Efficient conversion of microcrystalline cellulose to 1,2-alkanediols over supported Ni catalysts

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High yield of 1,2-alkanediols (70.4%) can be produced via one-pot catalytic hydrogenolysis of high-crystalline cellulose over Ni/ZnO catalysts.
Efficient conversion of microcrystalline cellulose to 1,2-alkanediols over supported Ni catalysts†

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Nickel supported on a variety of supports was evaluated in the batchwise hydrogenolysis of high-crystalline cellulose under hydrothermal conditions. The supports examined included Al2O3, kieselguhr, TiO2, SiO2, activated carbon (AC), ZnO, ZrO2 and MgO. All tested catalysts can effectively convert cellulose while the choice of supports plays a critical role in the product distribution and selectivity. The Ni catalysts favour the formation of industrially attractive 1,2-alkanediols such as 1,2-propanediol, ethylene glycol, 1,2-butanediol and 1,2-hexanediol. It was found that the bifunctional ZnO-supported Ni catalysts displayed superior activities and the best result was obtained on 20% Ni/ZnO which exhibited complete conversion of cellulose with up to 70.4% total glycol yields. Mechanism of the reaction involved was tentatively proposed by identifying the products formed.

1 Introduction

1,2-alkanediols with carbon numbers in the range of 2 to 6, such as ethylene glycol (EG), 1,2-propanediol (1,2-PD), and 1,2-butanediol (1,2-BD) are widely used as starting monomers for the production of polyesters, polyethers and polyurethanes. Currently, 1,2-alkanediols are mainly produced from petroleum-derived feedstocks via controlled functionalization of hydrocarbons.1 For example, EG and 1,2-PD are industrially produced by the selective epoxidation of olefins followed by catalytic hydration. However, due to the diminishing fossil fuel reservoirs together with the ever-deteriorating environment associated with the worldwide fossil-fuel-based industry, it is imperative to make use of alternative feedstocks for the production of chemicals and fuels.1,5 Cellulose, the most abundant non-food biomass resource on earth, presents a promising substitute for fossil fuel resources for the sustainable production of commodity chemicals and fuels which holds the possibility for carbon neutral technologies.5,8 More specifically, compared with traditional hydrocarbon feedstocks, cellulose is comprised of carbohydrate monomer which is rich in oxygen (~49.3%) and thus desirable to be converted into oxygenated chemicals. Hydrogenolysis of cellulose resulting in C-C and C-O cleavage is a promising pathway for the direct transformation of cellulose biomass into value-added chemicals and therewith, an entry point for future bio-refinery concepts. However, due to the robust crystalline structure of cellulose,9,10 it generally needs to be transformed into glucose via enzymatic hydrolysis or homogeneous acidic hydrolysis for further utilization. Unfortunately, cellulose is quite expensive and can hardly be reused; the use of homogeneous acid, on the other hand, often suffers from serious drawbacks of low selectivity, separation of products, corrosion and disposal of a large amount of neutralization waste.9 Recently, extensive attention was paid to the direct conversion of cellulose to polyols and glycols over heterogeneous catalyst in hot-compressed water (Table S1).9,15 Fukuoka and Dhepe were pioneers to report that cellulose can be directly converted into hexitols over a bifunctional Pt/Al2O3 catalyst at 463 K under H2, but the yield of hexitols was only around 30% after 24 h with sorbitol as the main product.9 Liu et al. successfully improved the transformation efficiency by conducting the reaction at an elevated temperature to make use of H2 released by high temperature water to promote the hydrolysis of cellulose, and they obtained a hexitols yield of 39.3% using Ru/C as the hydrogenation catalyst.15 Zhang and co-workers developed a series of tungstenic catalysts including Ni–W2O3/AC, WC/MC, and Ni-W/SBA-15, which can effectively catalyze cellulose conversion into ethylene glycol (EG) with a yield of as high as 76%.13,16,17 However, in all cases, a significantly large proportion (typically 15-40 %) of tungsten carbide or expensive support such as mesoporous carbon (MC) or mesoporous silica (SBA-15) in their catalysts is inevitable for high glycol yields.

