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 (Cs3PW12O40), which did not possess strong intrinsic acidity, efficiently catalysed the conversions of cellobiose and cellulose into sorbitol in water medium in H2 at \( \leq 433 \) K. The Bronsted acid sites generated in situ from H2 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 facilely transformed into valued chemicals and fuels in the subsequent step, is more desirable.\(^1\) 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.\(^2\) Moreover, H2 or liquid alkane fuels could also be produced from sorbitol via a catalytic aqueous reforming process.\(^3\)

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 \(-1,4\)-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\(^4d\) reported a Pt/Al2O3 catalyst for the conversion of cellulose to sorbitol and mannitol with a yield of 31% at 463 K in water in H2. Liu and Kou et al.\(^4b\) showed that Ru nanoclusters dispersed in acidic water (pH = 2) catalysed the conversion of cellobiose into sorbitol. Liu et al.\(^4c\) further combined the Ru/C catalyst with the reversibly generated H+ 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.\(^4d,e\) A few Ni-based catalysts also showed good performances in the same reaction.\(^5\) Zhang et al.\(^6\) developed a direct route for the hydrogenolysis of cellulose to ethylene glycol by using a Ni-promoted W2C/AC (AC = activated carbon) catalyst in water at 518 K. These systems, however, require relatively high temperatures (typically \( \geq 463 \) 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.\(^6c\) Recent studies showed that the combination of a strong mineral acid (H2SO4) or liquid heteropolyacid (H1PW12O40) with Ru/C afforded excellent yields of sugar alcohols.\(^7\) 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 H3PW12O40, may possess acidity even stronger than H2SO4.\(^8\) A few studies have shown that H3PW12O40 is active for the hydrolysis or alcoholysis of cellobiose or cellulose.\(^9,10\) 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+ are insoluble in water, and the CsH1−xPW12O40 with a proper Cs+ content was found to be water-tolerant and exhibit higher activity than H-ZSM-5 for the acid-catalyzed reactions in water medium.\(^8\) 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...
The Keggin-type Cs$_{3}$H$_{1+x}$PW$_{12}$O$_{40}$ was prepared by an established method (see ESI$^\dagger$ for experimental details). Colloidal Ru nanoparticles with a mean size of 1.6 nm (Fig. S1, ESI$^\dagger$), prepared by the reduction of RuCl$_3$ 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$_x$HPW$_{12}$O$_{40}$ and Cs$_x$PW$_{12}$O$_{40}$ with those on several other solid acid materials including Al$_2$O$_3$, TiO$_2$, ZrO$_2$, 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 and cellulose into sorbitol in water medium under relatively mild conditions (≤433 K).

The increase in H$_2$ pressure significantly increased cellobiose conversion was only 20%, and the main product was glucose.

This suggests that the acid-catalysed hydrolysis of the β,1,4-glycosidic bond is a slow step over these catalysts.$^\text{4e}$ On the other hand, the Ru/Cs$_x$HPW$_{12}$O$_{40}$ and Ru/Cs$_x$PW$_{12}$O$_{40}$ afforded outstanding sorbitol yields (93% and 86%). Our NH$_3$-TPD measurements confirmed that the Cs$_x$HPW$_{12}$O$_{40}$ possessed stronger acidity (Fig. S2, ESI$^\dagger$), and this could account for the excellent sorbitol yield of the Ru/Cs$_x$HPW$_{12}$O$_{40}$ catalyst. However, the superior sorbitol yield of the Ru/Cs$_x$PW$_{12}$O$_{40}$ catalyst is quite unexpected since Cs$_x$PW$_{12}$O$_{40}$ does not possess notable acidity (Fig. S2, ESI$^\dagger$).

We clarified that the Ru catalysts loaded on hydrogen-form Cs salts of tungstophosphates (Cs$_x$H$_{1+x}$PW$_{12}$O$_{40}$ with x < 3.0) showed similar sorbitol yields, which were slightly higher than that of the Ru/Cs$_3$PW$_{12}$O$_{40}$ (Table S1, ESI$^\dagger$). However, the recycling experiments revealed that the Ru/Cs$_3$PW$_{12}$O$_{40}$ was more stable than those hydrogen-form Cs salt-supported Ru catalysts. After 5 recycling uses, the sorbitol yield of the Ru/Cs$_3$PW$_{12}$O$_{40}$ became even slightly lower than that of the Ru/Cs$_3$PW$_{12}$O$_{40}$ (Fig. 2). Okuhara et al.$^\text{11}$ found that the treatment of Cs$_{2.5}$H$_{0.5}$PW$_{12}$O$_{40}$ in water at 393 K caused the leaching of the H$^+$-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$_3$HPW$_{12}$O$_{40}$ catalyst under hydrothermal conditions, and after repeated reactions, the acidity of the Ru/Cs$_3$HPW$_{12}$O$_{40}$ catalyst became similar to that of the Ru/Cs$_3$PW$_{12}$O$_{40}$ catalyst (Fig. S3, ESI$^\dagger$).

Further studies have been performed to understand the catalysis of the relatively stable Ru/Cs$_3$PW$_{12}$O$_{40}$ catalyst. We found that H$_2$ played a crucial role in the conversion of cellobiose. In the absence of H$_2$ (under 2 MPa N$_2$), cellobiose conversion was only ~20%, and the main product was glucose. The increase in H$_2$ 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$_2$. Thus, it is reasonable to speculate that the acidity generated on the Cs$_3$PW$_{12}$O$_{40}$ surface by spillover H species from the dissociation of H$_2$ on Ru nanoparticles may account for the superior catalytic performance of the Ru/Cs$_3$PW$_{12}$O$_{40}$ 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$^\dagger$).

In conclusion, our studies demonstrate that the Ru/Cs$_x$PW$_{12}$O$_{40}$ catalysts are efficient and stable for the conversion of cellobiose into sorbitol in water medium under mild conditions (≤433 K). The Ru/Cs$_x$HPW$_{12}$O$_{40}$ catalysts can also be used for the conversion of cellobiose into sorbitol at elevated temperatures (≥433 K). Further work is currently underway to investigate the catalytic performance of these catalysts under these conditions.
Moreover, the yield of glucose was also enhanced by loading a small amount of Ru onto the Cs₃PW₁₂O₄₀.

The generation of Bronsted acid sites from molecular H₂ was proposed by Hattori et al. 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/SO₂₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋_-...The Ru/Cs₃PW₁₂O₄₀ catalyst was also exploited for the conversion of ball-milled cellulose in water in H₂.

Table 1 Catalystic performances of the Ru/Cs₃PW₁₂O₄₀ catalyst for the conversion of ball-milled cellulose in water in H₂.°

<table>
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<th>Entry No.</th>
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<th>Glucose</th>
<th>Sorbitol</th>
<th>Mannitol</th>
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<td>0.1</td>
<td>1.0</td>
<td>40</td>
<td>3.1</td>
</tr>
</tbody>
</table>

° Reaction conditions: catalyst, 0.10 g; cellulose, 0.10 g; water, 15 cm³; H₂, 2 MPa; time, 24 h; ° The catalyst was pretreated in H₂ 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 cellulose and ball-milled cellulose into sorbitol in neutral water in the presence of H₂ under relative mild conditions. It is unexpected that the Ru/Cs₃PW₁₂O₄₀, which does not possess strong intrinsic acidity, shows superior sorbitol yield and good stability. It has been demonstrated that the H₂-originated Bronsted acid sites play a key role in the conversions of cellulose and cellulose into sorbitol over the present catalyst.

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Notes and references