J|A|C|S
COMMUNICATIONS

# One-Step Conversion of Cellobiose to $C_6$-Alcohols Using a Ruthenium Nanocluster Catalyst

Ning Yan,[†] Chen Zhao,[†] Chen Luo,[†] Paul J. Dyson,[‡] Haichao Liu,*[,†] and Yuan Kou*[,†]

*PKU Green Chemistry Center, Beijing National Laboratory for Molecular Sciences, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China, and The Institut des Sciences et Ingénierie Chimiques, Ecole Polytechnique, Fédérale de Lausanne, EPFL-BCH, CH-1015 Lausanne, Switzerland*

Received April 10, 2006; E-mail: yuankou@pku.edu.cn

The one-step conversion of cellulose to $C_6$-alcohols via green and energy efficient approaches has, as far as we are aware, not been reported. Such a process presents a considerable challenge, the two key problems being (1) finding a suitable solvent that dissolves the cellulose, and (2) the development of advanced catalytic chemistry for selective cleavage of the C−O−C bonds (glycosidic bonds) connecting glucose residues. The dissolution of cellulose has been recently realized by using ionic liquids as green solvents;[1] there is still no efficient method, such as selective hydrogenation, for the precise C−O−C cleavage under mild conditions, however. Cellobiose is a glucose dimer connected by a glycosidic bond and represents the simplest model molecule for cellulose. We disclose in this communication that the one-step conversion of cellobiose to $C_6$-alcohols can be realized by selectively breaking the C−O−C bonds via selective hydrogenation using a water-soluble ruthenium nanocluster catalyst under 40 bar $H_2$ pressure.

Sorbitol and glycerin, dideoxyhexitol, and trideoxyhexitol are under consideration as a new generation green energy platform, instead of syngas, to produce bio-fuels,[2,3] chemicals, and hydrogen.[4,5] Sorbitol is generally obtained via a two-step process, that is, hydrolysis of cellulose in acidic water and then by further hydrogenation. The process, especially hydrolysis under acidic conditions, is not energy efficient and also not as green as desired.[6,7] Direct conversion of cellulose requires the cleavage of two C−O−C bonds, one being the 1,4-$\beta$-glucoside bond connecting two adjacent glucose monomers and the other being contained in the glucose ring. It can be seen from Figure 1 that the cleavage of the 1,4-$\beta$-glycosidic bond may result in two different products: dehydrate-sorbitol when breaking the $C_1$−O bond (position **a**), and dehydroxy-glucose following cleavage of the other (position **b**).

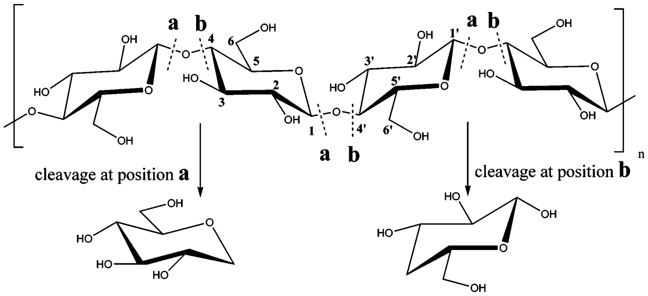


***Figure 1.*** Cellulose structure and the potential monomers formed following cleavage of the C−O−C bonds at position **a** or **b**.

To facilitate the discovery of a suitable catalyst, cellobiose was chosen as a model substrate, and four transition metals, Ru, Rh, Pd, and Pt, were examined. Metal nanoparticles were prepared by reduction of the appropriate metal salts in the presence of poly(*N*-vinyl-2-pyrrolidone) (PVP) in refluxing ethanol−water solution.[8−11] A typical micrograph of the ruthenium nanoparticles is shown in Figure 2. A narrow unimodal size distribution with a diameter of 2.4 ± 0.4 nm is observed. Rh, Pd, and Pt nanoparticles were found to have similar diameters of about 3 nm under related conditions.[11] The hydrogenation reactions were carried out in a Parr autoclave at 120 °C and 4 MPa $H_2$, and the products were analyzed by gas chromatography (GC), high-performance liquid chromatography (HPLC), and electrospray ionization mass spectroscopy (ESI-MS). Among them (Table 1, entries 1−4), Pd nanoparticles showed no activity, due perhaps to their instability under the reaction conditions (120 °C, 40 bar $H_2$). Pd black deposits were observed together with a colorless solution at the end of the reaction. Pt and Rh both exhibited good activities in the reaction, but the selectivities were poor. Ru was the only metal that exhibited high stability under the conditions (a temperature of 120 °C and a hydrogen pressure of 40 bar) and gave high activity and selectivity; that is, the cellobiose was quantitatively converted to $C_6$-alcohols.

