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ARTICLE

Chemoselective transfer hydrogenation of α, β-unsaturated carbonyl compounds using potassium formate over amine-grafted Ru/AlO(OH) catalysts

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Grafting of 3-(2-aminoethylamino) propyltrimethoxysilane onto Ru/AlO(OH) resulted in an active and highly chemoselective heterogeneous catalyst for the transfer hydrogenation of α, β-unsaturated carbonyl compounds to the corresponding allylic alcohols. Potassium formate was used as a sustainable hydrogen donor. A range of substrates including cinnamaldehyde, α-amylcinnamaldehyde, citral, 3-methyl-2-butenal, *trans*-2-pentenal, and *trans*-hexenal were selectivity hydrogenated at the C=O moiety with > 96 % selectivity. In comparison, the unmodified 1 wt. % Ru/AlO(OH) catalyzed hydrogenation of cinnamaldehyde at the C=C bond, yielding 3-phenylpropanal as the product. Higher loaded samples with 2 – 10 wt. % Ru exhibited 20 – 25 % selectivity to cinnamyl alcohol. The results show that low coordination sites were more selective to hydrogenation of the internal C=C than the terminal C=O bond. Immobilization of the amine via chemical bonding with hydroxyl groups of the AlO(OH) support blocks adjacent exposed metal sites, increasing the chemoselective reduction of C=O. Optimum results were achieved at an amine/Ru ratio of 6. The catalyst maintained high activity and chemoselectivity even after five cycles.

Introduction

The chemoselective hydrogenation of α, β-unsaturated carbonyl compounds to the corresponding allylic alcohols is an important step in the industrial synthesis of fine chemicals, in particular, pharmaceuticals, perfumes and cosmetics.[1-3] In terms of thermodynamics and kinetics, the hydrogenation of C=C bonds is easier than that of C=O bonds.[4] Although extensive studies have been done, the chemoselective synthesis of allylic alcohol via catalytic hydrogenation rather than by traditional stoichiometric reduction remains a challenge. Conventional hydrogenation catalysts based on supported Ni,[5] Pt,[6,7] Pd,[8] Ru,[9,10] and Rh[11] produce mainly saturated aldehydes/ketones. Therefore, much effort has been made to overcome this problem over the past decades. The use of promoters, different types of supports, and varying the metal particle size have been explored and discussed in reviews.[12,13] For cinnamaldehyde, the selectivity towards C=O hydrogenation could be improved if the Ru particle size for Ru/C increased from 3 nm to 16.8 nm.[14] A similar dependence on particle size was observed for supported Pt and Rh particles,[15] although for very small particles of ~ 1.5 – 2.5 nm, Zhu and Zaera found no preferential C=O selectivity.[16] The change in selectivity was attributed to a steric effect where the cinnamaldehyde molecule cannot adsorb with its plane parallel to the surface because of the aromatic ring. Theoretical calculations showed the phenyl ring encounters an energy barrier for distances less than 0.3 nm from the surface.[17,18] Hence, the molecule is tilted with the C=O extremity being closer to the surface than the C=C bond. In citral where no aromatic ring is present, this steric effect is absent, and no difference in the product distribution was observed with a change of the metal particle size.[19]

The choice of metal is another important factor in chemoselective hydrogenation. Gold shows an intrinsic selectivity toward hydrogenation of the conjugated C=O bond, forming 60 - 80 % yields of allylic alcohols.[20-22] Using theoretical calculations, Delbecq and Sautet rationalized that metals with larger d bands encounter stronger four-electron repulsions with the C=C bond, lowering the probability of its adsorption and hydrogenation.[23] This was supported by experimental results where the selectivity to allylic alcohols increased in the order Pd < Pt < Ir, Os.[12] The selectivity to the allylic alcohol can also be improved by using a second metal component. Examples of such bimetallic systems include Ru-Fe, Pt-Au, Pt-Sn, Ni-In, Pt-Fe, Cu-Cr and Sn-Pt supported on conventional silica, alumina, zeolites or active carbon.[24-30] Although the allylic alcohol selectivity was improved after the addition of a second metal, it was still very low, 40 - 70 %. It was observed that the formation of bimetallic particles with an electron-deficient metal component, such as Sn, Fe and Mn, acted as adsorption sites for the activation of the C=O bond.[31]

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The confinement of a bimetallic Pt-Ru catalyst in carbon nanotubes was reported to give relatively high selectivity of 70 – 90 % for the hydrogenation of cinnamaldehyde to cinnamyl alcohol.[32-34]

