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Selective hydrogenation of arenes to cyclohexanes in water catalyzed by chitin-supported ruthenium nanoparticles†

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The selective hydrogenation of aromatic compounds to cyclohexanes was found to be promoted by chitin-supported ruthenium nanoparticles (Ru/chitin) under near-neutral, aqueous conditions without the loss of C–O/C–N linkages at benzylic positions.

The catalytic hydrogenation of arenes is a straightforward and hugely important method by which cyclohexanes are produced.[1,2] However, a major issue with this transformation is the need to suppress the competitive hydrogenolysis of reactive carbon–heteroatom linkages (*e.g.* C–O and C–N bonds) at benzylic positions.[3,4] Attempts to address this problem typically focus on using acetic acid as a (co-)solvent in the presence of late transition metal catalysts such as PtO_2,[5a,b] Rh–PtO_2,[5c] RuO_2,[6a] Ru/Al_2O_3 [6b] and Rh/Al_2O_3.[7] The most frequently used catalysts are Ru/Al_2O_3 or, substantially more expensive, Rh/Al_2O_3. However, irrespective of the choice of catalyst, the use of acidic reaction media is incompatible with substrates bearing acid-sensitive functionalities such as epoxides and tertiary benzylic alcohols. Recently studied catalysts that have allowed the selective arene hydrogenation of benzyl alcohols or ethers in the absence of acidic additives include Rh/AlO(OH),[8a] Ru/MCM-41,[8b] Ru/CNF-P,[9a,b] Rh/CNF-T[9c] and Ru/HPS-NR_3Cl.[9d] In particular, Motoyama and Nagashima elegantly demonstrated the simultaneous tolerance of epoxide and benzylic C–O functionalities using Rh/CNF-T or Ru/HPS-NR_3Cl.[9c,d] However, with the exception of the Ru/HPS-NR_3Cl system, which utilized H_2O as a solvent,[9d] these reactions were typically run in hydrocarbons or polyethylene glycol.[10,11] The development of catalytic systems that operate under aqueous conditions remains strongly in demand, since it promises a route to functionalized, water-soluble cyclohexanes for applications in materials and biological sciences.[4g,12] We here disclose that chitin-supported ruthenium nanoparticles (Ru/chitin) efficiently catalyze arene hydrogenation under aqueous conditions without hydrogenolyzing C–O/C–N bonds at the benzylic positions.

In recent work we established that Ru/chitin serves as an efficient catalyst for the hydration of nitriles to amides under aqueous conditions.[13,14] Based on this result, we reasoned that Ru/chitin should also be suited to the chemoselective hydrogenation of functionalized arenes because the nitrile hydration operated under near-neutral conditions[13] and supported ruthenium nanoparticles are known to be good catalysts for arene hydrogenation.[6,8b,9a,b,10a–d,15] As shown in Table 1, the activity of Ru was tested in the hydrogenation of benzyl glycidyl ether (**1a**) to cyclohexylmethyl glycidyl ether (**2a**). This reaction allowed the monitoring of both reactivity and selectivity for arene hydrogenation over hydrogenolysis at the benzylic position or acid-/base-mediated opening of the oxirane ring.[9c,16] Currently known catalysts effective in this transformation are limited to just two tailor-made systems: Rh/CNF-T (rt, 12 h)[9c] and Ru/HPS-NR_3Cl (30 °C, 24 h).[9d,17] Ru/chitin can be prepared by simple impregnation–reduction using inexpensive $RuCl_3{\cdot}3H_2O$, $NaBH_4$ and commercially available chitin under aqueous conditions and in the absence of capping agents.[13] Results demonstrate that the hydrogenation of **1a** was effectively catalyzed by Ru/chitin. When a mixture of **1a** (1.0 mmol), H_2O (5 mL) and Ru/chitin (0.8 wt%, 0.008 mmol of Ru, 0.8 mol% Ru) was stirred at 50 °C under a H_2 atmosphere (2 MPa), the hydrogenation was completed within 1.5 h and cyclohexane **2a** was obtained in 98% yield (Table 1, entry 1). ICP-AES on the Ru/chitin catalyst before and after the hydrogenation cycle established that only negligible leaching of Ru (4.2 ppm) took place during the catalytic test. The hydrogenation proceeded in water with no detectable loss of the C–O linkages in the substrates, there being no appreciable formation of side products **3a–6a**. This result was reproducible (^{1}H NMR yields of **2a** in separate runs: 97, 95 and 97%). Product **2a** could be isolated in 84%

