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Conversion of Cellulose to Hexitols Catalyzed by Ionic Liquid-Stabilized Ruthenium Nanoparticles and a Reversible Binding Agent

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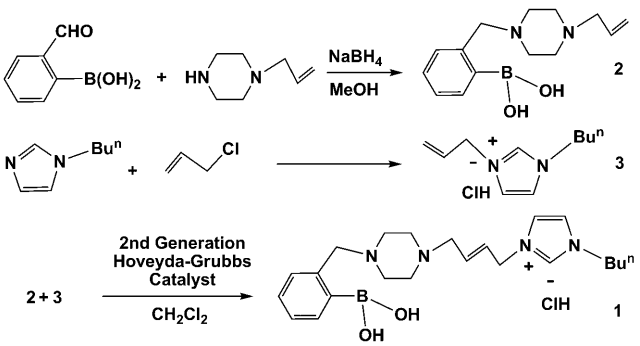
Biomass has recently attracted wide interest because it is recognized as a candidate for both new energy resources and as feedstocks to replace fossil fuels.[1] Because cellulose is the principal component of biomass, the conversion of cellulose to valuable chemicals is a major focus in biomass conversion.[1] Yet, the multiple hydroxyl groups of cellulose that form hydrogen bonds between adjacent polymers, and that create crystalline structures giving plants structural strength, also make cellulose particularly difficult to digest.[2] Three methods have been employed to overcome this problem:[2,3] a) acid-catalyzed cellulose hydrolysis, b) enzyme-catalyzed cellulose hydrolysis, and c) subcritical or supercritical water-catalyzed cellulose hydrolysis. Mineral acids are used to catalyze cellulose hydrolysis, creating glucose even under mild conditions. However, removal or neutralization of the acid is required after treatment, and the use of corrosive mineral acids causes environmental problems.[3] Furthermore, enzyme-catalyzed cellulose hydrolysis is not practical at present because it is expensive, and no satisfactory methods have been developed to recover the enzymes from the hydrolysate mixture.[3] Lastly, although hydrolysis in supercritical water at 374 °C is fast, it is difficult to inhibit secondary degradation of the generated monosaccharides. This degradation causes both low yields of glucose and subsequent inhibition of fermentation to ethanol because of the enzymatically toxic 5-hydroxymethylfurfural (5-HMF) produced.[3] Hence, there is a need to develop viable catalysts for rapid cellulose degradation that gives high conversion to hexitols with minimal environmental impact.

Transition metal nanoparticles as catalysts for organic transformations is attracting widespread attention.[4] This is because nanoparticle-based catalytic systems exhibit superior catalytic activities relative to their corresponding bulk materials,[5] and often higher selectivity when compared with conventional heterogeneous catalysts.[5] The particle size and surface structure are the most important factors dominating the catalytic selectivity of metal nanoparticle-based catalysts.[5g] For example, nanoparticles of Ru, Pd, and Pt are active catalysts for cellulose conversion to polyols.[6] The resulting sorbitol products were easily separated by extraction.[7]. However, the poor solubility of cellulose still hinders these catalytic processes.

To assist in solubility, ionic liquids have been used as a solvent in cellulose pretreatment and transformation.[8–11] In addition, the ionic liquid species can stabilize transition metal nanoparticles to sustain their small size, high surface area, and inhibit nanoparticle leaching.[12]

Further, it is well known that *o*-(*N*,*N*-dialkylaminomethyl) arylboronic acids can interact with sugars and diols through reversible covalent bonds.[13] We anticipated that boronic acids could break up the crystal packing of cellulose by reversible binding with the multiple hydroxyl groups, thereby improving solubility and catalytic activity. This should be especially effective when combined with the cellulose dissolving ability of ionic liquids, and hence we designed conjugate **1**.

Compound **1** was created by metathesis between boronic acid **2** and an *n*-butyl-3-imidazolium cation **3** (Scheme 1; see the Supporting Information for characterization). This cation



Scheme 1. Synthesis of boronic acid binding agent.

mimics that found in the ionic liquid 1-*n*-butyl-3-methylimidazolium chloride ([BMIM]Cl). Therefore, while compound **1** is insoluble in water, it is fully miscible with the ionic liquids 1-*n*-butyl-3-methylimidazolium chloride ([BMIM]Cl) and trihexyltetradecylphosphonium dodecylbenzene sulfonate ([THTdP][DBS]).