Most notably, supported Ni catalysts investigated in such
studies consistently exhibited poor performances towards the production of polyols, though non-noble Ni is generally considered as an efficient hydrogenation and hydrolysis catalyst. However, Vyver et al. successfully converted ball-milled cellulose to sugar alcohols with a yield of 56.5% over reshaped Ni particles at the tip of carbon nanofibers, and the selectivity of polyols with lower carbon chain was still poor. Comparatively few investigations on catalytic hydrogenolysis of cellulose were designed to produce C2–C3 polyols, which is the target of this work.

Herein we report the first observation that cheap and easily available supported Ni catalysts can effectively catalyze the conversion of high-crystalline cellulose into polyols, especially into 1,2-alkanediols with carbon number in the range of 2 to 6. The products can be widely used in antifreezes, cosmetics, drugs and as starting materials in esterification and etherification reactions, especially in unsaturated polyester resin (UPR) manufacture. When used in producing UPR, the monomeric polyols mixture acquired via this route can be used directly without further separation. Therefore, the production of 1,2-alkanediols from cellulose would be industrially important and reduce the dependence on petroleum.

Experimental
Materials
(1) Microcrystalline cellulose (Shanghai Chineway Pharm. Tech. Co., Ltd, Avicel® PH-101NF) were dried under vacuum at 378 K for 12 h before use.
(2) TiO₂ (P-25, Degussa, S BET = 55 m²·g⁻¹), SiO₂ (Qingdao Haiyang Chemical Co., Ltd, 80-120 mesh, S BET = 346 m²·g⁻¹), activated carbon (denoted as AC, Norit SX Ultra, S BET = 1300 m²·g⁻¹), γ-Al₂O₃ (Chinalco, S BET = 500 m²·g⁻¹), kieselguhr (Guangfu-chem, S BET = 31 m²·g⁻¹), MgO (Sinopharm Chemical Reagent Co., Ltd, S BET = 120 m²·g⁻¹) were dried at 393 K for 24 h before use. The high surface area zirconia (ZrO₂, S BET = 225 m²·g⁻¹) was prepared by the hydrolysis of zirconium chloride as reported by G.K. Chuaah et al.
(3) All the other chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd, and used as received.

Catalyst preparation
Preparation of Ni/ZnO: Nickel zinc hydroxycarbonate precursors were prepared by coprecipitation of a mixed solution of Ni(NO₃)₂·6H₂O and Zn(NO₃)₂·6H₂O with a solution of Na₂CO₃ under vigorous stirring at 343 K and a pH of 8.0 according to the preparation of Cu/ZnO. In detail, coprecipitation was performed in a reaction container filled with 400 mL of deionized water (343 K) by simultaneous mixing of an aqueous solution of metal nitrates (Ni(NO₃)₂·6H₂O and Zn(NO₃)₂·6H₂O, 1 M metal nitrate solution) with Na₂CO₃ (1.2 M) at constant pH (pH = 8). The nitrate solution was added at a constant rate of 25 mL·min⁻¹. The addition rate of the precipitation reagent (Na₂CO₃) was controlled to adjust the desired pH in the mother liquor which was monitored by measuring the pH value (Sartorius PB-10, Germany). After complete addition of the solutions, the resulting precipitates were aged under continuous stirring in the mother liquor at 353 K for 3 h. The suspensions were poured out of the reactor followed by separation of the precipitates from the mother liquor by vacuum filtration. The resulting filter cake was washed thoroughly with deionized water. Finally, the washed precipitate were dried at 393 K for 12 h, followed by calcination at 673 K in static air for 4 h (5 K·min⁻¹). Reduction of the catalysts were performed in pure H₂ atmosphere at 773 K at a heat ramp rate of 5 K·min⁻¹, followed by an isothermal period of 5 h at the final temperature. Prior to exposure to air, the catalysts were passivated by purging reactor with 1% O₂/N₂ for 5 h at room temperature. Ni/ZnO was also prepared using incipient wetness impregnation method (denoted as Ni/ZnO-IM), while the support ZnO was prepared according the preparation of nickel zinc hydroxycarbonate precursors described above.

