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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 H_2 of 0.8 MPa as sources of hydrogen, whereas Ru/Al_2O_3 catalyst is inactive in both reactions, indicating that the**
10 **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.[1] In order to avoid competition with food
15 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,[2] and therefore the conversion of cellulose has attracted significant attention as a
20 key issue in the utilisation of biomass.[3] Cellulose is a water-insoluble polymer composed of glucose units linked by β-1,4-glycosidic bonds,[2,4] and the hydrolysis-hydrogenation (abbreviated as hydrogenation) of cellulose gives sugar alcohols, which are versatile precursors to plastics, fuels and
25 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 H_2 pressure,[5] other groups have also reported the degradation of
30 cellulose to sorbitol[6] or ethylene glycol[7] using various supported metal catalysts under high pressures of H_2 ($\geq$ 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
35 disadvantages is the need for pressurised H_2. As an alternative to H_2 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
40 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.‡
45 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
50 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.
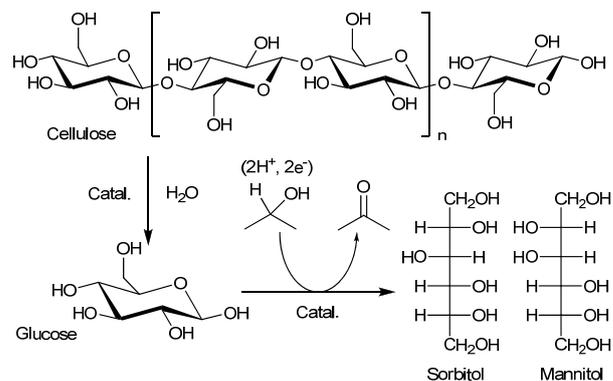
Scheme 1 Transfer hydrogenation of cellulose to sugar alcohols.

55 Accordingly, the selectivity based on the cellulose conversion for the sum of the sugar alcohols was 57%. 1,4-Sorbitan (1.4%), C_2-C_4 polyols (total 5.3%: ethylene glycol 0.8%, propylene glycol 1.8%, glycerine 1.2% and erythritol 1.5%), and glucose (0.7%) were produced as minor products. As the
60 source of hydrogen, 15% of 2-propanol (20 mmol) was converted to acetone, which was 22 times as much as the yield of the sugar alcohols (0.87 mmol). Thus, only 4.5% of the hydrogen species was utilised for the production of the sugar alcohols and the other part evolved as H_2 gas during the
65 reaction (see below). Ru/AC(W) (sugar alcohol yield 23%), Ru/BP2000 (14%) and Ru/XC72 (3.0%) were less active than Ru/AC(N), Ru/C-Q10 and Ru/CMK-3 (entries 7, 10, 11). Ru/TiO_2, Ru/ZrO_2 and Ru/Al_2O_3 were inactive for the reaction (entries 12-14), which indicates that the catalytic activity of
70 Ru greatly depends on the supports. It is notable that Ru/Al_2O_3 is an active catalyst for the hydrogenation of cellulose to sugar alcohols using H_2 gas of 5 MPa,[5] while it is completely inactive for the transfer hydrogenation (entry 14). Thus, we suggest that the active Ru species in this transfer
75 hydrogenation is different from that in the typical hydrogenation reaction with H_2. In the reactions using the inactive catalysts (entries 12-14), glucose and 5-hydroxymethylfurfural (5-HMF) formed instead of the hydrogenated products with almost no conversion of 2-
80 propanol. This is the same tendency as in the reactions without Ru catalysts (entries 1, 2), indicating that the hydrolysis of cellulose to glucose proceeds with or without catalysts[6a, 8-10] and that an active Ru species hydrogenates glucose to the sugar alcohols using a hydrogen species derived
85 from 2-propanol. Carbon-supported Rh, Ir, Pd, Pt and Au catalysts were also tested for the reaction (entries 16-20), but the sugar alcohols were not obtained. Therefore, we chose

