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Ni–Cu/ZnO-catalyzed Hydrogenolysis of Cellulose for the Production of 1,2-Alkanediols in Hot Compressed Water

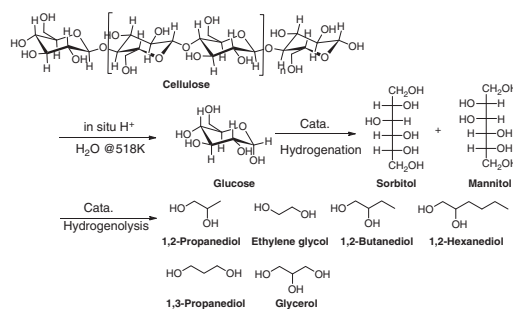Xicheng Wang,[1,2] Feng Wu,[1,3] Shengxi Yao,[1] Yijun Jiang,[1] Jing Guan,[1] and Xindong Mu*[1]
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Ni–Cu/ZnO catalysts with varied Ni-to-Cu mole ratio were prepared by coprecipitation and evaluated for the hydrogenolysis of high-crystalline cellulose. Ni and Cu species exerted synergetic effects in dehydroxylation reaction and C–C bond breakage for the formation of 1,2-alkanediols. Ni–Cu/ZnO with Ni-to-Cu ratio of 2:3 is highly selective toward 1,2-alkanediols (72.5%) under hydrothermal conditions (518 K, 4 MPa H_2), which also exhibits excellent activity in the conversion of real biomass.

Approaches for making use of cellulose, the most abundant and inedible biomass resource on earth, for the production of chemicals economically competitive with petro-based chemicals are under intensive research to maintain environmental and economical sustainability.[1–3] One-pot chemical transformation of cellulose to polyols over heterogeneous catalyst is one of the most promising routes for the effective utilization of cellulose in terms of catalyst separation, energy efficiency, and selectivity. Fukuoka and Dhepe were the first to report that a bifunctional Pt/Al_2O_3 could effectively catalyze the one-step conversion of cellulose into hexitols as major products.[4] By conducting the reaction at an elevated temperature to make use of H^+ generated by hot compressed water to promote the hydrolysis of cellulose, Luo et al. successfully improved the hexitol yield to 39.3% using Ru/C as the hydrogenation catalyst with a reaction time of 30 min,[5] showing that hot water was a promising reaction media for its distinct green-chemistry processing advantages in the utilization of robust cellulose.[1] More recently, Zhang and co-workers developed a series of tungstenic catalysts which can selectively catalyze cellulose conversion into ethylene glycol with a yield of 76%.[6–8] Most notably, supported Ni catalysts investigated in such studies consistently showed poor selectivity toward polyols,[6–9] though nonexpensive Ni is commonly considered an excellent hydrogenation and hydrogenolysis catalyst.[10] On the other hand, bifunctional Cu/ZnO catalyst has been used as an efficient dehydroxylation catalyst for hydrogenolysis of glycerol[11,12] and sorbitol.[13] This suggests to us that the combination of Ni and Cu may work well in the production of diols from cellulose, which is the objective of this work.

Herein, we report that ZnO-supported Ni–Cu bimetallic catalysts can effectively catalyze high-crystalline cellulose conversion into polyols in one pot (Scheme 1), especially into industrially attractive 1,2-alkanediols such as 1,2-propanediol (1,2-PDO), ethylene glycol (EG), 1,2-butanediol (1,2-BDO), and 1,2-hexanediol (1,2-HDO), demonstrating a totally distinctive product distribution compared to previously reported results.[4–6,14] The 1,2-alkanediols have wide promising applications in antifreezes, drugs, and as starting materials in esterification and etherification reactions. More specifically, the monomeric glycol mixtures can be used directly in unsaturated polyester resin manufacture without further separation, which will reduce the separation cost. In this study, the catalysts were also successfully used to convert real biomass (cornstalk and corncob) with remarkable 1,2-alkanediol selectivity.

Scheme 1. One-step conversion of cellulose to 1,2-alkanediols.

The catalysts were prepared by coprecipitation from mixed metal nitrate solution with Na_2CO_3[16] and evaluated in a 100-mL 316L stainless autoclave for batchwise conversion of microcrystalline cellulose with crystallinity index (CrI, estimated by Segal equation[15]) of 83%. After 0.15 g of catalyst and 0.5 g of cellulose were loaded, the reactor was purged four times with hydrogen to remove air, which was then pressurized to 4 MPa and programmed to 518 K for 30 min. Cellulose conversions were calculated by the weight loss of cellulose before and after the reaction and also confirmed by TOC.[6] Samples were identified by a gas chromatograph (GC, 7890A, Agilent, USA) coupled with a mass spectrometer (MS, 5975C, Agilent, USA). The peaks were matched according to NIST database. Quantitative analyses were carried out on both Varian GC450 and high-performance anion-exchange chromatograph with pulsed amperometric detection (IC, gold electrode detector, Dionex).