Ni/Al₂O₃, Ni/SiO₂, Ni/Kieselguhr, Ni/AC, Ni/ZrO₂, and Ni/MgO were prepared by incipient wetness impregnation using nickel nitrate as the precursor. The impregnation volume of metal solution was calculated using the measured incipient wetness of the support. Impregnation solutions were added dropwise and the supports were shaken thoroughly at about each 10% addition interval. After the addition, the vessel was capped for 12 h at room temperature after which the catalysts were dried at 393 K, calcined at 673 K for 4 h and then reduced at 773 K (1023 K for 20% Ni/Al₂O₃) in a pure H₂ flow for 5 h. The catalysts are generally labeled as x%Ni/support, in which x stands for the nominal weight loading of Ni.

Catalytic experiments
A general procedure to conduct the cellulose conversion is the same as reported before. All catalytic experiments were carried out in a batch system using a 100 mL stainless-steel autoclave. After 0.15 g catalyst, 0.5 g cellulose and 50 mL water were loaded, the reactor was purged four times with hydrogen to remove air, pressurized to 6 MPa hydrogen pressure at room temperature and finally programmed to 518 K for 2 h at a stirring speed of 800 RPM.

Product analysis
Samples were filtered through 0.22-µm-pore-size filters (Membrana) prior to analysis. The products in resultant solutions after reaction were identified by gas chromatograph (GC; 7890A, Agilent, USA) coupled with a mass spectrometer (MS, 5975C, Agilent, USA). The gas chromatogram-mass spectrometer (GC-MS) was equipped with a HP-INNOWax column (30 m × 0.25 mm; film thickness, 0.25 µm). The temperature of injection was at 250 °C. Argon was used as the carrier gas, and its flow rate was 0.3 mL·min⁻¹. The injection volume was 1 µL and the split ratio was 30:1. The temperature program for the column was held at 80 °C for 10 min and programmed to 220 °C at a ramping rate of 2 °C·min⁻¹ with a hold time of 30 min. The peaks are matched according to NIST database. For a better understanding of the intermediates in the hydrolysis of cellulose, sample with incomplete conversion (1 g cellulose; 0.15 g 20% Ni/ZnO; H₂O, 50 mL; temperature, 518 K; H₂ pressure, 6 MPa at room temperature; 800 RPM; reaction time 0.5 h) was analyzed on a Bruker maXis UHR-TOF (ultrahigh resolution time-of-flight) mass spectrometer (MS) (Bruker Daltonics Inc., Billerica, MA) with a electrospray source (ESI) in negative-ion mode through direct injection method via a syringe pump. Instrument settings were: capillary voltage: 2,800 V, dry gas: 4 L/min, dry gas temperature 180 °C, nebulizer gas: 0.3 bar, ion acquisition range:
m/z 50-1,500. The ion cooler parameters, including ion cooler RF, transfer time and prepulps storage, were changed accordingly to obtain idea sensitivity and responsiveness to molecules with a wide range of m/z value. Mass spectra data were submitted to ESI.

Compass (version 1.3, Data Analysis version 4.0) for molecular formula analysis.

Products were quantified by both gas chromatograph (GC) and ion chromatograph (IC). Diols were determined using a Varian 450-GC, equipped with a flame ionization detector (FID) and Galaxy workstation. The samples were injected (split ratio: 30) into a CP-Wax 58 (FFAP) column (Chrompack) of 25 m × 0.25 mm and 0.2 µm film thickness. The temperature program was from 60 °C (2 min) to 250 °C (8 min) at a rate of 20 °C min⁻¹. Injector and detector temperatures were 250 °C and 280 °C respectively. The carrier gas used was N₂ at 1 mL-min⁻¹. The FID used hydrogen at 30 mL-min⁻¹. The makeup gas was nitrogen at 29 mL-min⁻¹. Other products like glucose, sugar alcohols were determined by High-Performance Anion-Exchange Chromatography (IC, Dionex ICS-3000) with Pulsed Amperometric Detection (HPAEC-PAD, gold electrode detector, Dionex). The separation was carried out on a Dionex CarboPac MA1 column (4 × 250 mm) with a CarboPac MA1 guard column (4 × 50 mm) at 30 °C. The eluent flow rate was 0.4 mL·min⁻¹, eluted with a 500 mmol NaOH solution. Instrumental controls, data acquisition, and chromatographic integration were performed using Dionex Chromelone software.

