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# Polyoxometalate-supported ruthenium nanoparticles as bifunctional heterogeneous catalysts for the conversions of cellobiose and cellulose into sorbitol under mild conditions†

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**Ru nanoparticles loaded on a Keggin-type polyoxometalate (Cs<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>), which did not possess strong intrinsic acidity, efficiently catalysed the conversions of cellobiose and cellulose into sorbitol in water medium in H<sub>2</sub> at ≤433 K. The Brønsted acid sites generated *in situ* from H<sub>2</sub> have been demonstrated to play a key role in the formation of sorbitol.**

The transformation of cellulose, which is the main constituent of the most abundant renewable lignocellulosic feedstock and is non-edible, into chemicals and fuels has attracted much attention in recent years. Compared to other conversion routes such as high-temperature gasification and pyrolysis and enzymatic fermentation, a low-temperature and selective catalytic route for the transformation of cellulose into a platform molecule, which may be facily transformed into valued chemicals and fuels in the subsequent step, is more desirable.<sup>1</sup> Sorbitol is one of the promising platform molecules. It is widely used in food, cosmetic, medical and paper industries, and is also a building block in the synthesis of fine chemicals including vitamin C.<sup>2</sup> Moreover, H<sub>2</sub> or liquid alkane fuels could also be produced from sorbitol *via* a catalytic aqueous reforming process.<sup>3</sup>

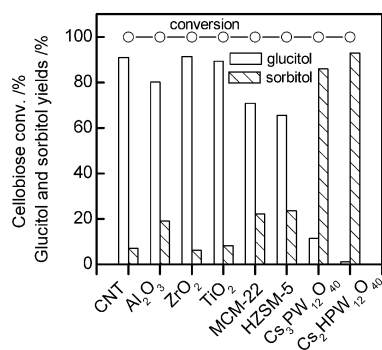
However, the catalytic transformation of cellulose under mild conditions is a challenging task because of the robust crystalline structure of cellulose. The studies on the conversion of cellobiose, which is a glucose dimer connected by the same β-1,4-glycosidic bond as in cellulose and is viewed as the simplest model of cellulose, would provide useful insights for the rational design of efficient catalysts for cellulose transformations. For the formation of sorbitol from cellobiose or cellulose, it is expected that a bifunctional catalyst combining

hydrolysis and hydrogenation functions is required. Fukuoka and Dhepe<sup>4a</sup> reported a Pt/Al<sub>2</sub>O<sub>3</sub> catalyst for the conversion of cellulose to sorbitol and mannitol with a yield of 31% at 463 K in water in H<sub>2</sub>. Liu and Kou *et al.*<sup>4b</sup> showed that Ru nanoclusters dispersed in acidic water (pH = 2) catalysed the conversion of cellobiose into sorbitol. Liu *et al.*<sup>4c</sup> further combined the Ru/C catalyst with the reversibly generated H<sup>+</sup> in hot water (518 K), converting cellulose to hexitols with a yield approaching 40%. We also demonstrated that Ru nanoparticles supported on carbon nanotubes (CNTs) bearing acidic groups catalyzed the conversions of cellulose or cellobiose into sorbitol.<sup>4d,e</sup> A few Ni-based catalysts also showed good performances in the same reaction.<sup>5</sup> Zhang *et al.*<sup>6</sup> developed a direct route for the hydrogenolysis of cellulose to ethylene glycol by using a Ni-promoted W<sub>2</sub>C/AC (AC = activated carbon) catalyst in water at 518 K. These systems, however, require relatively high temperatures (typically ≥ 463 K), which may cause problems in catalyst stability due to the strict hydrothermal conditions. Our mechanistic study for the Ru/CNT-catalysed cellobiose conversion unravelled that the hydrogenation proceeded much faster than the hydrolysis.<sup>4e</sup> Recent studies showed that the combination of a strong mineral acid (H<sub>2</sub>SO<sub>4</sub>) or liquid heteropolyacid (H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>) with Ru/C afforded excellent yields of sugar alcohols.<sup>7</sup> Therefore, the development of more efficient solid acid materials is the key to improving the performance of a bifunctional heterogeneous catalyst for the sorbitol formation under milder conditions.

