yield was greatly decreased. This is because high temperature was beneficial for dehydration of polyols, resulting in cyclization and partly polycondensation, and subsequent decrease in the total yield of identified polyol products.¹⁶ Similarly, the effect of reaction

pressure in the range of 4-8 MPa was investigated, the corresponding results are summarized in Table S2.[†] The yield of SOR and MAN increased with increasing pressure at 100% cellulose conversion, illustrating that hydrolysis of cellulose to glucose units was favored at high pressure, while the watersoluble oligomers were formed at low pressure, which were not detected by HPLC or GC. On the whole, reaction pressure has a positive effect on 1,2-PD yield, although it was slightly decreased at higher pressure (above 6.0 MPa) due to further hydrogenolysis of 1,2-PD to small molecular alcohols and CO or CO2, etc. These hydrogenolysis processes were verified by the effect of reaction time (Table S3[†]). The yield of SOR decreased with increasing reaction time, while that of 1,2-PD increased within 5 h, indicating that SOR gradually converted to 1,2-PD and other polyols (see Scheme 1). As expected, further extending time led to conversion of 1,2-PD to other by-products.

It was worth noting that the higher yield ratio of EG to 1,2-PD was obtained for the NiMg(0.25) catalyst compared to other single catalysts, as listed in Table 1, which was related to the basicity of MgO. Thus, addition of Ca(OH)₂ as a co-catalyst in the CuCr(4) catalyst for the hydrogenolysis of cellulose was conducted. As expected, the yield of EG was significantly increased, resulting in an increase in the yield ratio of EG to 1,2-PD. A maximum 1,2-PD and EG yield of 42.6% and 31.6% could be obtained. More low molecular weight polyols were formed with a base promoter, indicating that a C-C bond cleavage mechanism of the base-catalyzed retro-aldol condensation in hydrogenolysis was enhanced.¹³ Certainly, adding excessive alkali led to the further hydrogenolysis of 1,2-PD and EG, and a decrease in their yield. In the absence of a metal catalyst, the cellulose could be also converted over the Ca(OH)2 since 10.8% of conversion was obtained under similar conditions. This is because of the partial dissolution of $Ca(OH)_2$, the swelling or dissolution of cellulose could proceed under alkaline conditions.¹⁷

As same as the hydrogenolysis of glycerol, the reaction route and the hydrogenolysis rate were significantly changed under alkaline conditions or over alkaline catalysts.^{14,18} After adding a base, the higher yield of 1,2-PD and EG might be also attributed to the mechanism, such as the selective cleavage of C-C and C-O bonds and the bond cleavage rate, although the underlying reason is not clear. In the absence of a base, a widely accepted reaction mechanism of cellulose hydrolysis involves the activation of the glucosidic oxygen or pyranic oxygen by protonation,19 while that involves the random scissions of a glycosidic bond in the presence of a base. Meanwhile, the C-C bond cleavage based on the base-catalyzed retro-aldol condensation is also enhanced. The change in the reaction route is mainly responsible for the high yield of 1,2-PD and EG. In addition, Davis and Shanks suggested that the concentration of OH⁻ in the reaction mixture was mainly responsible for high hydrogenolysis performance.14 Nevertheless, the role of alkali metal ions in that needs to be further confirmed.

Catalyst recycling is important in metal-catalyzed liquidphase reactions. Therefore, we recycled the CuCr(4) catalyst

over three runs. Before reusing, the recovered catalyst was reduced as the first time. Table 1 shows that the reusability of catalysts was excellent, since the high conversion was maintained, although the 1,2-PD yield was slightly decreased from 36.3% to 25.3% after three runs. Inductively coupled plasma spectrometer (ICP) analysis of reaction solvents showed that the leaching of either copper or chromium is negligible (Cu: $2.1 \times 10^{-2} \text{ mg mL}^{-1}$, Cr: $4.4 \times 10^{-3} \text{ mg mL}^{-1}$). Thus, the increase of Cu particle size (Fig. S3⁺) and/or the slight deactivation due to the coverage of carbon species in the reaction (Fig. S5[†]) may be the main reason for a decrease in 1,2-PD yield. Similarly, the CuCr(4) 0.06 g Ca catalyst was recycled. The yield of 1,2-PD and EG decreased to 35.7% and 30.8% after two runs, respectively. ICP results (Cu: 1.8×10^{-2} mg mL⁻¹, Cr: 5.9×10^{-4} mg mL⁻¹, Ca: 0.58 mg mL⁻¹) indicated that the decrease of these yields was mainly related to the leaching of calcium.