We have previously found that AlO(OH)-entrapped Ru catalysts are highly efficient in the transfer hydrogenation of aldehydes and ketones.[35] However, the entrapped Ru particles in these catalysts were very small, in the order of 1.5 to 1.8 nm. Based on reported work, this should render them unselective for the hydrogenation α, β-unsaturated carbonyl compounds to allylic alcohols. We noted with interest that Noyori's group had previously reported that the carbonyl group in conjugated and unconjugated enals and enones was preferentially hydrogenated when amines were added to the homogeneous catalyst, $RuCl_2[P(C_6H_5)_3]_3$.[36] They proposed that the chemoselective hydrogenation occurs by a nonclassical metal-ligand bifunctional mechanism where a hydride on Ru and a proton of the NH_2 ligand are simultaneously transferred to the C=O function via a six-membered pericyclic transition state. Hence, we investigated whether amines can affect the chemoselectivity for a heterogeneous catalyst such as our AlO(OH)-entrapped Ru catalyst. A previous attempt to directly add ethylendiamine to a reaction mixture containing the heterogeneous catalyst, Ru/AlO(OH), gave only moderate yields of the allylic alcohols, 70 – 80 %.[37] Hattori et al.[38] prepared a heterogeneous Pd-ethylenediamine [10 % Pd/C(en)] complex catalyst for the chemoselective hydrogenation of aromatic ketones and aldehydes to corresponding benzyl alcohols. Although high yields, 80 – 100 %, were obtained, the reuse of the catalyst was not reported. Ghosh and Kumar[4] heterogenized $RuCl_2[P(C_6H_5)_3]_3$ by anchoring it onto the surfaces of mesoporous MCM-41 and MCM-48 functionalized with propylamine and propyl ethylenediamine. However, at 75 – 79 %, the selectivity for hydrogenation of the C=O group in α, β-unsaturated aldehydes was lower than for the homogeneous system.

In this study, we used potassium formate as the hydrogen source instead of gaseous hydrogen. Formates have advantages as hydrogen storage materials because they are non-combustible and easy to handle. The decomposition of formates to hydrogen and bicarbonate can be carried out under mild conditions.[39] A series of Ru/AlO(OH) samples with metal loading of 1 to 10 wt. % were prepared according to the sol-gel encapsulation process developed by the group of Park,[40-42] and modified by grafting of the following molecules: 3-aminopropyltrimethoxysilane (**1**), 3-(2-aminoethylamino) propyltrimethoxysilane (**2**) and 3-[2-(2-aminoethyl amino)ethyl amino] propyltrimethoxysilane (**3**) (Fig. 1). Upon contact with hydroxyl groups at the surface of the solid support, the trimethoxysilane moiety undergoes hydrolysis to chemically bind the molecule. The amine-grafted catalysts were assessed with regards to their effectiveness in changing the chemoselectivity during the reduction of cinnamaldehyde. It was also confirmed that they are truly heterogeneous. The best catalyst was then tested for the transfer hydrogenation of other α, β-unsaturated compounds.

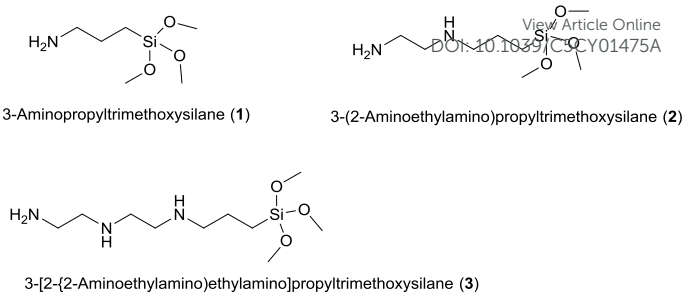

Fig. 1 Amines used in grafting of Ru/AlO(OH).

Experimental

Catalyst preparation

In a typical preparation for one gram of 1 wt. % Ru/AlO(OH), 20.6 mg $RuCl_3.xH_2O$ (0.1 mmol), 4 g (*sec*-$BuO)_3Al$ (16.5 mmol) and 2.4 mL 2-butanol (26.2 mmol) were added into a 50 mL round bottom flask equipped with condenser. After stirring the solution at 100 °C for 1 h, 4 mL water (22.2 mmol) was added and stirring was continued for another 30 min. The resulting black solid was filtered, washed with acetone, and dried in air at room temperature. Samples with ruthenium loadings of 2, 5, 8 and 10 wt. % were prepared by the same procedure.

Amines **1**, **2** and **3** were grafted onto the Ru/AlO(OH) samples. To prepare amine **2**-grafted 1 wt. % Ru/AlO(OH) with **2**/Ru molar ratio of 6, 1 g of 1 wt. % Ru/AlO(OH) (0.1 mmol Ru), 0.131 mL (0.6 mmol) amine **2** and 20 mL toluene were added into a 50 mL round-bottom flask equipped with a condenser. After refluxing for 24 h, the solid was filtered, washed with toluene followed by acetone, and dried at room temperature. The as-synthesized samples are denoted by **n**-x wt.% Ru-y where **n** stands for the amine precursor (**1**, **2** and **3**), x the ruthenium loading (1, 2, 5, 8 and 10 wt. %) and y the amine/Ru molar ratio (1, 2, 4, 6 and 8). A ruthenium-free amine **2**-grafted AlO(OH) was prepared by refluxing 1 g of AlO(OH) with 0.655 mL (3.0 mmol) amine **2** in toluene.