Polyoxometalates, *e.g.*, Keggin-type H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>, may possess acidity even stronger than H<sub>2</sub>SO<sub>4</sub>.<sup>8</sup> A few studies have shown that H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> is active for the hydrolysis or alcoholysis of cellobiose or cellulose.<sup>9,10</sup> However, in these systems, polyoxometalates functioned homogeneously in the liquid phase, and the separation and recovery of the catalyst from the product and the reaction medium would be problematic. On the other hand, the salts of Keggin-type polyoxometalates with large cations such as Cs<sup>+</sup> are insoluble in water, and the Cs<sub>x</sub>H<sub>3-x</sub>PW<sub>12</sub>O<sub>40</sub> with a proper Cs<sup>+</sup> content was found to be water-tolerant and exhibit higher activity than H-ZSM-5 for the acid-catalyzed reactions in water medium.<sup>8</sup> However, to date, few studies have been contributed to the cellulose or cellobiose conversions using heterogeneous polyoxometalate catalysts. Herein, we report a first study on the exploitation of

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† Electronic supplementary information (ESI) available: Experimental details, TEM micrograph of colloidal Ru nanoparticles, structural formulas of reactants and products, NH<sub>3</sub>-TPD profiles, catalytic performances of catalysts with different Cs contents and with different Ru loadings, pyridine-adsorbed FT-IR spectra for catalysts before and after repeated reactions, pyridine-adsorbed FT-IR for the Ru/Al<sub>2</sub>O<sub>3</sub> in H<sub>2</sub>, hydrolysis of cellulose in N<sub>2</sub> over the catalysts with and without H<sub>2</sub> pretreatment. See DOI: 10.1039/c1cc12506k



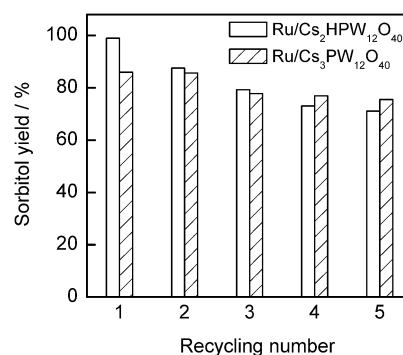
**Fig. 1** Catalytic performances of Ru catalysts loaded on various solid acid materials for the conversion of cellobiose in neutral water in H<sub>2</sub>. Reaction conditions: catalyst, 0.10 g; temperature, 413 K; cellobiose, 0.058 mol dm<sup>-3</sup>; water, 10 cm<sup>3</sup>; H<sub>2</sub>, 2 MPa; time, 6 h. Glucitol denotes 3-β-glucopyranosyl-D-glucitol.

Cs<sub>x</sub>H<sub>3-x</sub>PW<sub>12</sub>O<sub>40</sub>-supported Ru nanoparticles for the conversions of cellobiose and cellulose into sorbitol in water medium under relatively mild conditions (≤433 K).

The Keggin-type Cs<sub>x</sub>H<sub>3-x</sub>PW<sub>12</sub>O<sub>40</sub> was prepared by an established method (see ESI† for experimental details). Colloidal Ru nanoparticles with a mean size of 1.6 nm (Fig. S1, ESI†), prepared by the reduction of RuCl<sub>3</sub> with ascorbic acid at 353 K, were used as the precursors of Ru. The addition of white polyoxometalate powders into the colloidal solution decoloured the solution while the colour of the support was deepened, indicating the adsorption of Ru nanoparticles onto the support. The supported Ru catalysts were recovered by filtration, washed with deionised water and dried at 373 K. The loading of Ru was kept at 1.0 wt%.

We compared the catalytic performances of Ru catalysts loaded on the Cs<sub>2</sub>HPW<sub>12</sub>O<sub>40</sub> and Cs<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> with those on several other solid acid materials including Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub>, H-ZSM-5, MCM-22 and CNT for the conversion of cellobiose at 413 K. Fig. 1 shows that these catalysts exhibit almost 100% conversion of cellobiose, but the main product is 3-β-glucopyranosyl-D-glucitol, which is formed by the hydrogenolysis of a C–O band in one glucose ring of cellobiose (Scheme S1, ESI†), over most of these catalysts. This suggests that the acid-catalysed hydrolysis of the β-1,4-glycosidic bond is a slow step over these catalysts.<sup>4e</sup> On the other hand, the Ru/Cs<sub>2</sub>HPW<sub>12</sub>O<sub>40</sub> and Ru/Cs<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> afforded outstanding sorbitol yields (93% and 86%). Our NH<sub>3</sub>-TPD measurements confirmed that the Cs<sub>2</sub>HPW<sub>12</sub>O<sub>40</sub> possessed stronger acidity (Fig. S2, ESI†), and this could account for the excellent sorbitol yield of the Ru/Cs<sub>2</sub>HPW<sub>12</sub>O<sub>40</sub> catalyst. However, the superior sorbitol yield of the Ru/Cs<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> catalyst is quite unexpected since Cs<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> does not possess notable acidity (Fig. S2, ESI†).