Except for the major products summarized in Table 1 which include 1,2-PDO, EG, 1,2-BDO, 1,2-HDO, 1,3-PDO, glycerol, erythritol, sorbitol, mannitol, and glucose, some undesirable compounds were also formed, such as 5-hydroxymethylfurfural, lactic acid, and trace amount of mono alcohols with carbon number of 1–6. The carbon balance based on total organic carbon (TOC) analysis of the resultant liquid showed that negligible amount of gas product was produced. A typical set of GC and IC chromatograms (Figure 1) of products showed that the quantitative analysis using combination of GC and IC was very effective.

The conversion of cellulose without any catalyst was as high as 38% (Table 1, Entry 1) under the studied conditions, which

Table 1. Results of cellulose conversion over ZnO-supported catalysts[a]

| Entry | Catalyst[b] | Substrate | Conv.[c] /% | Selectivity based on carbon[d]/% | | | | | | | | | |
				1,2-PDO[e]	EG	1,2-BDO	1,2-HDO	Total[f]	1,3-PDO	Gly	Ery	Hexitols	Glucose
1	Blank	Cellulose	38	—	—	—	—	—	—	—	—	—	6.8
2	ZnO	Cellulose	42	—	—	—	—	—	—	—	—	—	3.0
3	5Cu·5ZnO	Cellulose	47	17.9	8.4	7.4	12.7	46.4	1.7	0.6	0.5	1.6	1.0
4	1Ni·4Cu·5ZnO	Cellulose	63	20.9	16.7	9.0	8.3	54.9	1.5	1.7	1.2	1.8	0.8
5	2Ni·3Cu·5ZnO	Cellulose	74	32.9	22.8	9.6	7.2	72.5	1.6	2.6	1.6	2.2	0.6
6	3Ni·2Cu·5ZnO	Cellulose	79	25.6	13.2	5.5	5.3	49.6	0.8	6.2	1.4	3.8	0.4
7	4Ni·1Cu·5ZnO	Cellulose	81	17.6	12.7	6.0	3.3	39.6	0.9	12.8	1.6	3.2	0.3
8	5Ni·5ZnO	Cellulose	86	16.5	12.2	2.2	1.2	32.1	0.6	17.2	1.2	4.5	0.1
9	2Ni·3Cu·5ZnO	Cellulose[g]	95	36.3	20.1	7.2	5.6	69.2	1.1	3.6	1.8	2.0	0.6
10	2Ni·3Cu·5ZnO	Glucose	100	25.6	10.9	5.3	0.7	42.5	1.3	5.7	2.9	6.2	0.0
11	2Ni·3Cu·5ZnO	Sorbitol	93	36.0	18.3	7.0	4.7	66.0	0.5	5.6	2.5	1.2	—
12	2Ni·3Cu·5ZnO	Glycerol	95	79.1	15.5	—	—	94.6	0.0	—	—	—	—
13	2Ni·3Cu·5ZnO	Cornstalk[h]	92	21.7	15.9	5.0	5.9	48.5	2.1	1.3	1.2	8.1	0.0
14	2Ni·3Cu·5ZnO	Corncob[h]	96	24.9	18.4	7.7	4.5	55.5	1.3	1.7	1.6	7.3	0.0
15	2Ni·3Cu·5ZnO-2[i]	Cellulose[g]	94	33.1	21.3	8.0	5.2	67.6	1.5	4.2	2.0	1.8	0.8
16	2Ni·3Cu·5ZnO-3[j]	Cellulose[g]	92	32.5	19.8	7.6	4.3	64.2	1.2	4.6	1.9	1.5	0.9
17	2Ni·3Cu·5ZnO-4[k]	Cellulose[g]	91	31.0	18.9	7.3	4.1	61.3	1.3	5.0	1.6	1.6	1.2