Table 1 Transfer hydrogenation of cellulose by supported metal catalysts.[a]

| Entry	Catalyst	Yield based on carbon /%								Cellulose conv.[e] /%	Yield of acetone /%
		Sorbitol	Mannitol	Sum of sorbitol and mannitol	Sorbitan	C_2-C_4 polyols[b]	Glucose	5-HMF[c]	Others[d]		
1	None	0	0	0	0	0	3.8	19.0	42.2	65.0	<0.1
2	AC(N)	0	0	0	0	0	1.5	12.8	50.6	64.9	<0.1
3	Ru/AC(N)	33.5	9.0	42.5	0.6	6.1	0.9	0	24.3[h]	74.4	15 (24)[j]
4[f]	Ru/AC(N)	36.3	10.6	46.9	0.9	6.7	1.1	0	29.6	85.2	15 (22)[j]
5[f]	Ru/AC(N)	2.0	0.4	2.4	0	0	4.4	11.6	88.6	107	1.6 (46)[j]
6[g]	Ru/AC(N)	29.5	8.3	37.8	1.4	6.9	0.7	0.3	35.8	82.9	–
7	Ru/AC(W)	18.5	4.2	22.7	0.4	4.8	1.2	0	32.7	61.8	15 (45)[j]
8	Ru/C-Q10	36.8	9.0	45.8	1.4	5.3	0.7	0	27.0	80.2	15 (22)[j]
9	Ru/CMK-3	35.7	9.3	45.0	1.4	7.1	0.8	0	26.9	81.2	15 (23)[j]
10	Ru/BP2000	11.6	2.4	14.0	0.3	3.0	1.3	2.1	59.1	79.8	14 (68)[j]
11	Ru/XC72	2.7	0.3	3.0	0.1	0	1.0	1.6	72.0	77.7	8.4 (190)[j]
12	Ru/TiO$_2$	0.1	0	0.1	0	0	3.5	12.8	60.0	76.4	0.6
13	Ru/ZrO$_2$	0	0	0	0	0	2.5	13.0	62.9	78.4	0.4
14	Ru/Al$_2$O$_3$	0	0	0	0	0	2.5	14.0	55.6[i]	72.1	0.7
15[g]	Ru/Al$_2$O$_3$	2.6	0.8	3.4	0	6.5	0.9	0.7	65.2	76.7	–
16	Rh/AC(N)	0	0	0	0	0	2.7	10.1	61.8	74.6	0.5
17	Ir/AC(N)	0	0	0	0	0	1.3	4.6	67.9	73.7	2.3
18	Pd/CMK-1	0	0	0	0	0	0.4	5.7	74.5	80.6	<0.1
19	Pt/CMK-3	0	0	0	0	0	1.1	0	80.9	82.0	4.9
20	Au/AC(N)	0	0	0	0	0	1.6	14.6	42.6	58.8	1.4

[a] Cellulose 324 mg (1.90 mmol), catalyst 50 mg (metal 2 wt%), water 30 mL, 2-propanol 10 mL (130 mmol), 463 K, 18 h. [b] Sum of erythritol, glycerine, propylene glycol and ethylene glycol. [c] 5-Hydroxymethyl furfural. [d] Others include soluble sugar compounds and unidentified ones. [e] Based on the carbon balance calculated from the weight difference after the reaction. [f] The reuse experiment using the residue of the experiment of the previous entry number and fresh cellulose of 324 mg. The conversion and yields are based on the fresh cellulose. [g] H$_2$ of 0.8 MPa was used instead of 2-propanol. Water 40 mL. [h] Cello-oligosaccharides 1.5%, cellobitol 1.0%, hexanetetrol 4.0% and unidentified 17.8% (Fig. S1). [i] Cello-oligosaccharides 1.9%, fructose 2.3%, levoglucosan 0.6%, furfural 1.3% and unidentified 49.5%. [j] Ratio of acetone yield against the sugar alcohols yield (mol/mol).

Ru/AC(N) as the typical catalyst hereafter because of its significant catalytic activity, good reproducibility and easy availability of the support.[11]

Reuse experiments of Ru/AC(N) were performed to verify its durability. The catalyst was separated by centrifugation from the reaction mixture and reused after drying at 383 K. The yields of sorbitol and mannitol were 36% and 11%, respectively, in the second use (entry 4), which were almost the same as those in the first run (sorbitol 34%, mannitol 9.0%). However, the catalyst was deactivated in the third run (entry 5). EDX and XRD analyses of the spent catalyst showed no change of the catalyst after the third use. Thus, the deactivation might be due to the strong adsorption of by-products on the active sites. The catalyst was usable twice and total TON of Ru for the production of the sugar alcohols was 170 in the reactions. In addition, the filtrate separated by polytetrafluoroethylene (PTFE) membrane (0.1 μm pore) after the first reaction was completely inactive for the transfer hydrogenation. Accordingly, we conclude that Ru/AC(N) is a heterogeneous catalyst for the transfer hydrogenation.