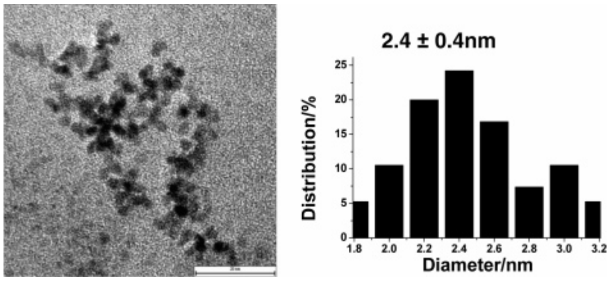


***Figure 2.*** TEM micrographs and particle histograms of polymer-stabilized ruthenium nanoparticles isolated from water (200 particles counted for the sample, scale bar = 20 nm).

It is interesting to note that our previous work has proved that Rh, Pd, and Pt nanoparticles prepared by the same method are all excellent catalysts for the hydrogenation of alkenes and arenes,[12] with the Ru nanoparticles being completely inactive.

To delineate to what extent that a two-step process, that is, hydrolysis followed by further hydrogenation, may occur, the influence of pH on the reaction was examined. Irrespective of the pH, no product with a carbon number less than six was detected by ESI-MS, and only trace amounts (<0.2 wt %) of small molecular weight alcohols, such as ethanol, were detected by GC, demonstrating the high specificity of the Ru nanoparticles in hydrogenation/hydrogenolysis of C−O−C bonds. Increasing the pH from 2 to 7 then to 10 resulted in an acceptable decrease in cellobiose conversion, but caused a dramatic change in product distribution (entries 4−6 in Table 1). Sorbitol was obtained quantitatively under acidic conditions (pH = 2), indicating the occurrence of a two-step process. At pH 7, 3-$\beta$-D-glucopyranosyl-D-glucitol (denoted

---

[†] Peking University.
[‡] Ecole Polytechnique.

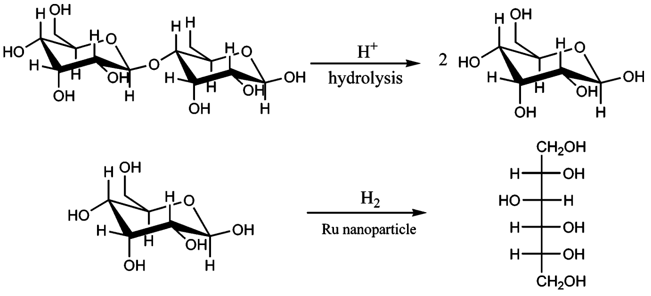
10.1021/ja062468t CCC: $33.50

***Table 1.*** Catalytic Hydrogenation of Cellobiose under Different Conditions

| | | | | Selectivity (%) | | | |
|---|---|---|---|---|---|---|---|
| entry | catalyst | pH | conv. (%) | sorbitol | glucose | A[d] | other polyols (mainly dideoxyhexitol) |
| 1[a] | Pd | 2 | 100 | 0 | 100 | 0 | |
| 2[a] | Rh | 2 | 100 | 6.9 | 66.9 | 0 | |
| 3[a] | Pt | 2 | 100 | 18.5 | 42.6 | 0 | |
| 4[a] | Ru | 2 | 100 | 100 | 0 | 0 | 0 |
| 5[a] | Ru | 7.0 | 87.8 | 26.4 | 1.6 | 64.8 | 7.2[c] |
| 6[a] | Ru | 10.0 | 75.6 | 24.0 | 3.2 | 55.7 | 17.1[c] |
| 7[b] | Ru/C | 7.0 | 100 | <1 | 0 | >99 | 0 |

[a] Reaction conditions: metal ($1.67 \times 10^{-3}$ mol/L); PVP: metal = 10 (mole ratio), temperature (120 °C), hydrogen pressure (40 bar), reaction time (12 h), cellobiose (7.31 mmol), using $H_2O$ (30 g) as solvent. [b] Reaction condition: the same as (a) except 0.1 g of 1% Ru/C was used as catalyst. [c] Due to the lack of standards, the data are obtained by subtracting the selectivity of glucose, sorbitol, and A from 100. The reliability of the data is ensured by the fact that no significant amount of other products (see Supporting Information for details) was detected in either the gas or liquid phases by IR and GC, and no other compounds in the liquid phase were found by ESI-MS except the ones listed in the table. [d] 3-β-D-Glucopyranosyl-D-glucitol.

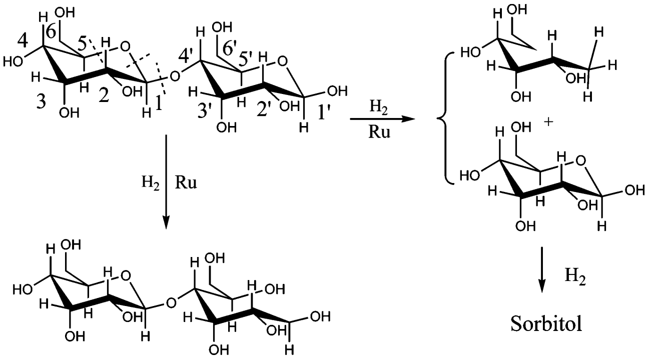
***Scheme 1.*** Proposed Reaction Mechanism under Acidic Conditions



as A in the Table), the corresponding sugar alcohol of cellobiose, is the main product (64.8% in a conversion of 87.8%) and the selectivity to sorbitol decreases to 26.4%. A small amount of glucose was also observed. ESI-MS and tandem MS analysis evidenced the appearance of dideoxyhexitol (7.2%). This very important “new” product was further observed in basic conditions. Under basic conditions (pH = 10), the selectivity to A and sorbitol slightly decreased to 79.7%, while that for the other $C_6$-alcohols (mainly dideoxyhexitol) increased from 7.2 to 17.1%, demonstrating the precise cleavage of the $C_1$−O in the glycosidic bond in cellobiose. On the basis of these findings, the reaction pathways depicted in Schemes 1 and 2 are proposed.

