Transfer hydrogenation of cellulose to sugar alcohols over supported ruthenium catalysts

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Ru/C catalysts are active for the conversion of cellulose using 2-propanol or H2 of 0.8 MPa as sources of hydrogen, whereas Ru/Al2O3 catalyst is inactive in both reactions, indicating that the Ru/C catalysts are remarkably effective for the cellulose conversion.

The conversion of renewable biomass to useful chemicals is one of the most important goals in green and sustainable chemistry. In order to avoid competition with food production, as seen in the last few years, non-food biomass should be used as a biomass resource for the manufacture of chemicals. Cellulose is the most abundant non-food biomass resource produced via photosynthesis, and therefore the conversion of cellulose has attracted significant attention as a key issue in the utilisation of biomass. Cellulose is a water-insoluble polymer composed of glucose units linked by β-1,4-glycosidic bonds, and the hydrolysis-hydrogenation (abbreviated as hydrogenation) of cellulose gives sugar alcohols, which are versatile precursors to plastics, fuels and pharmaceuticals. Therefore, sugar alcohols are among the major targets in the transformation of cellulosic biomasses.

Since we reported the conversion of cellulose to sorbitol and mannitol by supported Pt and Ru catalysts under H2 pressure, other groups have also reported the degradation of cellulose to sorbitol or ethylene glycol using various supported metal catalysts under high pressures of H2 (> 5 MPa). These solid catalysts have the advantage of easy separation and produce the desired chemicals in good yields under aqueous conditions. However, one of their disadvantages is the need for pressurised H2. As an alternative to H2 pressure, we investigated the transfer hydrogenation of cellulose using an alcohol and found that sugar alcohols are obtained as major products using the carbon-supported Ru catalysts (Scheme 1). To the best of our knowledge, the transfer hydrogenation of cellulose using heterogeneous catalysts has not previously been reported.

Table 1 summarises the results of the transfer hydrogenation of cellulose by various supported Ru catalysts using 2-propanol as a source of hydrogen without bases.†

Among the catalysts, the Ru carbons [Ru/AC(N), Ru/C-Q10 and Ru/CMK-3] gave the highest yields of sugar alcohols (entries 3, 8, 9). For example, the yields in the reaction using Ru/C-Q10 were 37% sorbitol and 9.0% mannitol for a total of 46% (0.87 mmol). The turnover number (TON) based on bulk Ru (0.01 mmol) for the sum of the sugar alcohols was 87. The conversion of cellulose was 80%, which was determined from the weight difference of the solid after the reaction.
Transfer hydrogenation of cellulose by supported metal catalysts.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Yield based on carbon %</th>
<th>Cellulose conv. %</th>
<th>Yield of acetone %</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Sorbitol</td>
<td>Mannitol</td>
<td>Sum of sorbitol and mannitol</td>
<td>Sorbitan C2-C4 polyols</td>
</tr>
<tr>
<td>1</td>
<td>None</td>
<td>0</td>
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<td>2</td>
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<td>3</td>
<td>Ru/AC(N)</td>
<td>33.5</td>
<td>9.0</td>
<td>42.5</td>
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<tr>
<td>4</td>
<td>Ru/AC(N)</td>
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<td>10.6</td>
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<td>5</td>
<td>Ru/AC(N)</td>
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<td>2.4</td>
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<td>Ru/AC(N)</td>
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<td>8.3</td>
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<tr>
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<td>Ru/AC(W)</td>
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<td>Ru/Al2O3</td>
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<td>Ru/AC(N)</td>
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</table>

**Notes:**
- Sorbitan C2-C4 polyols and others include soluble sugar compounds and unidentified ones.
- Based on the carbon balance calculated from the weight difference after the reaction.
- The catalyst was separated by centrifugation from the reaction mixture and reused after drying at 383 K.
- The reuse experiment using the residue of the experiment of the previous entry number 6.
- The catalyst was deactivated in the third run (entry 5).
- EDX and XRD analyses of the spent catalyst were performed to verify its durability.
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It is proposed that the active species for the transfer hydrogenation is a cationic Ru species. This work was financially supported by JSPS KAKENHI (20226016).

Notes and references

11 The optimisation of the reaction conditions using Ru/AC(N) catalyst is shown in the ESI: effect of the concentration of 2-propanol (Table S1), screening of the hydrogen source (Table S2).