Catalyst characterization

The surface area and pore volume of the catalysts were determined from nitrogen adsorption-desorption isotherms (Micromeritics Tristar 3000). Prior to measurement, each sample was degassed under nitrogen at 100 °C for 5 h. Powder x-ray diffractometry (XRD) was carried out using a Siemens D5005 diffractometer equipped with a Cu anode and variable slits. The diffractograms were measured for 2θ from 20° to 80° with a step size of 0.02° and a dwell time of 1s/step. Transmission electron microscopy (TEM) was performed using a JEOL JEM 3010 HRTEM. The ruthenium and nitrogen contents were measured by inductively coupled plasma-atomic emission spectroscopy (Thermo Jarrell Ash Duo Iris ICP-AES). X-ray photoelectron spectroscopy (XPS) was performed using a VG-Scientific ESCALAB Mark 2 spectrometer equipped with a hemispherical electron analyzer and a Mg Kα X-ray source (1253.6 eV, 300 W). All binding energies were calibrated using the C 1s peak at 284.5 eV as the reference.

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Catalytic testing

Typically, 1 mmol of the α, β-unsaturated carbonyl compound, 0.252 g (3 mmol) potassium formate, 0.27 mL (30 mmol) water and 5 mL (65 mmol) dimethylformamide (DMF) were added to a 25 mL round-bottom flask. After heating the reaction mixture to 100 °C under a flow of nitrogen, 100 mg Ru/AlO(OH) or 200 mg amine-grafted Ru/AlO(OH) was added. Samples were taken at regular intervals and analyzed by gas chromatography (GC) and gas chromatography mass spectrometry (GC-MS). For recycling tests, the used catalysts were recovered by centrifugation, washed with water followed by ethanol and dried at room temperature before reuse.

Results and discussion

Catalyst characterization

Grafting the 1 wt. % Ru/AlO(OH) with amines **1**, **2** and **3** affected the textural properties to a small extent, but the changes cannot be correlated with the chain length of the alkylamine (Table 1, Fig. S1). Increasing the amine **2**/Ru ratio from 1 to 8 resulted in a decrease of the surface area from 338 to 300 $m^2 g^{-1}$ as well as the pore volume from 0.95 to 0.72 $cm^3 g^{-1}$ (Fig. S2). When amine **2** was grafted onto samples with higher Ru loading, the textural properties were more severely affected (Fig. S3). The surface areas of ungrafted Ru/AlO(OH) with 2 – 10 wt. % Ru varied from 150 to 380 $m^2 g^{-1}$ with pore volumes of 0.18 to 0.90 $cm^3 g^{-1}$ (Table S1). The drastic decrease in surface area and porosity indicates severe pore blockage.

Table 1 Textural properties of amine-grafted Ru/AlO(OH)

Catalyst	Surface area ($m^2 g^{-1}$)	Pore volume ($cm^3 g^{-1}$)
1 wt. % Ru/AlO(OH)	425	1.01
1-1 wt. % Ru-6	309	0.83
2-1 wt. % Ru-6	299	0.78
3-1 wt. % Ru-6	355	1.05
2-1 wt. % Ru-1	338	0.95
2-1 wt. % Ru-2	328	0.80
2-1 wt. % Ru-4	310	0.79
2-1 wt. % Ru-8	299	0.72
2-2 wt. % Ru-6	235	0.58
2-5 wt. % Ru-6	42.2	0.12
2-8 wt. % Ru-6	1.91	0.02
2-10 wt. % Ru-6	0.11	0.02

Despite the textural changes, the Ru particle size was only slightly increased after grafting. The average Ru particle sizes for the 1 and 10 wt. % Ru/AlO(OH) were 1.5 and 1.8 nm, respectively (Fig. 2a and b). After grafting with amine **2**, the particles were ~ 1.6 – 1.7 nm (Fig. 2c and d). Due to the small metal particle size, no Ru-related peaks could be observed in the X-ray diffractograms.

The Ru and N contents for grafted 1 wt. % Ru/AlO(OH) were determined by ICP-AES. The amine-grafted 1 wt. % Ru/AlO(OH) contained 0.72 to 0.79 wt.% Ru, which is slightly lower than the 0.84 wt. % measured in the ungrafted sample (Table 2). The amount of amine grafted onto the sample agrees well with the expected values. For an expected amine/Ru ratio of 6, the value obtained from ICP was between 6.53 and 7.12.