The conversions of cellulose were calculated by the weight variation before and after the reaction and also verified based on total organic carbons (TOC) data obtained by a liquiTOC II analyzer (Elementar Analysensysteme Hanau, Germany) using the equation: Conversion_TOC = (moles of total organic carbon in the resultant liquid)/(moles of carbon in cellulose charged into the reactor determined by a CHNS analyzer)×100%. Since the TOC conversion was very close to weight conversion (the difference smaller than 3%) implying that only a small amount of carbon-containing gas generated, the gas products were not analyzed in our study. The yield of polyols was calculated based on carbon balance (Appendix in ESI). The qualitative results showed that the solid residue was readily filtered out and dried at 333 K to calculate the conversion of cellulose.

Characterization

The X-ray powder diffraction (XRD) patterns of cellulose and catalysts were obtained with a Bruker D8 Advance X-ray powder diffraction meter under Ni-filtered Cu-Kα radiation. N₂ adsorption-desorption experiments were performed with a Micromeritics ASAP 2020 surface area and porosity analyzer. NH₃-TPD, CO₂-TPD and H₂-TPR experiments were performed with a Micromeritics Autochem II chemisorption analyzer. ICP experiments were carried out on a Thermo IRIS Intrepid II XSP atomic emission spectrometer to determine chemical composition of catalysts and metal leaching after reaction.

Results and discussion

The substrate used in this study was Avicel® PH-101 microcrystalline cellulose and the crystallinity index (CrI) was estimated by XRD analysis according to the empirical method developed by Segal and coworkers using the following equation:

\[
\text{CrI} = \frac{I_{002} - I_{amorph}}{I_{002}} \times 100
\]

where \(I_{002}\) is the maximum intensity of the (002) lattice diffraction and \(I_{amorph}\) is the intensity diffraction at 18-20 degrees. The XRD peak height method is the most widely used method to determine CrI, which allows rapid comparison of cellulose samples. XRD patterns of fresh cellulose, cellulose reacted with/without a catalyst under the studied conditions were shown in Fig. 1. The CrI of the fresh cellulose was as high as 83%, and the treatment of cellulose under hydrothermal conditions with/without a catalyst for 30 min at 518 K did not change the crystal structure of cellulose according to the XRD patterns. The CrI of the samples treated without a catalyst and with 20% Ni/ZnO were 84% and 86%, respectively, showing only a slight increase in the CrI. This indicated that the cellulose was very stable under investigated conditions and the reaction took place at the crystal surface. After reaction, the cellulose residue settled to the bottom of the reactor, and maintained powder form and the solid residue was readily filtered out and dried at 333 K to calculate the conversion of cellulose.

Under the investigated conditions, the product distribution is very complex according to the qualitative analysis by the GC-MS, IC analysis (Fig. S1 and Fig. S2 in ESI) and electrospray ionization mass information acquired from the UHR-TOF analysis (Appendix in ESI). The qualitative results showed that the degradation products included methanol, i-propanol, ethanol, n-propanol, n-butanol, 1,2-propanediol (1,2-PD), ethylene glycol (EG), 1,3-propanediol (1,3-PD), 1,2-butanediol (1,2-BD), 1,2-hexanediol (1,2-HD), glycerol, erythritol, sorbitol, mannitol, glucose and some other unsaturated and/or deoxidation products as a result of dehydroxylation reaction and C–C bond breakage. A set of typical GC and IC spectra of cellulose degradation products was shown in Fig. S2 (see ESI), suggesting that the quantitative analysis procedure combining GC and IC was an effective way to separate the products. The identification with UHR-TOF demonstrated nearly all the intermediates during the transformation of cellulose (Fig. S4 and Appendix in ESI). The result showed that molecular weight of the products was mostly within 400, suggesting disaccharide and monosaccharide were formed dominantly as the incipient degradation intermediates by