[a]*Reaction conditions*: catalyst, 0.15 g; substrate, 0.5 g; H_2O, 50 mL; temperature, 518 K; H_2 pressure, 4 MPa (RT); 800 rpm; reaction time, 0.5 h. [b]The catalysts were labeled as xNi·yCu·zZnO, where x, y, and z refer to the molar ratio of the metals in the preparation. [c]Cellulose conversions were calculated by the weight loss of cellulose in the reaction. [d]The selectivity was based on carbon. [e]Abbreviations: PDO: propanediol, EG: ethylene glycol, BDO: butanediol, HDO: hexanediol, Gly: glycerol; Hexitols: sorbitol + mannitol. [f]Sum of 1,2-alkanediol selectivity. [g]Ball-milled cellulose was charged as substrate. [h]The conversion and selectivity were based on pentose and hexose. [i, j, k]2Ni·3Cu·5ZnO in the second, third, and forth runs for ball-milled cellulose conversion.
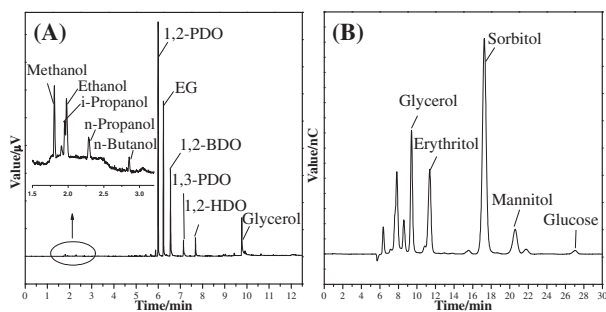

Figure 1. Chromatograms of liquid sample after reaction of cellulose over 2Ni·3Cu·5ZnO at 518 K, 4 MPa H_2 for 30 min: (A) GC and (B) IC.

was ascribed to the hydrolysis catalyzed by in situ formed H^+ ions.[5] The addition of ZnO gained a rise to 42% cellulose conversion, indicating that the degradation product underwent further reaction over ZnO and thus promoted the reaciton. When the hydrogenation species (Ni or Cu) was introduced, obvious increase of cellulose conversion was observed, leading to a colorless solution versus brown solution when no hydrogenation catalysts were used. Among the catalysts investigated, 2Ni·3Cu·5ZnO (the numbers refer to the mole ratio of the metals in the preparation) displayed the best 1,2-alkanediol selectivity (72.5%) with 74% cellulose conversion (Table 1, Entry 5). Within the fraction of 1,2-alkanediols, 1,2-PDO (32.9%) and EG (22.8%) are the major products followed by 1,2-BDO (9.6%) and 1,2-HDO (7.2%). Besides the 1,2-alkanediols, other products including glycerol, erythritol, sorbitol, mannitol, and glucose which could be regarded as the precursors of diols, reached a total selectivity of 7.0%. This system offered glycol selectivity

superior to the combined homogenous acid and noble metal catalyzed hydrogenolysis of cellulose[14] with different product distributions compared to previous work.[4–6]

The catalytic performance as well as the product distributions differed greatly as a result of varying Ni/Cu ratio in the catalyst. In the absence of Ni, 5Cu·5ZnO could achieve 47% conversion with 46.4% total 1,2-alkanediol selectivity, and the selectivity to glycerol was only 0.6% (Table 1, Entry 3). Indeed, Cu/ZnO was very effective in the hydrogenolysis of glycerol to 1,2-PDO.[12] When a little Ni was added to the catalyst, notable increase of cellulose conversion was observed and the selectivity to 1,2-alkanediols improved to 54.9%. Further increase of Ni/Cu molar ratio to 2/3 led to a more significant improvement, which showed 74% conversion with a total selectivity to 1,2-alkanediols of as high as 72.5%. Though higher conversions were obtained with higher Ni/Cu molar ratio, the selectivity to 1,2-alkanediols decreased, suggesting that the higher Ni content led to more cracking reactions which favored the formation of the undesired by-products. 5Ni·5ZnO showed 86% conversion of cellulose with only 32.1% selectivity to 1,2-alkanediols and relatively high glycerol selectivity (17.2%). When glycerol was used as substrate, 94.6% selectivity toward glycols (1,2-PDO and EG) was obtained, confirming the role of combining Ni and Cu in the formation of diols as a result of C–C/C–O cleavage (Table 1, Entry 12). The results showed the Ni and Cu played synergetic roles in the hydrogenolysis of cellulose which involved hydrolysis, hydrogenation, as well as C–C and C–O hydrogenolysis. The increase of conversion was ascribed to good hydrogenation activity catalyzed by Ni, while the selectivity depended on both Ni and Cu. The formation of new species, namely, Ni–Cu alloys as indicated by the XRD patterns and H_2-TPR characterization
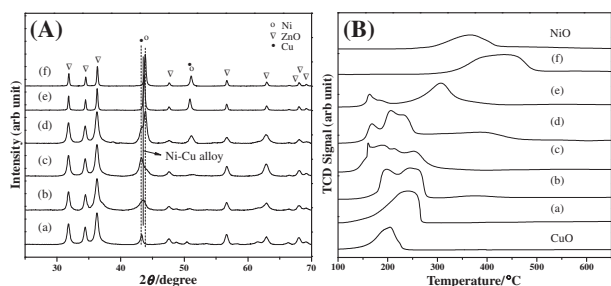
Figure 2. Powder X-ray diffraction patterns (A) and H$_2$-TPR profiles (B) of Ni–Cu/ZnO catalysts: (a) 5Cu·5ZnO, (b) 1Ni·4Cu·5ZnO, (c) 2Ni·3Cu·5ZnO, (d) 3Ni·2Cu·5ZnO, (e) 4Ni·1Cu·5ZnO, and (f) 5Ni·5ZnO.