In conclusion, we have presented a green approach of efficient conversion from high concentration cellulose to polyols directly. The CuCr catalysts exhibited excellence in anti-coking and a good catalytic performance. This provides a possibility for scale-up in industrial application. The maximum 1,2-PD and EG yield of 42.6% and 31.6% at 100% conversion was obtained over CuCr(4) catalysts with Ca(OH)₂ as a co-catalyst, while the actual role of the Ca promoter in deciding the products distribution needs to be further investigated. For a rational control of the products distribution and efficient conversion of high concentration cellulose into renewable fuels and chemicals, further designing the catalyst and understanding this catalytic system has become the focus of research.

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Notes and references

- A. J. Ragauskas, C. K. Williams, B. H. Davison, G. Britovsek, J. Cairney, C. A. Eckert, W. J. Frederick Jr., J. P. Hallett, D. J. Leak, C. L. Liotta, J. R. Mielenz, R. Murphy, R. Templer and T. Tschaplinski, *Science*, 2006, **311**, 484.
- 2 L. T. Fan, M. M. Gharpuray and Y. H. Lee, in *Cellulose Hydrolysis Biotechnology Monograph*, Springer, Berlin, 1987, p. 211.
- 3 A. Fukuoka and P. L. Dhepe, *Angew. Chem., Int. Ed.*, 2006, 45, 5161.
- 4 C. Luo, S. Wang and H. Liu, Angew. Chem., Int. Ed., 2007,
 46, 7636; Y. Liu, C. Luo and H. Liu, Angew. Chem., Int. Ed., 2012, 51, 3249.

- 5 W. Deng, X. Tan, W. Fang, Q. Zhang and Y. Wang, *Catal. Lett.*, 2009, 133, 167; H. Wang, L. Zhu, S. Peng, F. Peng, H. Yu and J. Yang, *Renewable Energy*, 2012, 37, 192.
- 6 S. J. You, I. G. Baek, Y. T. Kim, K. E. Jeong, H. J. Chae, T. W. Kim, C. U. Kim, S. Y. Jeong, T. J. Kim, Y. M. Chung, S. H. Oh and E. D. Park, *Korean J. Chem. Eng.*, 2011, 28, 744.
- 7 H. Kobayashi, Y. Ito, T. Komanoya, Y. Hosaka, P. L. Dhepe, K. Kasai, K. Hara and A. Fukuoka, *Green Chem.*, 2011, 13, 326.
- 8 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.
- 9 X. Wang, L. Meng, F. Wu, Y. Jiang, L. Wang and X. Mu, Green Chem., 2012, 14, 758; S. Van de Vyver, J. Geboers, M. Dusselier, H. Schepers, T. Vosch, L. Zhang, G. Van Tendeloo, P. A. Jacobs and B. F. Sels, ChemSusChem, 2010, 3, 698.
- 10 Z. Ma, Z. Xiao, J. A. van Bokhoven and C. Liang, *J. Mater. Chem.*, 2010, 20, 755; Z. Xiao, Z. Ma, X. Wang, C. T. Williams and C. Liang, *Ind. Eng. Chem. Res.*, 2011, 50, 100 (2010) (20

2031; Z. Xiao, S. Jin, X. Wang, W. Li, J. Wang and C. Liang, *J. Mater. Chem.*, 2012, 22, 16598; Z. Xiao, C. Li, J. Xiu, X. Wang, C. T. Williams and C. Liang, *J. Mol. Catal. A: Chem.*, 2012, **365**, 24.

- 11 C. H. Liang, F. P. Tian, Z. L. Li, Z. C. Feng, Z. B. Wei and C. Li, *Chem. Mater.*, 2003, **15**, 4846.
- 12 X. Ni, B. Zhang, C. Li, M. Pang, D. Su, C. T. Williams and C. Liang, *Catal. Commun.*, 2012, 24, 65.
- C. Luo, S. Wang and H. Liu, Angew. Chem., Int. Ed., 2007, 46, 7636; J. Sun and H. Liu, Green Chem., 2011, 13, 135.
- 14 E. P. Maris and R. J. Davis, J. Catal., 2007, 249, 328;
 D. G. Lahr and B. H. Shanks, *Ind. Eng. Chem. Res.*, 2003, 42, 5467.
- 15 R. Bechara, G. Wrobel and M. Daage, *Appl. Catal.*, 1985, **16**, 15.
- 16 N. Li and G. W. Huber, *J. Catal.*, 2010, 270, 48;
 C. Montassier, J. C. Ménézo, J. Moukolo, J. Naja,
 L. C. Hoang and J. Barbier, *J. Mol. Catal.*, 1991, 70, 65.
- 17 Y. Yu, X. Lou and H. Wu, Energy Fuels, 2008, 22, 46.
- 18 S. Xia, R. Nie, X. Lu, L. Wang, P. Chen and Z. Hou, J. Catal., 2012, 296, 1.
- 19 A. Cabiaca, E. Guillon, F. Chambon, C. Pinel, F. Rataboul and N. Essayem, *Appl. Catal., A*, 2011, **402**, 1.