![Fig. 1 Powder X-ray diffraction pattern of microcrystalline cellulose (Avicel® PH-101NF) (a) fresh cellulose, (b) cellulose treated without a catalyst for 30 min, (c) cellulose reacted with 20% Ni/ZnO for 30 min.](image)
hydrolysis of glucosidic bond at the terminal group. Almost all the products had a carbon number less than 30, indicating that only oligosaccharides with no more than five monomers were formed in the course of in-situ H\textsuperscript{+} catalyzed hydrolysis. Furthermore, a large amount of unsaturated products containing \(\text{C}=\text{O}\) and \(\text{C}≡\text{O}\) bonds, were identified by UHR-TOF analysis which were also verified by Fehling’s and KMnO\textsubscript{4} solutions.

The results of cellulose conversion and yields of the major products which included 1,2-PD, EG, 1,3-PD, 1,2-BD, 1,2-HD, were summarized in Table 1. The undesired minor byproducts were not quantified in this work. The yields were calculated based on carbon, which gave a clear and balanced definition of the selectivity towards different products. The concept carbon efficiency (CE), defined as the ratio of all the carbon in the 1,2-alkanediols and other products summarized in Table 1 to that in the substrate, was introduced to assess the atom economy of the reaction.

The conversion of cellulose without any catalyst was as high as 68\% (Table S2, entry 24) under the studied condition, giving a brown solution, which darkened in colour as a result of exposure in air after sampling. This confirmed the hydrolysis of cellulose into oligosaccharides catalyzed by in-situ produced H\textsuperscript{+} ions\textsuperscript{12,19}. The introduction of the Ni catalysts greatly enhanced the conversion of cellulose and colourless solutions could be obtained when a certain catalyst was charged into the reactor (Fig. S3). Among the catalysts investigated, the Ni/ZnO catalysts were observably more effective and selective in producing 1,2-alkanediols, giving markedly higher yield of 1,2-alkanediols compared with other catalysts in this work. After 2 h at 518 K and 6 MPa H\textsubscript{2}, 15\% Ni/ZnO catalyst gave a 94\% conversion of cellulose with a total glycol yield of 51.0\% and the CE equaled 69.0\% (entry 1). Within the fraction of 1,2-alkanediols, 1,2-PD (23.6\%) and EG (16.7\%) are the main products, followed by 1,2-BD (7.4\%), 1,2-HD (2.4\%), and 1,3-PD (0.9\%) being analyzed most abundantly. This unoptimized system already offered glycol yields superior to the combined homogenous acid and noble metal catalysed hydrogenolysis of cellulose.\textsuperscript{11} Except for these glycols, other polyols including glycerol, erythritol, sorbitol, mannitol and glucose, which could be considered as the precursors for glycols, reached a total yield of 16.8\%. When the metal loading was increased to 20\%, the cellulose charged was completely converted with a CE of 84.5\% and the yields of 1,2-PD, EG, 1,2-BD, 1,3-PD, 1,2-HD were 34.4\%, 19.1\%, 10.1\%, 2.1\% and 4.7\%, respectively, amounting to a total glycol yield of 70.4\% (entry 2). To the best of our knowledge, this is the highest glycol yield obtained to date over Ni catalysts. All these products are commercially value-added ch-
emicals originated from petroleum nowadays. Further increasing in the metal loading to 30% led to only a slight decline in selectivity towards 1,2-PD and when the metal loading was increased to 40%, the conversion of cellulose was decreased to 90.0% and the yield towards diols drastically dropped to 44.9%. The Ni particle size slightly increased as a result of increase in metal loading according to the XRD patterns (Fig. 2, Table 2). The mean diameters of Ni particles of 15% Ni/ZnO, 20% Ni/ZnO, 30% Ni/ZnO, and 40% Ni/ZnO were 14 nm, 15 nm, 17 nm, and 18 nm respectively, calculated by the Scherrer’s equation. TEM study of the catalysts was also conducted (Fig. S5), but it is very difficult to distinguish Ni particle from ZnO support as a result of similar contrast between Ni and Zn. The NH3-TPD (Fig. 3 left) and CO2-TPD (Fig. 3 right) characterization showed that Ni/ZnO catalysts had both acidic and basic sites on the surface and both acidity and basicity changed as a result of metal loadings. Ni/ZnO with amphoteric nature, possibly played multifunctional roles in the transformation of cellulose, where ZnO is active for dehydration step and nickel is a hydrogenation active species. The dehydration catalyzed by ZnO is critical in the formation of intermediates from cellulose, which are precursors of glycols, and thus determined the overall conversion of cellulose. This is also the case in the hydrogenolysis of sorbitol and glycerol for the production of glycols. The decrease in conversion at higher Ni content might be due to the insufficient amount of surface active ZnO indicated by the lower BET surface area and less acidic and basic sites in the TPD profiles. Nitrogen adsorption studies on Ni/ZnO catalysts showed that the surface area decreased as a result of increase in metal loading (Table 2), which possibly led to less surface active ZnO sites (Fig. 3) together with worse dispersion of Ni, leading to a slightly increase in the Ni size according to the XRD patterns. In addition, more nickel would lead to more cracking products such as monoalcohols. 