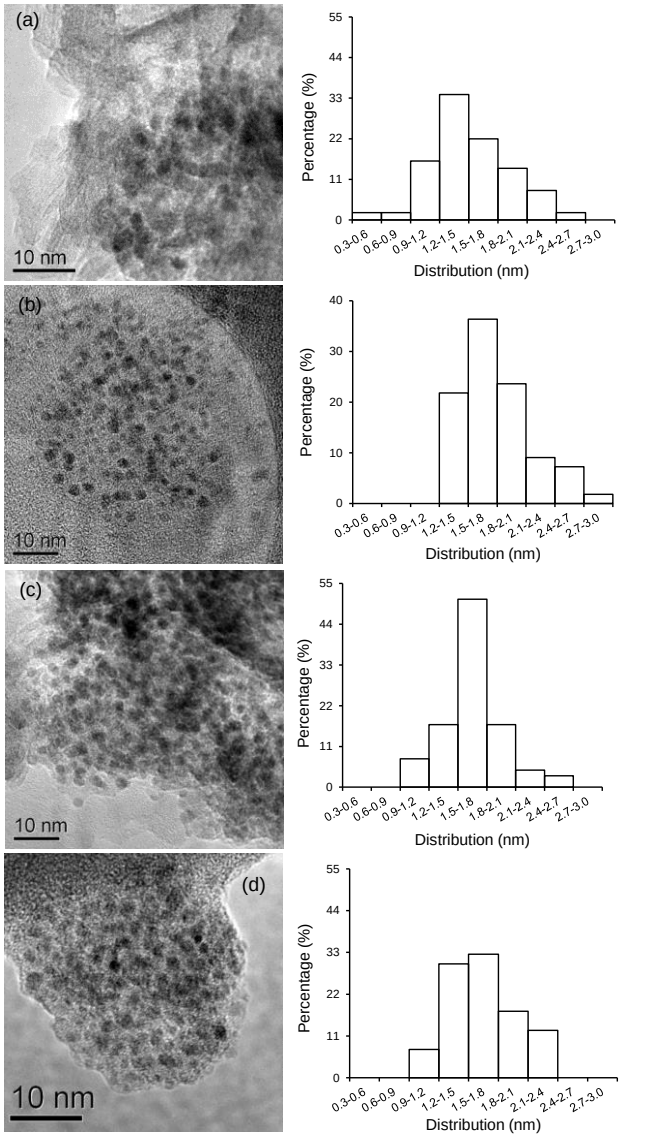

Fig. 2 TEM images and particle size distribution for (a) 1 and (b) 10 wt. % Ru/AlO(OH) and amine **2** grafted- (c) 1 and (d) 10 wt. % Ru/AlO(OH) at **2**/Ru of 6.

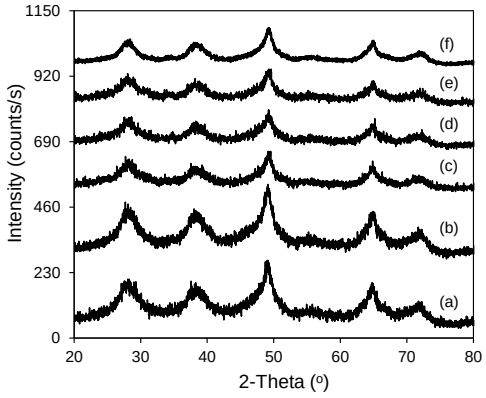

Fig. 3 XRD diffractograms for (a) 1 wt. % Ru/AlO(OH) and amine **2**-grafted 1 wt. % Ru/AlO(OH) with different **2**/Ru molar ratio of (b) 1, (c) 2, (d) 4, (e) 6 and (f) 8.

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Table 2 Ruthenium and nitrogen contents for the amine-grafted 1 wt. % Ru/AlO(OH)

Catalyst	Ru (wt. %)	N (wt. %)	Molar ratio of amine/Ru	
			Expected	Measured
1 wt. % Ru/AlO(OH)	0.84	-	-	-
1-1 wt. % Ru-6	0.79	0.78	6	7.12
2-1 wt. % Ru-6	0.79	1.47	6	6.70
3-1 wt. % Ru-6	0.72	1.96	6	6.53
2-1 wt. % Ru-1	0.83	< 0.5	1	< 2
2-1 wt. % Ru-2	0.81	0.57	2	2.54
2-1 wt. % Ru-4	0.86	1.11	4	4.66
2-1 wt. % Ru-8	0.76	1.67	8	7.95

X-ray photoelectron spectroscopy (XPS) was carried out to determine if there is any electronic interaction between the amine and ruthenium. Due to grafting of **2**, the carbon 1s peak was very strong and overlapped with the ruthenium 3d signal. Hence, we examined the nitrogen 1s signal for any changes. The nitrogen 1s signal of AlO(OH) grafted with amine **2** (40 wt. %) can be deconvoluted into two peaks. The peak with binding energy at 397.96 eV is assigned to free or unprotonated nitrogen (denoted as N_S) while that at 399.91 eV is assigned to protonated nitrogen (denoted as N_S^+). The protonated nitrogen results from the reaction of -NH_2 or -NH groups with -OH groups on the AlO(OH) support.[43,44] In comparison, for the amine **2**-grafted Ru/AlO(OH) sample, the nitrogen 1s signal was broader (Fig. 4), and at least three peaks are required to adequately deconvolute the signal, with the new peak at 398.69 eV (denoted as N_{Ru}^+). This binding energy agrees with that reported for a free nitrogen coordinated to ruthenium.[4] The interaction between ruthenium and nitrogen shifts the lone electron pair on the nitrogen atom towards the metal, resulting in the observed increase of the nitrogen binding energy from 397.96 eV to 398.69 eV. The appearance of this new peak suggests that some of the amine molecules are either directly grafted onto the ruthenium particles or are grafted to the alumina surface sufficiently close to the metal particle to allow for ruthenium-nitrogen interaction.