Scheme 1 shows the reaction pathways in acidic media. The mechanism involves $H^+$-promoted hydrolysis of glycosidic bonds, followed by catalytic hydrogenation of glucose to sorbitol. While in neutral and basic media (see Scheme 2), the situation is quite different. The product A is simply arising from a classic hydrogenation of the cellobiose. The presence of a new compound with a formula of $C_6H_{14}O_4$, which is a saturated tetraols (containing 4 OH groups) as demonstrated by MS analysis (see Supporting Information S2−S6 and corresponding analysis), and the absence of any compound with a formula of $C_6H_{14}O_5$ or $C_6H_{12}O_5$ are indicative of the removal of the oxygen atom in the $C_1$−O−$C_5$ bonds in combination with the cleavage of the $C_1$−O bond involved in the glycosidic bonds. Had the $C_{4'}$−O bond been broken, the principle products would have been 4-dehydroxy glucose ($C_6H_{12}O_5$) or 2-dehydroxy sorbitol ($C_6H_{14}O_5$). Thus, dideoxyhexitol and sorbitol are the final products; that is, the experimentally observed sorbitol observed at different pH originates from different reaction pathways, as explained by the schemes.

***Scheme 2.*** Proposed Reaction Mechanism under Neutral and Basic Conditions



Dispersed Ru nanoparticles, for example, supported on a surface, would reasonably expect to have a similar catalytic performance. Surprisingly, unlike that of the water-soluble Ru nanoparticles, active carbon-supported ruthenium catalyst (entry 7) shows no such catalytic activity under the same reaction conditions.

In conclusion, selective cleavage of C−O bonds leading to a novel catalytic hydrogenation reaction has been realized with a Ru nanocluster catalyst. A new approach, the one-step conversion of cellobiose to $C_6$-alcohols, can for the first time be achieved via precise cleavage of the glycosidic bonds. Preliminary investigations demonstrate that cellulose can also be converted to $C_6$-alcohols using the Ru nanocluster catalyst in [bmim]Cl ionic liquid, and while a conversion of 15% was observed, further experiments are in progress to improve the conversion. Nevertheless, the concept established in this work opens up a new opportunity for the transformation of cellulose to valuable chemicals, such as bio-fuels.

**Acknowledgment.** This work was financially supported by the National Science Foundation of China (Project Nos. 20533010, 20473002.).

**Supporting Information Available:** Synthesis of the ruthenium nanoparticles, and the procedures and experiment data for cellobiose hydrogenation reactions. This material is available free of charge via the Internet at http://pubs.acs.org.

## References

(1) Swatloski, R. P.; Spear, S. K.; Holbrey, J. D.; Rogers, R. D. *J. Am. Chem. Soc.* **2002**, *124*, 4974−4975.
(2) Huber, G. W.; Cortright, R. D.; Dumesic, J. A. *Angew. Chem., Int. Ed.* **2004**, *43*, 1549−1551.
(3) Huber, G. W.; Chheda, J. N.; Barrett, C. J.; Dumesic, J. A. *Science* **2005**, *308*, 1446−1450.
(4) Cortright, R. D.; Davda, R. R.; Dumesic, J. A. *Nature* **2002**, *418*, 964−967.
(5) Huber, G. W.; Shabaker, J. W.; Dumesic, J. A. *Science* **2003**, *300*, 2075−2077.
(6) Sharkov, V. I. *Angew. Chem., Int. Ed.* **1963**, *2*, 405−492.
(7) Robinson, J. M.; Burgess, C. E.; Bently, M. A.; Brasher, C. D.; Horne, B. O.; Lillard, D. M.; Macias, J. M.; Mandal, H. D.; Mills, S. C.; O’Hara, K. D.; Pon, J. T.; Raigoza, A. F.; Sanchez, E. H.; Villarreal, J. S. *Biomass Bioenergy* **2004**, *26*, 473−483.
(8) Yu, W.; Liu, M.; Liu, H.; Ma, X.; Liu, X. *J. Colloid Interface Sci.* **1998**, 439−444.
(9) Borsla, A.; Wilhelm, A. M.; Delmas, H. *Catal. Today* **2001**, 389−395.
(10) Teranishi, T.; Miyake, M. *Chem. Mater.* **1998**, *10*, 594−600.
(11) Teranishi, T.; Hosoe, M.; Miyake, M. *Adv. Mater.* **1997**, *9*, 65−67.
(12) Mu, X. D.; Evans, D. J.; Kou, Y. *Catal. Lett.* **2004**, *97*, 151−154.

JA062468T