The mean diameters of Ni particles of 15% Ni/ZnO, 20% Ni/ZnO, 30% Ni/ZnO, and 40% Ni/ZnO were 14 nm, 15 nm, 17 nm, and 18 nm respectively, calculated by the Scherrer’s equation. TEM study of the catalysts was also conducted (Fig. S5), but it is very difficult to distinguish Ni particle from ZnO support as a result of similar contrast between Ni and Zn. The NH3-TPD (Fig. 3 left) and CO2-TPD (Fig. 3 right) characterization showed that Ni/ZnO catalysts had both acidic and basic sites on the surface and both acidity and basicity changed as a result of metal loadings. Ni/ZnO with amphoteric nature, possibly played multifunctional roles in the transformation of cellulose, where ZnO is active for dehydration step and nickel is a hydrogenation active species. The dehydration catalyzed by ZnO is critical in the formation of intermediates from cellulose, which are precursors of glycols, and thus determined the overall conversion of cellulose. This is also the case in the hydrogenolysis of sorbitol and glycerol for the production of glycols. The decrease in conversion at higher Ni content might be due to the insufficient amount of surface active ZnO indicated by the lower BET surface area and less acidic and basic sites in the TPD profiles. Nitrogen adsorption studies on Ni/ZnO catalysts showed that the surface area decreased as a result of increase in metal loading (Table 2), which possibly led to less surface active ZnO sites (Fig. 3) together with worse dispersion of Ni, leading to a slightly increase in the Ni size according to the XRD patterns. In addition, more nickel would lead to more cracking products such as monoalcohols.

### Table 2 Nitrogen adsorption studies on Ni/ZnO catalysts

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<th>Catalyst</th>
<th>S&lt;sub&gt;BET&lt;/sub&gt;&lt;sup&gt;a&lt;/sup&gt; (m&lt;sup&gt;2&lt;/sup&gt;·g&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>Pore volume (cm&lt;sup&gt;3&lt;/sup&gt;·g&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>Average Pore diameter (nm)</th>
<th>Ni crystallite size&lt;sup&gt;b&lt;/sup&gt; (nm)</th>
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<td>15% Ni/ZnO</td>
<td>22.2</td>
<td>0.14</td>
<td>27.4</td>
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<tr>
<td>20% Ni/ZnO</td>
<td>21.3</td>
<td>0.14</td>
<td>26.5</td>
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<tr>
<td>30% Ni/ZnO</td>
<td>18.2</td>
<td>0.13</td>
<td>25.9</td>
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<tr>
<td>40% Ni/ZnO</td>
<td>16.2</td>
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<td>18</td>
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<tr>
<td>20% Ni/ZnO-IM</td>
<td>12.1</td>
<td>0.13</td>
<td>18.0</td>
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<sup>a</sup> BET method;  <sup>b</sup>Determined by XRD characterization

