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Rapid synthesis of unsaturated alcohols under mild conditions by highly selective hydrogenation†

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Ir–ReO$_x$/SiO$_2$ acted as a highly active and selective heterogeneous catalyst for the hydrogenation of unsaturated aldehydes to unsaturated alcohols in water at low H$_2$ pressure (0.8 MPa) and low temperature (303 K). The catalysis is derived from the synergy between Ir metal and ReO$_x$.

Selective hydrogenation of unsaturated aldehydes including α,β-unsaturated aldehydes produces unsaturated alcohols, which are important intermediates in the synthesis of fine chemicals like flavor, fragrance and pharmaceutical compounds.[1] Thermodynamically and kinetically, a C═C bond is more easily hydrogenated than a C═O bond and so the selective hydrogenation of unsaturated aldehydes to unsaturated alcohols is still a challenging task. Conventional hydrogenation catalysts such as Pd, Rh, Ni and Pt mainly provide saturated aldehydes or saturated alcohols as over-hydrogenated compounds.[2] Traditionally, excellent C═O selectivity is obtained by the stoichiometric $NaBH_4$ or $LiAlH_4$ reduction. However, this method has some drawbacks such as handling of the reducing agent and production of equivalent salts. To overcome these problems, significant efforts have been made to search for catalytic systems that are able to efficiently and selectively hydrogenate C═O bonds of the substrates having both C═O and C═C bonds using hydrogen (H_2) as a reductant. To date various homogeneous and heterogeneous effective catalysts have been developed and high selectivity has been achieved in some cases. Homogeneous catalysts have been intensively investigated because of their high activity and selectivity, and many studies were performed using Ru, Rh, Ir, W and other metals with some ligands.[3–5] Noyori and Bullock have reported an efficient catalyst of an Ru complex with phosphine ligands for selective hydrogenation of various unsaturated aldehydes and ketones.[3,4] However, in the aspect of the catalyst/substrate separation and reusability, heterogeneous catalysts are desired to be developed. Effective heterogeneous catalysts that show high selectivity have been prepared using various techniques[6–12] such as introducing additives,[6,7] modifying the active metal with second metal components,[8] tuning the particle sizes of catalysts[9] or using oxide supports that strongly interact with the active metals.[10] However, most of the catalysts sacrifice the activity to attain high selectivity,[7,11,12a] resulting in much lower activity than that of conventional noble metal catalysts. For the hydrogenation of crotonaldehyde to crotyl alcohol, which is one of the most difficult reactions to proceed selectively, Nishiyama[12a] reported 100% selectivity of crotyl alcohol using Sn-modified silica-coated Pt catalysts, but the yield (4.1%) and turnover frequency (TOF) based on the amount of Pt (0.5 h^{-1}) were very low. In contrast, Mitsudome[12b] demonstrated the highest yield of 87% with the AgNP@CeO_2 catalyst, but the TOF (4.9 h^{-1}) was very low in spite of high temperature (423 K) and high H_2 pressure (1.5 MPa). In total, the previously reported yield and TOF did not exceed 87% and 126 h^{-1}, respectively, which are far from the satisfactory level (Table S1, ESI†). Moreover, these catalysts suffer from high temperature ($\geq$323 K), high H_2 pressure ($\geq$2 MPa) or use of organic solvents. No catalyst presented both high activity and selectivity under mild and eco-friendly reaction conditions. Therefore, a novel catalysis system to accomplish both high activity and high selectivity in an environmentally benign solvent such as H_2O and under the mild conditions such as low H_2 pressure and low temperature is desired to be developed.

Ionic hydrogenation is an effective method to selectively hydrogenate polarized double bonds such as carbonyl group as known using homogeneous catalysts such as Ru complexes.[3–5] When H_2 is used as a reductant, it is heterolytically cleaved into hydride and proton species. As reported in our previous studies on hydrogenolysis of polyols, Ir–ReO$_x$/SiO$_2$ (ref. 13*a*) can be an efficient catalyst to produce hydride species on the catalyst. Therefore, Ir–ReO$_x$/SiO$_2$ may be a new catalyst for selective and active hydrogenation of C═O bonds by ionic hydrogenation. Our results indeed demonstrate that the Ir–ReO$_x$/SiO$_2$ catalyst acts as a highly active and selective catalyst in the selective hydrogenation of various unsaturated aldehydes to unsaturated alcohols in H_2O even at a low H_2 pressure of 0.8 MPa and a low temperature of 303 K.