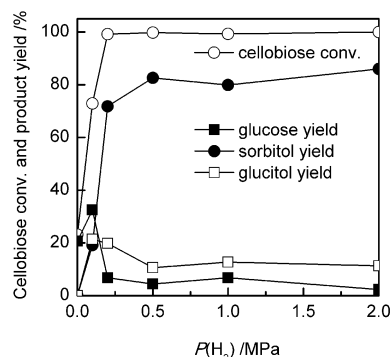
We clarified that the Ru catalysts loaded on hydrogen-form Cs salts of tungstophosphates (Cs<sub>x</sub>H<sub>3-x</sub>PW<sub>12</sub>O<sub>40</sub> with  $x < 3.0$ ) showed similar sorbitol yields, which were slightly higher than that of the Ru/Cs<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> (Table S1, ESI†). However, the recycling experiments revealed that the Ru/Cs<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> was more stable than those hydrogen-form Cs salt-supported Ru catalysts. After 5 recycling uses, the sorbitol yield of the Ru/Cs<sub>2</sub>HPW<sub>12</sub>O<sub>40</sub> became even slightly lower than that of



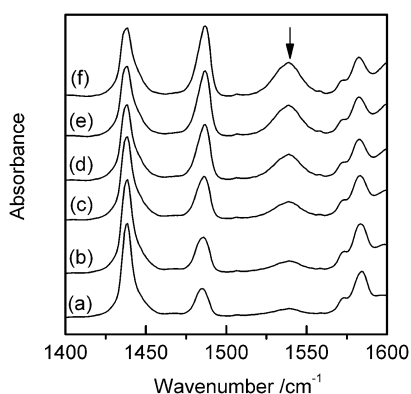
**Fig. 2** Changes of sorbitol yield during the recycling uses of Ru/Cs<sub>2</sub>HPW<sub>12</sub>O<sub>40</sub> and Ru/Cs<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> for the conversion of cellobiose. Reaction conditions: catalyst, 0.10 g; temperature, 413 K; cellobiose, 0.058 mol dm<sup>-3</sup>; water, 10 cm<sup>3</sup>; H<sub>2</sub>, 2 MPa; time, 6 h.

the Ru/Cs<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> (Fig. 2). Okuhara *et al.*<sup>11</sup> found that the treatment of Cs<sub>2.5</sub>H<sub>0.5</sub>PW<sub>12</sub>O<sub>40</sub> in water at 393 K caused the leaching of the H<sup>+</sup>-rich hydrophilic moiety into water, resulting in a significant decrease in Brønsted acidity. Our studies also revealed the leaching of protons from the Ru/Cs<sub>2</sub>HPW<sub>12</sub>O<sub>40</sub> catalyst under hydrothermal conditions, and after repeated reactions, the acidity of the Ru/Cs<sub>2</sub>HPW<sub>12</sub>O<sub>40</sub> catalyst became similar to that of the Ru/Cs<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> catalyst (Fig. S3, ESI†).

Further studies have been performed to understand the catalysis of the relatively stable Ru/Cs<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> catalyst. We found that H<sub>2</sub> played a crucial role in the conversion of cellobiose. In the absence of H<sub>2</sub> (under 2 MPa N<sub>2</sub>), cellobiose conversion was only ~20%, and the main product was glucose. The increase in H<sub>2</sub> pressure significantly increased cellobiose conversion and sorbitol yield (Fig. 3). The yield of glucose, which should be formed by the acid-catalysed hydrolysis of cellobiose, also increased by feeding a low pressure of H<sub>2</sub>. Thus, it is reasonable to speculate that the acidity generated on the Cs<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> surface by spillover H species from the dissociation of H<sub>2</sub> on Ru nanoparticles may account for the superior catalytic performance of the Ru/Cs<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> catalyst. This speculation was further supported by the experimental fact that the presence of Ru was also required for obtaining higher cellobiose conversion and sorbitol yield (Fig. S4, ESI†).



**Fig. 3** Dependence of catalytic performances of the Ru/Cs<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> catalyst for the conversion of cellobiose on H<sub>2</sub> pressure. Reaction conditions: catalyst, 0.10 g; temperature, 413 K; cellobiose, 0.058 mol dm<sup>-3</sup>; water, 10 cm<sup>3</sup>; time, 6 h. Glucitol denotes 3-β-glucopyranosyl-D-glucitol.