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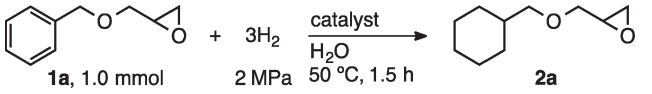
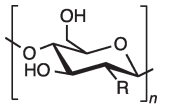
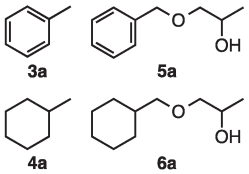
Table 1 Hydrogenation of **1a** to **2a**[a]



Entry	Catalyst	Conv. of **1a**[b] (%)	Yield of **2a**[b] (%)	Combined yield of **3a** and **4a**[c] (%)	Combined yield of **5a** and **6a**[b] (%)
1	Ru/chitin	>99	98	<1	<1
2	None	<1	<1	<1	<1
3	Chitin	4	<1	<1	<1
4	$RuCl_3{\cdot}3H_2O$	>99	75	6	12
5	RuO_2[d]	1	<1	1	<1
6	Ru/cellulose	>99	97	2	<1
7	Ru/chitosan	47	41	<1	<1
8	Ru/γ-Al_2O_3	40	36	3	<1
9	Ru/C	51	43	4	1
10	Ru/Al_2O_3[d,e]	19	15	2	<1
11	Rh/Al_2O_3[d,e]	>99	92	5	<1
12	Ru/C[d,e]	>99	87	4	7
13	Rh/C[d,e]	>99	24	25	38
14	Pd/C[d,f]	96	<1	25	69





[a] Conditions: **1a** (1.0 mmol), catalyst (0.8 mol% Ru) and H_2O (5 mL) at 50 °C for 1.5 h under H_2 (2 MPa). [b] Determined by ^1H NMR using mesitylene as an internal standard. [c] GC-MS yield using *n*-octane as an internal standard. [d] Purchased from commercial suppliers. [e] 5 wt% Ru or Rh. [f] 10 wt% Pd.

yield after removal of the catalyst and SiO_2 column chromatography, with Ru contamination proving lower than the detection limit of ICP-AES (<1 ppb). Results demonstrate that both ruthenium and chitin were necessary for selective arene hydrogenation (entry 1 *vs.* entries 2–5). Moreover, heterogeneous catalysts prepared analogously to Ru/chitin but using cellulose, chitosan, γ-Al_2O_3 or carbon promoted arene hydrogenation but with lower selectivity (entries 6–9). Among these, hydrogenation with Ru/cellulose[15c] was also found to be distinctly effective, although appreciable amounts of side-products were formed through hydrogenolysis (Table 1, entry 6). Results obtained using commercially available catalysts are summarized in entries 10–14. Rh/Al_2O_3 (Sigma-Aldrich) proved efficient (**2a**: 92% yield) but induced partial hydrogenolysis to **3a** or **4a** (entry 11). Lastly, Ru/C (TCI)[18] was also a moderately good catalyst (**2a**: 87% yield) but caused competing epoxide ring-opening (entry 12).[19]

Results in Table 2 demonstrate that Ru/chitin-promoted selective arene hydrogenation was compatible with benzylic C–O or C–N linkages in alcohol, ether, amide and amino functionalities in a wide range of substrates (**1b**–$\mathbf{k_{Na}}$). The corresponding cyclohexanes **2b**–$\mathbf{k_{Na}}$ were obtained in good-to-excellent isolated yields, with the products typically being isolated by distillation or column chromatography after simply removing the catalyst by filtration or centrifugation. Hydrogenation of significantly acid-sensitive benzyl alcohols **1d** and

Table 2 Catalytic hydrogenation of arenes (**1**) to cyclohexanes (**2**) with Ru/chitin[a]