Table 2. Composition analysis of substrates

Substrate	CrI[a] /%	Component/wt %[b]				
		Cellulose	Hemicellulose	Lignin	Ash	Others
Cornstalk	72	35.0	20.8	22.5	4.0	17.7
Corncob	58	34.6	30.6	9.4	2.5	22.9

[a]CrI (crystallinity index): estimated by XRD analysis according to the Segal equation. [b]According to NREL analytical method.

may also contribute to the good activity of the Ni–Cu/ZnO catalysts (Figure 2). When glucose, the monomer unit in cellulose, was charged as substrate, only 42.5% total 1,2-alkanediol selectivity was obtained with complete glucose conversion (Table 1, Entry 10), implying that the hydrolysis of cellulose by in situ H$^+$ is the rate-determining step. The slowly generated glucose underwent fast hydrogenation to form more stable sorbitol, which was further converted to glycols (Table 1, Entry 11).

In our study, the pulverized cornstalk and corncob were used as real feedstock in the hydrogenolysis reaction. The composition of the raw materials was determined according to the NREL analytical methods,[17] and the results are listed in Table 2. When cornstalk and corncob were used as feedstocks over the most promising catalyst 2Ni·3Cu·5ZnO, efficient conversion of the substrates with target products was demonstrated (Table 1, Entries 13 and 14). The higher conversion could be explained by the lower degree of cellulose crystallization (Figure 3 and Table 2) compared to the Avicel microcrystalline cellulose (CrI = 83%), which was justified by almost complete conversion of ball-milled cellulose with a CrI of 18% (Table 1, Entry 9). A higher selectivity to 1,2-PDO and EG was observed in the conversion of corncob than cornstalk, which could be ascribed to the higher content of pentoses than those in cornstalk.

Finally, the durability of 2Ni·3Cu·5ZnO was investigated in recycling tests with ball-milled cellulose as substrate. After each run, the used catalyst was separated by centrifugation and washed with deionized water and used in the next run. Similar conversions (based on fresh cellulose) of ball-milled cellulose were achieved in the next three runs with a slight reduction in the 1,2-alkanediol selectivity (Table 1, Entries 15–17). The XRD patterns of the used catalyst showed that no obvious changes were observed (Figure S1).[16] ICP-AES analysis of the resultant liquid showed that negligible amount of Ni and Cu was leached in the liquid. When the leaching liquid (catalyst treated with water without substrate) was used to convert cellulose, the resultant solution was brown and a total 1,2-alkanediol selectivity
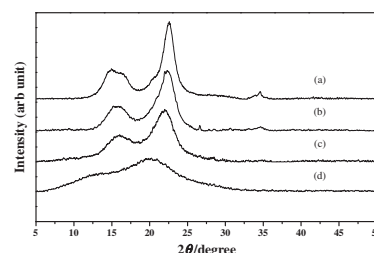

Figure 3. Powder X-ray diffraction patterns the substrates: (a) micro-crystalline cellulose (Avicel® PH-101NF), (b) cornstalk, (c) corncob, and (d) ball-milled cellulose (Avicel® PH-101NF).

of only 1.3% was obtained at 40% cellulose conversion, suggesting that the leaching was only partially responsible for the loss of catalytic activity. The products possessing chelating groups may be another factor which can facilitate leaching and poisoning, thus leading to the loss of catalyst activity.[3]

In summary, ZnO-supported Ni–Cu catalysts were successfully applied to the hydrogenolysis of cellulose and real biomass substrates (cornstalk and corncob) with 1,2-alkanediols as major products under hydrothermal conditions. The activity, selectivity, and product distribution depended strongly on the mole ratio of Ni and Cu, which played synergetic roles for the formation of 1,2-alkanediols during the reaction. Further work is under way to design more active catalysts for rational control of product distribution.

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