After achieving **1**, we checked if it would stabilize metal nanoparticles as do free ionic liquids. Ruthenium nanoparticles were prepared and stabilized with [BMIM]Cl and [THTdP][DBS] as previously reported (mole ratio of [BMIM]Cl/**1** or [THTdP][DBS]/**1** = 45:1).[12] The resulting Ru nanoparticles were analyzed with transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS) to determine their particle

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size and oxidation states. The TEM image shows that the nanoparticles are small with an average size of approximately 4.0 nm, with a narrow size distribution (Figure 1). These results

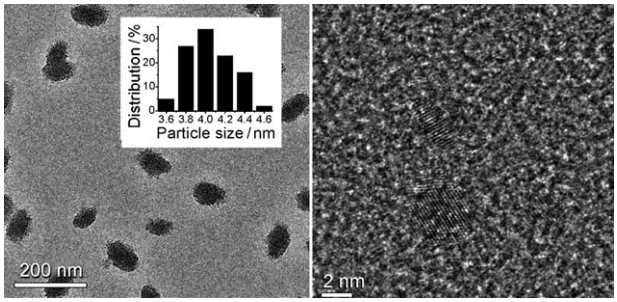

Figure 1. TEM images and particle histograms of [BMIM]Cl/1 (mole ratio = 45:1) stabilized Ru^0 nanoparticles (150 particles counted).

are comparable with other reported results.[14,15] The XPS spectrum (see the Supporting Information, Figure S1) shows typical Ru^0 absorptions at 280.20 and 284.40 eV for $3d_{5/2}$ and $3d_{3/2}$, respectively, with a $\Delta = 4.20$ eV, which is consistent with the literature results.[16] All preparative work was carried out in an argon atmosphere to guard against oxide formation, and accordingly no evidence was found in the XPS results for the existence of RuO contamination.[14]

In the absence of **1**, a conversion of 15% was achieved for cellulose hydrogenation to hexitols using a Ru nanocluster catalyst in [BMIM]Cl.[8] However, when using varying hydrogen donors in the presence of **1**, cellulose was successfully converted to hexitols in high yield (Table 1). It was found that both ionic liquids [BMIM]Cl and [THTdP][DBS] were equally effective in runs in which the hydrogen source was sodium formate (Table 1, entries 4 and 6). Furthermore, in the absence of ruthenium nanoparticles and hydrogen, cellulose was smoothly hydrolyzed to α-glucose using compound **1** with a 95% conversion to glucose after 5 h at 80 °C, which shows that **1** is crucial in activating the cellulose polymer chains. Compound **1** and

Table 1. Catalytic hydrogenation of cellulose[a]

Entry	Catalyst	Conv. [%]	Yield [%][b] G	S	M	
1	[BMIM]Cl	< 5				
2	[BMIM]Cl+**1**	95	87			
3	[BMIM]Cl+**1**+Ru	90 (FA)			76	7[c]
4	[BMIM]Cl+**1**+Ru	100 (SF)			94	
5	[BMIM]Cl+**1**+Ru	98 (H_2)			89	3[c]
6	[THTdP][DBS] +**1**+Ru	100 (SF)			93	

[a] FA = HCO_2H, SF = HCO_2Na, G = glucose, S = sorbitol, M = mannitol. Reaction conditions: **1** (0.1 mmol), Ru^0 nanoparticles (10.0 μmol), [BMIM]Cl (0.8 g, 4.5 mmol) or [THTdP][DBS] (1 mL), cellulose (1 g), sodium formate (0.1 g, 1.5 mmol) or formic acid (70 mg, 1.5 mmol) or H_2 (10 atm); reaction temperature 80 °C; reaction time 5 h. The hexitol products were analyzed by NMR spectroscopy, GC and EI-MS. [b] Isolated yield. [c] Based on GC analysis.

the nanoparticles were easily recovered from the reaction mixture by diluting with water, decanting the aqueous phase, and washing the obtained residue with water to remove any traces of hexitols. Activity was maintained after 5 runs with sodium formate as the hydrogen donor, whereas the Ru catalysts loss was less than 3 ppm, based on the inductively coupled plasma (ICP) analysis.