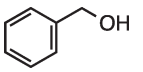
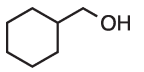
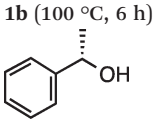
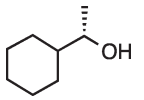
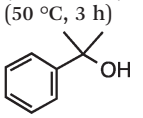
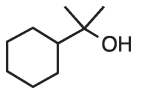
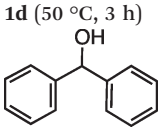
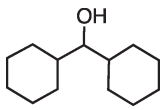
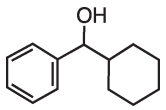
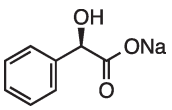
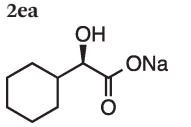
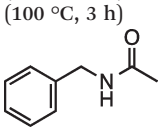
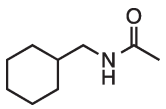
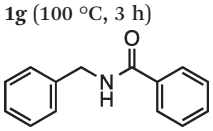
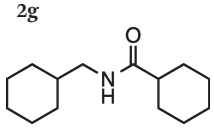
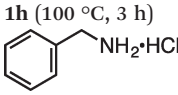
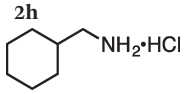
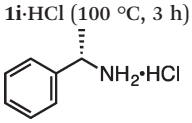
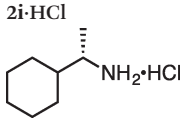
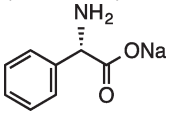
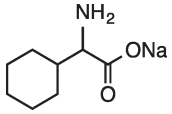
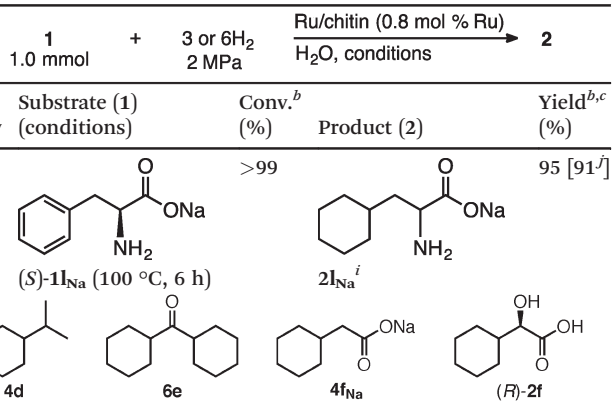
Entry	Substrate (**1**) (conditions)	Conv.[b] (%)	Product (**2**)	Yield[b,c] (%)
1	 **1b** (100 °C, 6 h)	>99	 **2b**	90 [66[d]]
2	 (*S*)-**1c** (*S* : *R* = 97 : 3)[e] (50 °C, 3 h)	>99	 (*S*)-**2c** (*S* : *R* = 94 : 6)[e]	95 [92]
3	 **1d** (50 °C, 3 h)	>99[f]	 **2d**	90 [88]
4	 **1e** (50 °C, 6 h)	>99[f]	 **2e**	79 [75]
			 **2ea**	13 [17]
5	 (*R*)-$\mathbf{1f_{Na}}$ (*S* : *R* = 1 : 99)[g] (100 °C, 3 h)	91[f]	 (*R*)-$\mathbf{2f_{Na}}$ (*S* : *R* = 1 : 99)[e]	85 [82[h]]
6	 **1g** (100 °C, 3 h)	>99	 **2g**	99 [93]
7	 **1h** (100 °C, 3 h)	>99	 **2h**	97 [95]
8	 **1i**·HCl (100 °C, 3 h)	>99	 **2i**·HCl	93 [92]
9	 (*S*)-**1j**·HCl (*S* : *R* = 99 : 1)[e] (100 °C, 3 h)	>99	 (*S*)-**2j**·HCl (*S* : *R* = 96 : 4)[e]	96 [91]
10	 (*S*)-$\mathbf{1k_{Na}}$ (100 °C, 3 h)	>99	 $\mathbf{2k_{Na}}$[i]	96 [90[j]]

Table 2 *(continued)*

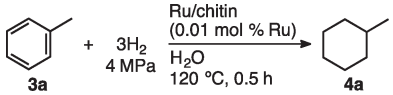


Entry	Substrate (1) (conditions)	Conv.[b] (%)	Product (2)	Yield[b,c] (%)
11	(*S*)-**1l**$_{Na}$ (100 °C, 6 h)	>99	**2l**$_{Na}$[i]	95 [91[j]]
	4d		**6e**	
	4f$_{Na}$		(*R*)-**2f**	