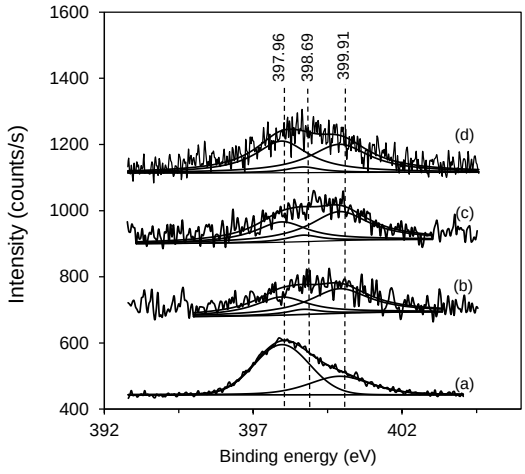
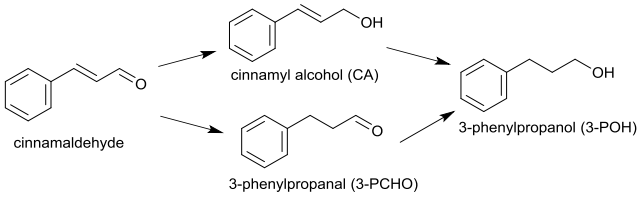


Fig. 4 Nitrogen 1s XPS spectra for the amine **2**-grafted (a) AlO(OH) and 1 wt. % Ru/AlO(OH) with amine **2**/Ru molar ratio of (b) 1, (c) 2 and (d) 6.

Effect of Ru loading

The chemoselectivity for C=O reduction in α, β-unsaturated carbonyl compounds was investigated using cinnamaldehyde as a model compound. The hydrogenation of either the C=C or the C=O group leads to the formation of 3-phenylpropanal (3-PCHO) or cinnamyl alcohol (CA), respectively (Scheme 1). These two products can be further reduced to 3-phenylpropanol (3-POH).



Scheme 1 Reaction pathways in the hydrogenation of cinnamaldehyde.

The effect of Ru loading of Ru/AlO(OH) was investigated at a constant substrate to catalyst ratio (S/C) of 100. Over 1 wt. % Ru/AlO(OH), the transfer hydrogenation of cinnamaldehyde with potassium formate was very fast with a high initial TOF of 190 h^{-1} (Table 3, entry 1). Initially, the reaction was fully selective to the hydrogenation of the C=C group, forming 3-phenylpropanal as the sole product (Fig. 5). The hydrogenation of the C=O group in 3- phenylpropanal occurred only after all cinnamyl aldehyde had been consumed, clearly showing the

Table 3 Effect of Ru loading on the transfer hydrogenation of cinnamaldehyde over Ru/AlO(OH)

Entry	Ru loading (wt. %)	Time (h)	Conv. (%)	Sel. (%)			TOF[a] (h^{-1})
				CA	3-PCHO	3-POH	
1	1	1.5	100	0	100	0	190
2	2	1.5	96	18	71	11	104
3	5	1.5	97	25	51	24	84
4	8	2	98	20	60	20	46
5	10	2	98	22	64	14	38

Reaction conditions: 1 mmol cinnamaldehyde, 3 mmol HCOOK, 15 mmol H_2O, 5 mL DMF, catalyst (1.0 mol % Ru, S/C of 100), 100 °C, N_2 protection. [a]Calculated from the conversion after 20 min.

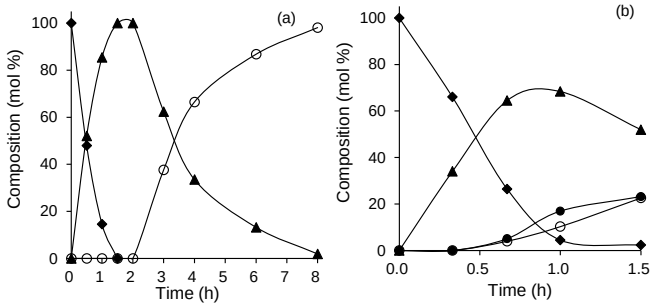


Fig. 5 Kinetic profile for the transfer hydrogenation of cinnamaldehyde using Ru/AlO(OH) with Ru loading of (a) 1 and (b) 2 wt. %. (♦) cinnamaldehyde (●) cinnamyl alcohol (▲) 3-phenylpropanal (○) 3-phenylpropanol.

difference in C=C to C=O reduction rates. Cinnamyl alcohol was not observed throughout the reaction. However, using catalysts with higher Ru loading of 2 - 10 wt. %, up to 25 % selectivity to cinnamyl alcohol could be obtained (Table 3, entries 3-5 and Fig. S4). Once formed, the cinnamyl alcohol did not react further so that its selectivity did not change significantly with conversion. These results are consistent with the effect of particle size on cinnamyl alcohol selectivity that had been previously observed for Ru/C and for graphite-supported Pt and Rh catalysts.[15] The decrease in TOF with higher loading is a consequence of the bigger size of the Ru particles. Bigger particles have more atoms at planar sites than at the more exposed kinks, corners and steps. The results suggest that the latter are more active for hydrogenation than the planar sites. Being coordinatively unsaturated, these sites are also easier to be accessed by the internal C=C bond, thus lowering the selectivity to cinnamyl alcohol.