As described above, H$_2$ was produced during the transfer hydrogenation reactions, whose partial pressure reached 0.8 MPa in the closed reactor from the chemical equilibrium (Eq. 1) at 463 K in the initial period of 0.5 h. It is noteworthy that the reduction of the dead volume in the reactor decreases the evolution of H$_2$ and improves the utilisation efficiency of 2-propanol as the equilibrium shifts to the left-hand side. Considering this phenomenon, we expected that the hydrogenation of cellulose would proceed at a H$_2$ pressure as low as 0.8 MPa without 2-propanol by using Ru/AC(N) catalyst. In fact, the reaction gave good yields of the sugar

alcohols (sorbitol 30%, mannitol 8.3%, entry 6), whereas Ru/Al$_2$O$_3$, which is a typical active catalyst for the hydrogenation of cellulose with H$_2$ of 5 MPa, was significantly less active (sorbitol 2.6%, mannitol 0.8%, entry 15) under the same reaction conditions. This result indicates that the active species of Ru/AC(N) is different from that of Ru/Al$_2$O$_3$.

$$(CH_3)_2CH–OH \Leftrightarrow (CH_3)_2C=O + H_2 \quad (1)$$
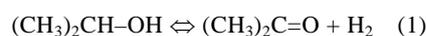
To identify the active species for the transfer hydrogenation, XRD analysis was performed for Ru/AC(N) and Ru/Al$_2$O$_3$. Fig. 1 represents the XRD patterns of AC(N), Ru/AC(N) and the differential pattern of Ru/AC(N) minus AC(N). AC(N) gave a broad scattering pattern of amorphous carbon ($2\theta = 23°$, 43° and 80°) and sharp diffraction peaks of quartz, which is an impurity of AC(N) [Fig. 1(a)]. After the impregnation of Ru, no diffraction peaks of Ru metal appeared in the XRD [Fig. 1(b, c)], even when the Ru loading was increased to 10 wt% (Fig. S2). These data show that the Ru species on AC(N) was highly dispersed and/or not fully reduced to zero-valent particles during the catalyst preparation. We performed H$_2$-temperature programmed reduction (TPR) of Ru/AC(N) (Fig. S3), and 4 peaks appeared at 410, 530, 670 and 860 K with the H/Ru atomic ratios of 13, 3.5, 2.9 and 11, respectively. The second or the third peaks might be assigned to the reduction of the Ru species by correlating the peak areas with the Ru concentration, suggesting tri- or tetra-valent Ru. Other peaks are due to the reduction of the surface functional groups on the carbon support such as quinones and aromatic rings. In the XPS analysis, the electron binding energy of Ru 3p$_{3/2}$ for
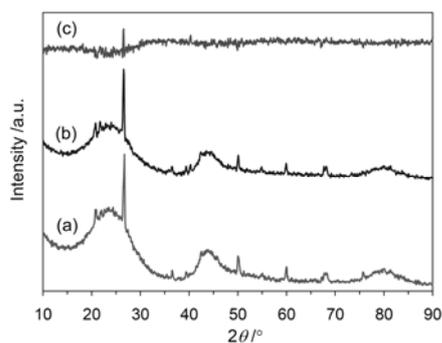
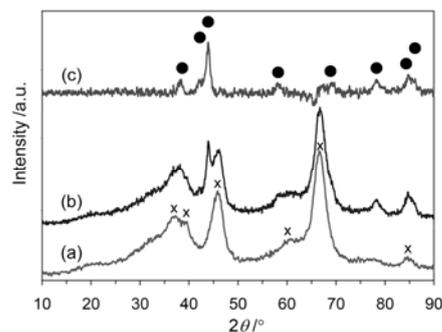**Fig. 1** XRD patterns of (a) AC(N), (b) Ru/AC(N) and (c) the differential pattern of (b)–(a).