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† Electronic supplementary information (ESI) available: Details of characterization methods and NMR spectra. See DOI: 10.1039/c3cc41526k

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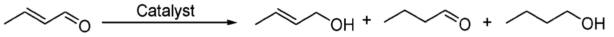
Table 1 Selective hydrogenation of crotonaldehyde by various catalysts[a]



			Selectivity (%)		
Entry	Catalyst	Conv. (%)	Crotyl alcohol	Butanal	1-Butanol
1	Ir–ReO_x/SiO_2-0.5	34.9	91.7	4.0	3.8
2	Ir–ReO_x/SiO_2-1	43.0	92.0	3.4	4.1
3	Ir–ReO_x/SiO_2-2	44.3	91.1	3.9	4.4
4	Ir–ReO_x/SiO_2-3	38.6	91.9	3.3	4.2
5	Rh–ReO_x/SiO_2-0.5	96.9	0.3	76.3	23.2
6	Pd–ReO_x/SiO_2-0.5	94.3	0.9	94.8	4.1
7	Ru–ReO_x/SiO_2-0.5	21.4	33.0	48.0	19.0
8	Pt–ReO_x/SiO_2-0.5	2.0	19.5	56.2	21.3
9	5% Pt/C	66.5	3.6	79.1	13.0
10	5% Ru/C	28.1	6.8	82.0	9.9
11	5% Rh/C	98.3	0	96.5	2.4
12	5% Pd/C[b]	>99	0	96.1	3.5
13	4% Ir/SiO_2	5.4	63.7	31.8	2.0
14	3.6% Re/SiO_2	0.1	0	0	0
15	None	0	—	—	—

[a] Reaction conditions: crotonaldehyde 3.0 mmol, H_2O 3.0 g, catalyst 50 mg, T = 303 K, P_{H_2} = 8 MPa, t = 0.1 h. [b] Catalyst 10 mg.

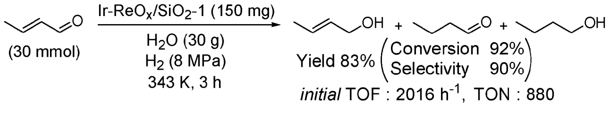
Table 2 Effect of H_2 pressure[a]

				Selectivity (%)		
Entry	P_{H_2} (MPa)	t (h)	Conv. (%)	Crotyl alcohol	Butanal	1-Butanol
1	8	0.1	43.0	92.0	3.4	4.1
2	4	0.25	37.0	91.1	3.7	4.0
3	2	0.5	36.7	93.1	2.6	3.7
4	0.8	1	43.3	95.0	3.4	1.3
5	0.1	4	34.8	93.8	2.6	3.2

[a] Reaction conditions: crotonaldehyde 3.0 mmol, H_2O 3.0 g, Ir–ReO_x/SiO_2-1 50 mg, T = 303 K.

We prepared a series of ReO_x modified SiO_2-supported metal catalysts with various noble metal components and with the same Re/M molar ratio (Re/M = 0.5): M–ReO_x/SiO_2-0.5 (M = Ir, Rh, Pd, Ru, Pt) and a series of Ir–ReO_x/SiO_2-X (X = 0.5, 1, 2, 3), where X is the Re/Ir molar ratio. The selective hydrogenation of crotonaldehyde to crotyl alcohol in water at 303 K and 8 MPa H_2 was carried out as a model reaction for the optimization of metal components and/or compositions (Table 1). Among the M–ReO_x/SiO_2-X (entries 1–8) and conventional hydrogenation catalysts such as carbon-supported transition metal catalysts (entries 9–12), Ir–ReO_x/SiO_2 catalysts showed the highest selectivity (>90%). It should be noted that both the activity and selectivity of Ir–ReO_x/SiO_2 were much higher than those of Ir/SiO_2 (entry 13) and ReO_x/SiO_2 (entry 14). These results suggest that the synergy between Ir and ReO_x generates the high activity and high selectivity of Ir–ReO_x/SiO_2 simultaneously. In the aspect of activity, selectivity and Re metal amount, Ir–ReO_x/SiO_2-1 is an optimal catalyst for the hydrogenation of crotonaldehyde. Time-course of the selective hydrogenation of crotonaldehyde was measured (Fig. S1, ESI†). After 8 h, the yield of crotyl alcohol reached 90% with 91% selectivity. This yield is higher than the ones reported for heterogeneous catalysts (Table S1, ESI†).

A gram-scale experiment (Scheme 1) was carried out using 2.1 g (30 mmol) of crotonaldehyde in 30 g of water using Ir–ReO_x/SiO_2-1 (150 mg, Ir = 0.1 mol%) at 343 K for 3 h to provide crotyl alcohol in 83% yield at 92% conversion and 90% selectivity. The turnover number (TON) and *initial* TOF[14] based on the total Ir metal were calculated to be 880 and 2016 h^{-1}, respectively. To the best of our knowledge, these values are much higher than those reported previously for heterogeneous catalysts (max TOF = 126 h^{-1},[12c] max TON = 66[12d] based on the total metal, as given in Table S1, ESI†). Based on the surface number of Ir (dispersion = 0.16[13a]), Ir–ReO_x/SiO_2-1 showed a high TON of 5500 and an *initial* TOF of 12 600 h^{-1}.