Effect of ethylenediamine

Ethylenediamine (EDA) was directly added to a reaction mixture for transfer hydrogenation of cinnamaldehyde with 1 wt. % Ru/AlO(OH) as catalyst. This affected the rate of reaction as well as the selectivity. For EDA/Ru of 0.3, an induction time of 1.5 h was observed before the onset of reaction (Fig. S5). During the reaction, the selectivity to cinnamyl alcohol decreased from 82 % initially to 43 % after 22 h. The induction time was shorter, 0.5 - 1 h, for higher EDA/Ru ratios of 0.5 – 3. However once the reaction started, the rate was similar and cinnamyl alcohol was formed with selectivity of 91 – 97 % from the beginning of the reaction (Table 4). In contrast to the reaction using an EDA/Ru ratio of 0.3, here the high cinnamyl alcohol selectivity was maintained even at long reaction times up to 24 h (Fig. S5b). However, the color of the reaction mixture changed from light yellow (the color of cinnamaldehyde) to dark brown, suggestive of ruthenium leaching to form a homogeneous Ru-EDA complex. This complex is itself catalytically active, because the reaction continued after the solid catalyst was removed from the reaction solution by hot filtration (Fig. S6).

Table 4 Effect of EDA/Ru on the transfer hydrogenation of cinnamaldehyde

Entry	EDA/Ru (mol/mol)	Time (h)	Conv. (%)	Sel. (%) CA	3-PCHO	3-POH
1	0	1.5	100	0	100	0
2	0.1	2	100	0	34	66
3	0.3	4	96	80	0	20
4	0.5	2.5	96	91	0	9
5	1	3	96	93	0	7
6	2	3	97	97	0	3
7	3	3	96	97	0	4

Reaction conditions: 1 mmol cinnamaldehyde, 3 mmol HCOOK, 15 mmol H_2O, 5 mL DMF, 100 mg 1 wt. % Ru/AlO(OH), 100 °C, N_2 protection.

Amine-grafted Ru/AlO(OH)

To prevent the leaching of Ru, the amine-bearing molecules were grafted onto 1 wt. % Ru/AlO(OH). For the **1**-grafted catalyst, the initial TOF was only 63 h^{-1} (Table 5) which is threefold lower compared to the ungrafted 1 wt. % Ru/AlO(OH), 190 h^{-1} (Table 3). The low reaction rate can be due to partial coverage of active sites on the Ru particles by the grafted amine. These active sites are required for formate decomposition and transfer hydrogenation. Although some cinnamyl alcohol was formed, the main product was 3-phenylpropanol. The cinnamyl alcohol selectivity decreased from 33 % initially to only 22 % at 96 % conversion (Fig. S7). This shows that a significant fraction of the coordinatively unsaturated active sites was still present despite grafting with amine **1**. When **2** was grafted on 1 wt. % Ru/AlO(OH), the TOF was even lower, 13 h^{-1}, indicating an even higher coverage of the Ru surface by the amine. However, from the onset of reaction, the main product was cinnamyl alcohol with much smaller amounts of 3-phenylpropanal and 3-phenylpropanol (Fig. 6). After 7 h, 96 % conversion was attained with selectivity to cinnamyl alcohol of 95 %. The catalyst grafted with **3**, which contains three amino groups, had an even lower TOF of 6 h^{-1}, but at 91 %, the selectivity to cinnamyl alcohol was not improved over that of the **2**-grafted sample. Hence, amine **2** was the most effective modifier for high cinnamyl alcohol yield.

Table 5 Hydrogenation of cinnamaldehyde over 1 wt. % Ru/AlO(OH) modified with different amines.

Catalyst	Time (h)	Conv. (%)	Sel. (%) CA	3-PCHO	3-POH	TOF[a] (h^{-1})
1-1 wt. % Ru-6	1.5	96	22	21	57	63
2-1 wt. % Ru-6	7	96	95	0	5	13
3-1 wt. % Ru-6	21	97	91	0	9	6

Reaction conditions: 1 mmol cinnamaldehyde, 3 mmol HCOOK, 15 mmol H_2O, 5 mL DMF, 200 mg catalyst (2 mol % Ru, S/C of 50), 100 °C, N_2 protection. [a]Calculated from the conversion after 3 h.

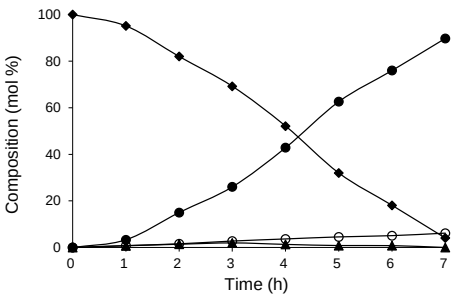


Fig. 6 Reaction profile for the transfer hydrogenation of cinnamaldehyde over the amine **2** grafted-1 wt. % Ru/AlO(OH) at amine/Ru molar ratio of 6. (♦) cinnamaldehyde (●) cinnamyl alcohol (▲) 3-phenylpropanal (○) 3-phenylpropanol.