Fig. 2 XRD patterns of (a) Al_2O_3, (b) Ru/Al_2O_3 and (c) the differential pattern of (b)–(a). Circles: Ru metal. x: γ-Al_2O_3.

Ru/AC(N) catalyst was 463.1 eV, which is in the range of tri- to tetra-valent states and higher than that for Ru metal (461.9 eV, Fig. S4). Fig. S5 shows the curve fitting of the XPS data for Ru/AC(N), and the spectrum was fitted by those of RuO_2 (99.7%) and Ru metal (0.3%), giving a similar electron state to that of RuO_2. It is thus indicated that the Ru species on AC(N) is not metal but tetra- or tri-valent. Fig. 2 shows the XRD patterns of Al_2O_3, Ru/Al_2O_3 and the differential pattern of Ru/Al_2O_3 minus Al_2O_3. The pattern of Al_2O_3 indicated the presence of γ-Al_2O_3 phase [Fig. 2(a)]. After the loading of Ru, the diffraction pattern of Ru metal was observed with the peaks of γ-Al_2O_3 [Fig. 2(b)]. The differential pattern [Fig. 2(c)] clearly showed the peaks of Ru metal, marked with black circles. The mean diameter of Ru particles was 9 nm, calculated by the Scherrer's equation, which was reported as the best particle size for the selective hydrogenation of cellobiose using H_2 of 5 MPa.[12] Therefore, we conclude that the highly dispersed cationic Ru species is active for the transfer hydrogenation reaction, whereas Ru metal nanoparticles are inactive for this reaction.

In summary, Ru/AC(N), Ru/C-Q10 and Ru/CMK-3 catalysts were active for the transfer hydrogenation of cellulose to sugar alcohols. Ru/AC(N) also catalysed the hydrogenation of cellulose at a H_2 pressure as low as 0.8 MPa. The catalytic activity of Ru/AC(N) is significantly different from those of the typical catalysts for the cellulose hydrogenation such as Ru/Al_2O_3, which require high pressures of H_2. It is proposed that the active species for the transfer hydrogenation is a cationic Ru species.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [analysis methods of products, characterisation procedures of the catalysts, XRD, H_2-TPR, XPS, optimisation of the reaction]. See DOI: 10.1039/b000000x/
‡ The catalyst supports used in this study are as follows. CMK-1 and CMK-3 were synthesised according to procedures in the literature.[13] Carbon (C-Q10, BET surface area 840 m^2 g^{-1}) was prepared using an amorphous silica (Q-10, Fuji Silysia) in the same manner as for CMK-3. Activated carbons were purchased from Wako (activated charcoal), denoted as AC(W) and Aldrich (SX Ultra, Norit), denoted as AC(N). Carbon blacks (VULCAN XC72 and BP2000) were supplied from Cabot. Other supports are TiO_2 (P-25, Degussa), ZrO_2 (JRC-ZRO-2, Catalysis Society of Japan) and Al_2O_3 (JRC-ALO-2, Catalysis Society of Japan).

Supported Ru catalysts (Ru metal loading 2 wt%) were prepared by a conventional impregnation method as follows: $RuCl_3$ aq. (0.202 mmol in 5 mL of water) was dropped into a mixture of a catalyst support (1.00 g) and water (20 mL), and the mixture was stirred for 16 h. After drying *in vacuo*, the solid was reduced in a fixed-bed flow reactor with H_2 (30 mL min^{-1}) at 673 K for 2 h. In the cases using oxide supports, the precursors were calcined with O_2 (30 mL min^{-1}) at 673 K before the H_2 reduction.

Transfer hydrogenation of cellulose was carried out in a stainless steel (SUS316) high-pressure reactor (OM Lab-Tech MMJ-100, 100 mL). Cellulose (Merck, Avicel) was milled using ZrO_2 balls at 60 rpm for 4 days. The milled cellulose (324 mg, 1.90 mmol glucose units, containing 4.8 wt% physisorbed water), supported Ru catalyst (50 mg), water (30 mL) and 2-propanol (10 mL) were charged in the reactor (glucose unit/Ru = 190), and then purged with 1 atm of N_2 or He. The mixture was heated to 463 K and maintained at this temperature for 18 h with stirring at 600 rpm. The analysis methods of products and the characterisation procedures of the catalysts are described in the ESI.

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