Based on previous reports and our results, we propose the following steps are involved in the mechanism. Firstly, upon boronic acid-based receptor **1** incubation with cellulose, binding occurs with the 1,2-diols present along the polymeric chain of cellulose. Compared with a mixture of [THTdP][DBS] and **1** in CD_2Cl_2, after suspending with cellulose at 30 °C for 2 h, a broad peak at $\delta = -1.1$ ppm emerged in the ^{11}B NMR spectra (see the Supporting Information, Figure S5), which supports complex formations between **1** and multiple hydroxyl groups in cellulose. The affinity of boronic acids to diols is enhanced at neutral pH,[13] such as in most of our conditions. However, when formic acid/Na^+ formate is used, the reaction mixture is slightly acidic (pH ca. 5–6), which lowers the affinity between **1** and the cellulose. Under any pH we use, the binding of **1** with cellulose is proposed to solubilize the polysacchloride. Cellulose hydrolysis to glucose is then followed by glucose hydrogenation to hexitols by the Ru nanoparticle catalysts. Furthermore, when formic acid/Na^+ formate is used as the hydrogen donors, the ionic liquid stabilizes ruthenium nanoparticle catalysts, which likely also enhances the hydrogen release; it has been reported that the ruthenium complexes are effective catalysts for this release.[17] Lastly, dissociation of binding agent **1** from the free glucose and hexitol allows **1** to play its role again. Our proposed catalytic process for cellulose hydrolysis and hydrogenation is shown in Figure 2.

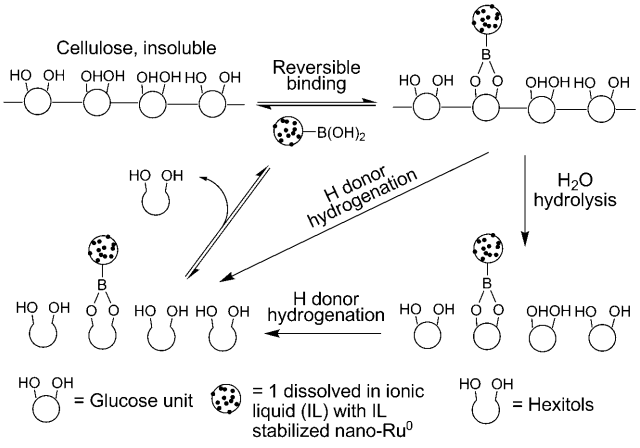

Figure 2. Catalytic conversion of cellulose to hexitols by reversible interaction.

In conclusion, we have successfully synthesized a conjugate between an ionic liquid moiety and a boronic acid binding agent **1**. Compound **1** is an effective catalyst when combined with an ionic liquid-stabilized ruthenium nanoparticle catalyst for cellulose conversion to hexitols. The catalyst can be recycled with sustained activity.

Experimental Section

General Procedure

All operations were operated under argon atmosphere with a glove box or standard Schlenk line. α-Cellulose (microcrystalline, powder), 1-*n*-butyl-3-methylimidazolium chloride ([BMIM]Cl) and other reagents were purchased from Aldrich. The ionic liquid trihexyltetradecylphosphonium dodecylbenzenesulfonate [THTdP][DBS] was provided by IL-TECH Inc. Ruthenium nanoparticles were produced according to literature.[12] ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Fourier-Transform multinuclear spectrometer at 400 and 100.6 MHz, relative to an external Me_4Si (TMS) standard. ^{11}B NMR spectra were recorded on a Bruker 400 analyzer at 128.38 MHz. Infrared (IR) spectra were measured by using a BIO-RAD spectrophotometer with a KBr pellets technique. The MS was measured on a Thermo Finnigan MAT XP95 analyzer using the EI model. ICP analysis was carried out on a VISTA-MPX, CCD simultaneous ICP-OES analyzer. XPS was carried out on an ESCALAB 250 analyzer, and TEM measurements were carried out on a JEOL Tecnai-G^2, FEI analyzer at 200 kV. GC analysis was performed on a PerkinElmer, Clarus 500 GC analyzer on a DB-1 column (30 m × 0.32 mm × 1.00 μm) with an isothermal temperature of 250 °C. Detail experimental procedures are available in the Supporting Information.