The amine **2**/Ru molar ratio was next optimized (Table 6). Compared to the ungrafted 1 wt. % Ru/AlO(OH, the initial TOF decreased by seven-fold to 27 h^{-1} for **2**/Ru ~ 1. However, it levelled off at 10 – 13 h^{-1} for higher **2**/Ru of 2 to 8. The selectivity to cinnamyl alcohol changed from 0 in the ungrafted catalyst to 54 % and 89 % for **2**/Ru ratios of 1 and 2 (Fig. S8). Increasing the ratio of **2**:Ru further up to 8 resulted in a

selectivity of 91 to 95 %. The optimum **2**/Ru molar ratio was 6 with a cinnamyl alcohol selectivity of 95 %. Even after 5 runs, this catalyst gave high yields of cinnamyl alcohol, showing its robustness (Fig. 7). The absence of leaching was confirmed because the conversion stopped after the catalyst had been removed by hot filtration when the conversion had reached 30 % (Fig. S9). The cinnamyl alcohol selectivity was similarly improved in catalysts with higher Ru loading, rising from 20 – 25 % up to 94 – 96 % after grafting with 6 equiv. of amine **2** (Table 6, entries 7 - 10). However, the reaction rate was lower than over grafted 1 wt. % Ru/AlO(OH). The TOF was only 5 h^{-1} for the grafted 2 wt. % Ru/AlO(OH), and fell below 1 h^{-1} for catalysts with 5, 8 and 10 wt. % Ru loading.

Table 6 Hydrogenation of cinnamaldehyde over amine **2**-modifed Ru/AlO(OH)

Entry	Catalyst	Time (h)	Conv. (%)	Sel. (%) CA	Sel. (%) 3-PCHO	Sel. (%) 3-POH	TOF[a] (h^{-1})
1	**2**-1 wt. % Ru-1	5	98	54	0	46	27
2	**2**-1 wt. % Ru-2	8	98	89	1	10	12
3	**2**-1 wt. % Ru-4	7	97	91	2	7	12
4	**2**-1 wt. % Ru-6	7	96	95	0	5	13
5[b]	**2**-1 wt. % Ru-6	10	96	90	2	8	12
6	**2**-1 wt. % Ru-8	8	96	94	1	5	10
7	**2**-2 wt. % Ru-6	14	94	95	0	5	5
8	**2**-5 wt. % Ru-6	18	95	94	1	5	0.9
9	**2**-8 wt. % Ru-6	20	97	94	1	5	0.8
10	**2**-10 wt. % Ru-6	23	98	96	0	4	0.8

Reaction conditions: 1 mmol cinnamaldehyde, 3 mmol HCOOK, 15 mmol H_2O, 5 mL DMF, catalyst (2.0 mol % Ru, S/C of 50), 100 °C, N_2 protection. [a]Calculated from the conversion after 3 h. [b]Fifth run.

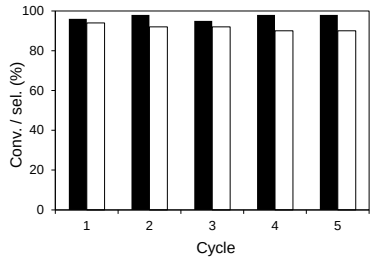


Fig. 7. Reuse of **2**-1 wt.% Ru-6 in transfer hydrogenation of cinnamaldehyde.

The improved selectivity to cinnamyl alcohol for the grafted Ru/AlO(OH) can be attributed to a steric blocking of the sites that gives rise to C=C hydrogenation and/or to an electronic effect. As deduced from the increasing selectivity with metal particle size, the coordinatively unsaturated sites at steps or kinks are most likely involved in the C=C hydrogenation. If the grafting onto the AlO(OH) support occurs such that the tethered amine group is within reach of the ruthenium crystallite, it can block these sites via coordination with the NH_2 group (Fig. 8). Amine **1** with one amino group is shorter (0.64 nm as estimated using Materials Studio) than the amines **2** (0.93 nm) and **3** (1.37 nm). The probability that upon grafting, it will be near enough to interact with the Ru particle is therefore smaller for **1** than for the longer amines **2** and **3**, especially given the low metal density of only 1 wt. %. Hence, amines **2** and **3** have a bigger reach and can interact with ruthenium particles within its vicinity through the primary and secondary amine moiety. Ruthenium atoms located at the steps and kinks on the sides of a metal particle are more likely to interact with the amine rather than those atop the particles (Fig. 8). As a result, adsorption of the internal C=C bond to these highly exposed ruthenium sites is blocked, resulting in an increase in the selectivity for hydrogenation at the terminal C=O. The more extensive coverage of the metallic catalyst by amines **2** and **3** as compared to **1** is seen in the decrease in TOF with longer chain length. Besides exerting a steric effect, the interaction of the amino group with Ru results in an increase in electron density at the metal, as indicated by the appearance of a new N peak at 398.69 eV in the XPS spectrum of the grafted catalyst. This enhances the binding with the partially positive carbon end of the C=O group in cinnamaldehyde. In addition, the hydrogen bonding between the NH_2 group and the C=O end group can activate the C=O bond by perturbing its electron distribution.[4] In contrast, the internal C=C group is rich in electrons and therefore becomes less susceptible to hydrogen transfer due to the repulsion from the more electron rich Ru active sites. Hence, the selectivity changes, and hydrogenation occurs preferentially at the C=O group.