[a] Conditions: **1** (0.50 or 1.0 mmol), Ru/chitin (0.8 mol% Ru), H_2O (5 mL) and H_2 (2 MPa). [b] Determined by ^{1}H NMR using mesitylene as an internal standard. [c] Isolated yield in parentheses. [d] Low yield due to the volatile nature of the product. [e] Absolute configuration and optical purity were determined by a polarimeter and chiral GC analyses. [f] Side-products were detected: entry 3, **4d** (3%); entry 4, **6e** (7%); entry 5, **4f**$_{Na}$ (6%). [g] As indicated by the supplier. [h] Yield of carboxylic acid (*R*)-**2f** after the addition of HCl aq. [i] Optical purity was not determined. [j] Yield of **2**·HCl after the addition of HCl aq.

1e proceeded without loss of the C–O bonds (Table 2, entries 3 and 4).[20] Marginal amounts of side-products were detected when using **1d**–**f**$_{Na}$ (entries 3–5). The absolute configurations of (*S*)-**1c**, (*R*)-**1f**$_{Na}$ and (*S*)-**1j**·HCl were retained under our reaction conditions (entries 2, 5 and 9).[21] Unfortunately, double hydrogenation of dibenzyl ether or dibenzylamine·HCl was sluggish due to low reactivity and competitive hydrogenolysis at the benzylic positions.[22] However, arene **1h** could be doubly hydrogenated to give the dicyclohexyl analogue **2h** in excellent yield (entry 7). By virtue of the aqueous conditions used, hydrophilic sodium carboxylates **1f**$_{Na}$ and **1k**$_{Na}$ as well as ammonium salts **1i**·HCl and **1j**·HCl could be effectively converted to give the corresponding salts of substituted cyclohexanes (entries 5, 8–10). In particular, the hydrogenation of **1k**$_{Na}$ to **2k**$_{Na}$ represents an important route for preparing non-standard amino acid-bearing hydrophobic cyclohexyl rings from more accessible aromatic analogues.[4g,12] In a similar vein, the hydrogenation of sodium phenylalanate (**1l**$_{Na}$) with Ru/chitin also gave the corresponding cyclohexyl-bearing amino acid **2l**$_{Na}$ in high yield (entry 11). The substrate scope of other typical aromatic rings is summarized in Table S3.†

The hydrogenation of toluene (**3a**) by Ru/chitin in water showed a turnover frequency (TOF) of 6000 h^{-1} and a turnover number (TON) of 3000 based on the amount of consumed H_2 (eqn (1)). These values are higher than or comparable to those in previously reported hydrogenations of **3a** in water with other Ru or Rh catalysts (Ru: TOF and TON, 10–2700 h^{-1} and 240–2700; Rh: 100–11 000 h^{-1} and 300).[4e,9d,10]



(1)

The reusability of the Ru/chitin catalyst was tested over seven consecutive reductions of **1a**, with the catalyst being recovered by centrifugation each time. Results indicated only a modest loss of catalytic activity and selectivity (hydrogenation of **1a**: 1st run, 98% yield; 2nd run, 96% yield; 3rd run, 94%; 4th run, 90%; 5th run, 89%; 6th run, 87%; 7th run, 87%, Table S4†). This behavior was investigated by HRTEM analysis (Fig. 1). Analysis after either 1 or 6 hydrogenation cycles suggested that the nanoparticles continued to incorporate pristine metal, with an observed *d*-spacing of 2.14–2.17 Å attributed to the Ru(002) plane of Ru^0. However, nanoparticle sintering was clearly observed after repeated testing, with the mean particle size growing from 2.3 ± 0.3 nm in the fresh catalyst (Fig. 1a) to 3.5 ± 0.8 nm after 6 hydrogenation cycles (Fig. 1c). TEM, EDX and XRD analyses of the as-prepared Ru catalysts (Fig. S1–S9†) suggest that 2–3 nm nanoparticles represent both the most efficient and selective of the catalysts tested. Interestingly, results point to the inexpensive polysaccharide supports chitin and cellulose accommodating such particles (Table S5 and Fig. S10†) more readily than other commercially available supports do when using the same preparative route. Though one commercially sourced Ru/C catalyst