Further reaction led to a decline in glycol yield. The product distributions changed with time, even at complete conversions, indicating that the polyols underwent further degradation. The conversion of cellulose at different reaction time showed that 2 h was enough to gain excellent performance over 20% Ni/ZnO. As comparison, 20% Ni/ZnO was also prepared using incipient wetness impregnation method, while the support ZnO was prepared according the preparation of nickel zinc hydroxycarbonate precursors. The activity of 20% Ni/ZnO prepared by impregnation method (labeled as 20% Ni/ZnO-IM) was comparable to that of 15% Ni/ZnO prepared using coprecipitation method, with 96% conversion of cellulose and a total glycol yield of 47.1% (Table 1, entry 5), which was poorer than the 20% Ni/ZnO catalysts, but still much better than the other catalysts in our study. H2-TPR analysis showed that 20% Ni/ZnO-IM seemed to be easier to get reduced as shown in Fig. S5 (see ESI), and the Ni crystallite size of Ni/ZnO-IM was about 23 nm, much larger than that of Ni/ZnO. The BET surface area of 20% Ni/ZnO-IM (12.2 m<sup>2</sup>·g<sup>-1</sup>) was much lower than that of 20% Ni/ZnO (21.3 m<sup>2</sup>·g<sup>-1</sup>), suggesting a worse nickel dispersion on ZnO support prepared via impregnation method thus leading to lower glycol yields. Furthermore, the acidity and basicity of Ni/ZnO prepared via incipient wetness impregnation method were much lower that the counterpart 20% Ni/ZnO prepared via coprecipitation.

Our study showed a remarkably different product distribution...
with a higher selectivity for 1,2-PD, 1,2-BD, and 1,2-HD compared to the previous work, indicating Ni is less active in C-C bond breaking than W based catalysts, but more active than Pt (entries 13, 14), and Ru in C-C bond cleavage under the conditions studied. Ni is active in both C-C and C-O bond cleavage, giving complex mixtures containing significant amounts of partially deoxygenated products and light polyols such as 1,2-PD, 1,2-BD and 1,2-HD.

With the same metal loading of 20%, for Ni catalysts supported on various supports, including Al₂O₃, kieselguhr, TiO₂, SiO₂, AC, ZrO₂, and MgO, the catalytic performances were quite different from the Ni/ZnO catalyst. The conversions of cellulose over all the catalysts for 2 h were nearly 100% except for 83% conversion on 20% Ni/ZrO₂, while the selectivity towards glycols differed greatly. Ni supported on ZrO₂ exhibited superior glycol selectivity than on TiO₂, Al₂O₃ and kieselguhr, and all these catalysts showed different product distributions compared to 20% Ni/ZnO. The yield ratio of 1,2-PD to EG was about 1.8 over 20% Ni/ZnO whereas this value was almost 1 over the other catalysts. Only very small amounts of target products were formed with yields of 8.3% and 11.1% respectively when using SiO₂ and AC as carriers. When combinations of supported Ni catalysts (Ni/Al₂O₃, Ni/Kieselguhr, Ni/ZrO₂) and ZnO were used to convert the cellulose (Table S2, entries 20-22, see ESI), the glycols yield gained slight increase compared with when no ZnO was added, confirming the ZnO role described previously. These results strongly suggested that the nature of the supports significantly influenced the catalytic performance of the Ni catalysts in the conversion of cellulose. Liu et al. attributed surface acid-basicities of supports to their different dehydrogenation/hydrogenation activities which consequently influenced the xylitol reaction pathways catalyzed by supported Ru catalysts. However, in our study, the apparent acidity of the supported Ni catalysts, as indicated by the NH₃-TPD test (See Fig. 5), did not directly correspond to the catalytic activity under investigated condition, and this is in consistence with Fukuoka’s work. The acidic sites on the support surface may not play a critical role under the reaction conditions. However, the basic sites of the supports seem to be critical for the activity and selectivity of the catalysts. The strong basic sites of Ni/ZnO observed from the CO₂-TPD (located at 650 K) may contributed to the excellent activity in the transformation of cellulose. The catalysts were also characterized by using H₂-TPR (H₂ TPR profiles in Fig. S7), and it was shown that the reducibility of the metal precursor species and the catalytic properties of the reduced material depended strongly on the nature of the support and the preparation procedure. However, it was difficult to correlate the reducibility to the catalytic activity under investigated condition. Besides the strong surface basic sites, what else affects the catalytic performance of the Ni catalysts in this study needs further investigation. Precious metal catalysts, 5% Pt/AC and 5% Pt/Al₂O₃ were also used for the reaction, but the glycol yields were very low and the carbon efficiency was much lower than the supported Ni catalysts (entries 13, 14).