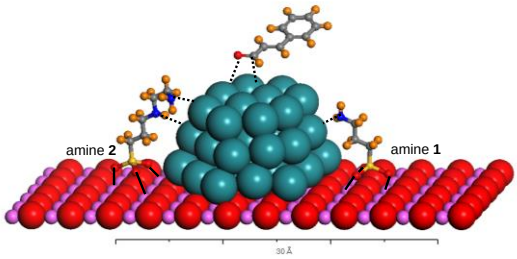


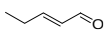
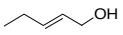
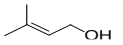
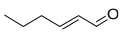
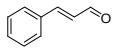
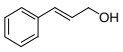
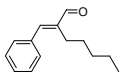
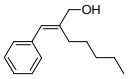
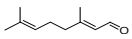
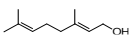
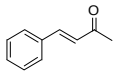
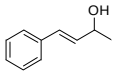
Fig. 8 Proposed interaction of amines **1** and **2** with Ru particle and adsorption of cinnamaldehyde.

Activity for various substrates.

The **2**-grafted 1 wt. % Ru/AlO(OH) was tested for the catalytic transfer hydrogenation of various α, β-unsaturated carbonyl compounds. The linear substrates, *trans*-2-pentenal and *trans*-2-hexenal, were easily reduced to the corresponding α, β-unsaturated alcohols with selectivity > 96 % (Table 7, entries 1 and 3). With branched substrates, 3-methyl-2-butenal and citral, the rate of reaction was lower and a longer time of 10 h and 24 h were needed to reach > 90 % conversion (Table 7, entries 2 and 6). However, the selectivity to the allylic alcohols was always high, 96 % and 98 %, respectively. Of the aryl-containing α, β-unsaturated aldehydes tested, cinnamaldehyde reacted much faster than α-amyl cinnamaldehyde (Table 7, entries 4 and 5). This is understandable from the bigger molecular size of α-amyl cinnamaldehyde as compared to cinnamaldehyde. It is noteworthy that citral, which due to its two C=C and one C=O bonds is considered one of the most difficult α, β-unsaturated aldehydes to be hydrogenated to the allylic alcohol,[45] was

converted to the unsaturated alcohol in excellent yields (Table 7, entry 6). Geraniol and nerol were obtained with 98 % chemoselectivity at 90 % conversion of citral. Such reaction efficiency, notably the absence of citronellal owing to C=C hydrogenation, is unique when compared with previously reported results.[3] α, β-Unsaturated ketones are challenging substrates because of the steric hindrance at the carbonyl group. Nevertheless, even for benzalacetone, 90 % conversion was reached after 24 h although the selectivity to the unsaturated alcohol, 4-phenyl-3-buten-2-ol, was only 67 % (Table 7, entry 7).

Table 7. Catalytic transfer hydrogenation of various α, β-unsaturated carbonyl compounds

Entry	Substrate	Product	Time (h)	Conv. (%)	Sel. (%)
1			7	100	97
2			10	100	96
3			5	100	96
4			7	100	95
5			18	93	98
6			24	90	98
7			24	90	67

Reaction conditions: 1 mmol substrate, 3 mmol HCOOK, 15 mmol H_2O, 5 mL DMF, 200 mg amine **2**-grafted 1 wt. % Ru/AlO(OH) (2/Ru at 6), 100 °C, N_2 protection.

Conclusion

The catalytic transfer hydrogenation of cinnamaldehyde using potassium formate proceeded smoothly over a 1 wt. % Ru/AlO(OH) catalyst. Hydrogenation of the C=C bond was very rapid, so that 3-phenylpropanal was the sole product at full conversion of the unsaturated aldehyde, while at longer times, hydrogenation to 3-phenylpropanol occurred. Higher Ru loadings of 5 - 10 wt. % gave 20 – 25 % selectivity to cinnamyl alcohol. High yields of cinnamyl alcohol, > 95 %, were obtained after grafting the catalyst with 3-(2-aminoethylamino)propyl trimethoxysilane. The optimum catalyst had an amine/Ru molar ratio of 6. A variety of other α, β-unsaturated carbonyl compounds were also chemoselectively hydrogenated to the corresponding allylic alcohols with yields of > 95 %. The amine-modified 1 wt. % Ru/AlO(OH) catalyst maintained its high activity and selectivity over at least five cycles.

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3-(2-aminoethylamino) propyl groups grafted on Ru/AlO(OH) greatly increase chemoselectivity in transfer hydrogenation of α, β-unsaturated carbonyl compounds to allylic alcohols.

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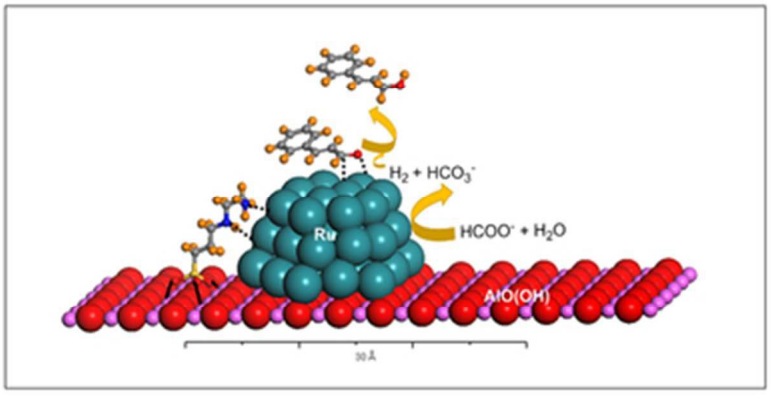

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