**Fig. 4** Pyridine-adsorbed FT-IR spectra of Ru/Cs<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> in H<sub>2</sub> with different pressures at 303 or 323 K. (a) At 303 K after pretreatment in H<sub>2</sub> at 573 K followed by evacuation, (b) 12.8 kPa H<sub>2</sub> and 303 K, (c) 19.2 kPa H<sub>2</sub> and 323 K, (d) 25.6 kPa H<sub>2</sub> and 323 K, (e) 33.3 kPa H<sub>2</sub> and 323 K, (f) 44.8 kPa H<sub>2</sub> and 323 K.

Moreover, the yield of glucose was also enhanced by loading a small amount of Ru onto the Cs<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>.

The generation of Brønsted acid sites from molecular H<sub>2</sub> was proposed by Hattori *et al.*<sup>12</sup> and this kind of reversible acidity has found applications in the hydroisomerisation and cracking of alkanes over a few metal oxide-supported transition metal catalysts such as Pt/SO<sub>4</sub><sup>2-</sup>-ZrO<sub>2</sub>. Fukuoka and Dhepe<sup>4a</sup> assumed that such reversible Brønsted acidity might contribute to the conversion of cellulose over a Pt/Al<sub>2</sub>O<sub>3</sub> catalyst. To gain evidence for the generation of such Brønsted acidity, we have performed FT-IR studies of the adsorbed pyridine (Fig. 4). The Ru/Cs<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> catalyst was pretreated in H<sub>2</sub> at 573 K, followed by evacuation at the same temperature, and then, was exposed to pyridine at 423 K for 0.5 h. After evacuation and cooling down to 303 K, FT-IR spectra were recorded. After the introduction of H<sub>2</sub>, an IR band at 1540 cm<sup>-1</sup>, which was attributable to pyridine adsorbed on the Brønsted acid sites, grew significantly, confirming the generation of the Brønsted acid sites in the presence of H<sub>2</sub>. We performed the same pyridine-adsorbed FT-IR studies over the Ru/Al<sub>2</sub>O<sub>3</sub>, which was selected as an example of other supported Ru catalysts. However, we did not observe the generation of Brønsted acid sites over the catalyst in H<sub>2</sub>, and this may have caused its low activity in sorbitol formation (Fig. S5, ESI<sup>†</sup>). Our results described in this work clearly demonstrate the unique role of such H<sub>2</sub>-originated Brønsted acidity in the conversion of cellobiose into sorbitol over the Ru/Cs<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> catalyst, which does not possess notable intrinsic acidity.

The Ru/Cs<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> catalyst was also exploited for the conversion of ball-milled cellulose in water medium in H<sub>2</sub>. Table 1 shows that sorbitol is the main product, and the yield of sorbitol increases with temperature and can reach 43% at 433 K. The pretreatment of the Ru/Cs<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> by H<sub>2</sub> at 573 K for 5 h did not significantly change the sorbitol yield. The hydrolysis of cellulose in an N<sub>2</sub> atmosphere at the same temperature only provided very low yields of glucose irrespective of catalyst pretreatment (Table S2, ESI<sup>†</sup>), further suggesting the key role of the presence of gaseous H<sub>2</sub>.

**Table 1** Catalytic performances of the Ru/Cs<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> catalyst for the conversion of ball-milled cellulose in water in H<sub>2</sub><sup>a</sup>

Entry No.	Temperature/K	Yield (%)			
		Cellobiose	Glucose	Sorbitol	Mannitol
1	393	0	0.1	1.1	0
2	403	0.1	0.2	5.5	0.2
3	413	0.2	0.2	12	0.6
4	423	0.2	0.2	25	1.2
5	433	1.0	0.3	43	2.1
6 <sup>b</sup>	433	0.1	1.0	40	3.1

<sup>a</sup> Reaction conditions: catalyst, 0.10 g; cellulose, 0.10 g; water, 15 cm<sup>3</sup>; H<sub>2</sub>, 2 MPa; time, 24 h. <sup>b</sup> The catalyst was pretreated in H<sub>2</sub> at 573 K for 5 h.

In conclusion, we have found that the Keggin-type polyoxometalate-supported Ru nanoparticles exhibit unique catalytic behaviours for the conversions of cellobiose and ball-milled cellulose into sorbitol in neutral water in the presence of H<sub>2</sub> under relative mild conditions. It is unexpected that the Ru/Cs<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>, which does not possess strong intrinsic acidity, shows superior sorbitol yield and good stability. It has been demonstrated that the H<sub>2</sub>-originated Brønsted acid sites play a key role in the conversions of cellobiose and cellulose into sorbitol over the present catalyst.

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