In the absence of any catalysts, a large quantity of 5-hydroxymethylfurfural (HMF), a product of the facile acid catalyzed dehydration of hexoses, was formed in the hydrothermal treatment of cellulose and glucose. The formation of HMF can be attributed to the acidic role of subcritical water rather than the autocatalysis by acidic product formed.

The conversion of glucose, the monomer unit in cellulose,
under the same reaction condition over 20% Ni/ZnO (entry 15) gave much lower glycol yield (44.8% with CE of 56.6%) than those of cellulose, with HMF, levulinic acid, lactic acid and other deoxygenated products obtained according to GC-MS analysis. The isomerisation and dehydration catalysed by reversely formed H+ were possibly the key steps to obtain HMF (Scheme 1), and there was a rate-mating between in-situ H+ catalyzed hydrolysis and Ni/ZnO catalyzed hydrogenolysis in the conversion of cellulose, with the hydrolysis being the rate-determining step. In agreement with previous reports carried out on heterogeneous catalysts,3,15 hydrolysis of cellulose was a slow process and the glucose could be instantaneous hydrogenated. When cellulose was used, the small amount of glucose slowly generated by proton-catalyzed hydrolysis of the glycosidic bonds, would be readily converted into hexitols and glycols under hydrogenolysis. However, when the leaching liquid was used to convert cellulose, the resultant solution was brown, similar with that no catalyst existed. After the second run, the metal leaching was significantly less than the first run; ~3% for Ni, ~2% for ZnO over the second run (Table S1, entry 23, see ESI). This suggested that the leaching of the catalysts was only partially responsible for loss in the catalytic activity and the conversion of cellulose to 1,2-alkanediols as a critical heterogeneous catalysis. The XRD patterns of the used catalyst (Fig. 4) showed that the catalyst retained its original form without significant changes. In Ni catalyzed hydrogenation, poisoning of the catalyst by organic fragments produced by side cracking reactions would be another reason for the deactivation.34 The intermediate components during reaction such as organic acids possess strongly chelating groups, which can facilitate leaching and poisoning of the catalytically active phases.4

Conclusions

In summary, we have demonstrated that simple supported Ni catalysts allow the high-yield production of industrially attractive 1,2-alkanediols from microcrystalline cellulose under H2 in hot-compressed water via combined steps involving hydrolysis, hydrogenation and hydrogenolysis. All Ni catalysts investigated could effectively catalyze the one-pot conversion of microcrystalline cellulose and the supports played a critical role in the product distribution and selectivity. The best result was obtained by using 20% Ni/ZnO as the catalyst, with complete cellulose conversion and remarkable glycol yield of 70.4%, which is the highest value obtained so far on supported Ni catalysts. The relatively poor hydrothermal stability of the Ni/ZnO catalyst partially responsible for the decrease in the repeated runs. Further research is undergoing to improve the selectivity and stability of current catalysts, and to achieve the rational design of catalysts for the direct conversion of carbohydrates to the desired diol/polyol products.

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Notes and references