Synthesis of Compound **2**: A literature procedure was used to synthesize compound **2**.[13a] In brief, 2-formylbenzeneboronic acid (0.309 g, 2.0 mmol) was dissolved in dry methanol (10 mL), and a solution 1-allylpiperazine (0.258 g, 2.0 mmol) in methanol (5 mL) was added dropwise over 30 min at room temperature in a glovebox. After stirring for 2 days at room temperature, sodium borohydride (0.139 g, 3.5 mmol) was added to the reaction mixture in two parts within 2 h, and the mixture was further reacted for 4 h. The solvent was removed in vacuum, and dichloromethane (20 mL) was added to the residue. The solid precipitate was removed by filtration and the filtrate was concentrated to 5 mL followed by purification with chromatography (SiO_2, eluted with a mixted solvent of methanol/dichloromethane 1:10) to produce **2** (0.395 g, 76%).

Synthesis of Compound **3**: 1-Butylimidazole (5.0 mL, 37.3 mmol) and allyl chloride (40 mL, 485.9 mmol, great excess) were added to a 100 mL round bottom flask equipped with a magnetic stir bar. The resulting mixture was left reacting for one week with continuous stirring. After removing all the solvent under reduced pressure, the obtained residue was washed with hexane and diethyl ether followed by drying in vacuum to produce pure product **3** (6.5 g, 86.8%).

Synthesis of Compound **1**: A literature procedure was used to conduct the reaction.[18] Compounds **2** (0.260 g, 1.0 mmol) and **3** (0.200 g, 1.0 mmol) were dissolved in dichloromethane (10 mL). The second generation Hoveyda–Grubbs catalyst (62.7 mg, 0.1 mmol) was added to the solution. The resulting mixture was left stirring for one week in a glove box at room temperature. After removing all the solvents under reduced pressure, the obtained residue was purified by precipitation from dichloromethane solution with pentane followed by drying in vacuum to give **1** (0.27 g, 62%).

Cellulose Conversion to Hexitols

Microcrystalline α-cellulose, purchased from Aldrich, was pretreated with acetic acid according to literature to produce nanoscaled cellulose (ca. 200 nm) for hydrolysis reactions.[19] Compound **1** (43.3 mg, 0.1 mmol) was added to [BMIM]Cl (0.8 g, 4.5 mmol) or [THTdP][DBS] (1 mL) containing Ru^0 nanoparticles (10.0 μmol) with vigorous stirring for 2 h at 80 °C. The resulting catalyst composite was then added to a mixture of pretreated cellulose (1 g) and sodium formate (0.1 g, 1.5 mmol) or formic acid (70.0 mg, 1.5 mmol) in deionized water (15 mL). When hydrogen was used, the reaction vessel was then saturated with H_2 (10 atm). The reaction was conducted at 80 °C for 5 h before quenching with cold methanol followed by diluting with deionized water (40 mL). For a control experiment, neither **1** nor Ru^0 nanoparticles were added; only [BMIM]Cl was used. Any unreacted cellulose was then collected by filter or centrifugation and dried in vacuum. Cellulose conversion was determined by the change in weight of cellulose used before and after the reactions. Catalyst composite with ionic liquid was recovered by decanting the solution. The recovered catalyst was washed with deoxygenated deionized water and dried in vacuum for the subsequent run. The results are listed in Table 1. The hexitols products were purified by flash chromatography (Al_2O_3-SiO_2, eluted with a mixed solvent of methanol/dimethyl sulfoxide/water 3:5:1) and analyzed by NMR spectrscopy, GC, and MS. For GC analysis, samples were prepared according to literature.[20] The above hexitols (20.0 mg) were added to a solution of acetic anhydride/pyridine 10:1 (10 mL) for 4 h at 80 °C. The solutions were then concentrated by evaporation under a stream of argon before subjecting to GC analysis. Results are shown in the Supporting Information (Figure S6).

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