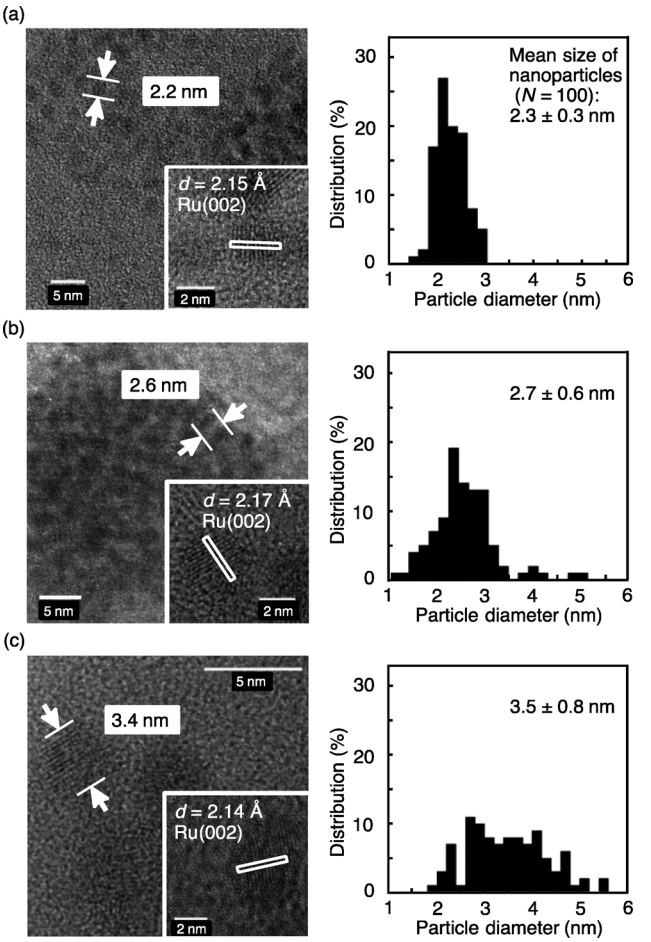


Fig. 1 TEM images and particle size distributions of Ru/chitin: (a) as prepared, (b) after 1 cycle and (c) after 6 cycles of hydrogenation of **1a**.

contains comparably-sized nanoparticles, the selectivity is lower than Ru/chitin or Ru/cellulose (Fig. S8 and Table S5†).

In summary, we have prepared 2–3 nm chitin-supported ruthenium nanoparticles in the absence of additional capping agents. They have promoted efficient hydrogenation of arenes to cyclohexanes under near-neutral, aqueous conditions, with hydrogenation taking place to the exclusion of hydrogenolysis of normally reactive C–O and C–N linkages. Of importance, preliminary data point to the use of this readily available, environmentally benign support material being synonymous with the generation of nanoparticles whose dimensions provide both excellent conversion and selectivity. Ongoing work is seeking to more precisely investigate morphological changes exhibited by Ru/chitin in order to counteract the modest loss of activity after multiple hydrogenation cycles and to assess the possibility of developing these systems in a microfluidic context.

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16 **2a** can also be a (co-)monomer for preparing epoxide resins.

17 (*a*) Ref 9*c*: **1a** (0.5 mmol), Rh/CNF-T (10 mg, 0.2 wt% Rh, 0.04 mol% Rh), H_2 (1 MPa), *n*-hexane (1 mL), rt, 12 h; **2a**, >99% yield; (*b*) Ref 9*d*: **1a** (1 mmol), Ru/HPS-NR_3Cl (0.3 mol% Ru), H_2 (3 MPa), H_2O (1 mL), 30 °C, 24 h; **2a**, 96% yield.

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22 Hydrogenation of dibenzyl ether (100 °C, 6 h, 91% conv.) gave a mixture of bis(cyclohexylmethyl) ether (27%), benzyl cyclohexylmethyl ether (38%), **2b** (7%) and other unidentified products. Hydrogenation of dibenzylamine·HCl (100 °C, 5 h, >99% conv.) gave a mixture of bis(cyclohexylmethyl)amine·HCl (21%) and **2i**·HCl (74%).