Scheme 1 Scale-up reaction for the hydrogenation of crotonaldehyde over Ir–ReO_x/SiO_2-1.

Next, the effect of H_2 pressure on the hydrogenation of crotonaldehyde was examined (Table 2). The activity is decreased by the decrease in H_2 pressure. In contrast, the dependence of selectivity on H_2 pressure is not so strong, and at 0.8 MPa of H_2 pressure the highest selectivity is obtained (95%). In general, selective hydrogenation of unsaturated aldehydes has been carried out at high pressure ($\geq$2.0 MPa) or high temperature ($\geq$323 K). It should be noted that this reaction system is a first example achieving high selectivity and adequate activity in H_2O at low H_2 pressure (<1.0 MPa) and ambient temperature (303 K). In total, we selected the 0.8 MPa H_2 pressure as an optimal H_2 pressure in the following study.

To verify whether the observed catalysis is derived from Ir–ReO_x/SiO_2 or leached Ir species, the selective hydrogenation of crotonaldehyde was carried out under the optimal conditions and the Ir–ReO_x/SiO_2-1 catalyst was removed from the reaction mixture by filtration at approximately 60% conversion of crotonaldehyde. After the removal of the catalyst, the filtrate was reacted under the same conditions. In this case, no reaction proceeded (Fig. S2, ESI†). Moreover, it was confirmed using coupled plasma atomic emission spectroscopy (ICP-AES) that no Ir species was present in the filtrate (<0.1 ppm). These results indicate that the observed catalysis is intrinsically heterogeneous.

A further advantage of this catalytic system is its reusability. We conducted the reuses of Ir–ReO_x/SiO_2 for the selective hydrogenation of crotonaldehyde (Fig. S3, ESI†). The catalyst can be easily retrieved from the reaction mixture by filtration. For each successive use, the catalyst was washed with water three times to remove the products, followed by drying at 383 K for 12 h and calcination in air at 773 K for 1 h.[13e] After this treatment, the recovered catalyst was reused at least three times without a marked loss of its high catalytic efficiency. XRD, TEM and XAFS analyses, and the CO adsorption experiment of Ir–ReO_x/SiO_2 showed that the state of Ir–ReO_x/SiO_2 hardly changed before and after the reaction (Fig. S4–S9 and Tables S2–S5, ESI†), which indicates that Ir–ReO_x/SiO_2 is very robust under the reaction conditions. The structure of Ir–ReO_x/SiO_2 was as follows: supported Ir is in the metallic state and the Re species form low-valent ($\sim$+3) oxide clusters (ReO_x) that partially cover the Ir metal surface.[13a,b,e]

The substrate scope of the selective hydrogenation is listed in Table 3. Hydrogenation of α,β-unsaturated aldehydes over

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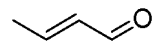
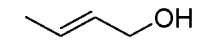
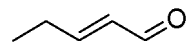
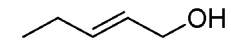
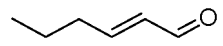
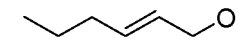
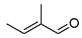
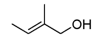
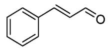
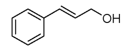
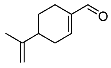
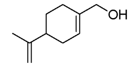
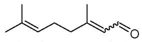
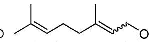
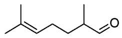
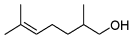
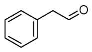
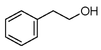
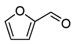
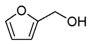
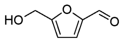
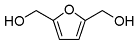
Table 3 Selective hydrogenation of various unsaturated aldehydes over Ir–ReO_x/SiO_2 [a]

Entry	Aldehyde	Product	t (h)	Conversion (%)	Yield (%)	Selectivity[b] (%)		
						Product	AL	SA
1			8	99	90	91	0	8
2			5	>99	90	90	0	9
3			4	95	87	92	2	6
4			6	96	89	93	0	6
5			6	99	95 (91[c])	96	0	4[e]
6			8	85	70	82	3[d]	15[f]
7	 (*cis* / *trans* = 27 /63)	 (*cis* / *trans* = 26 /64)	6	91	88	97	0	3[g]
8			6	93	78	84	0	14
9			6	80	80	>99	0	1
10			6	>99	>99 (97[c])	>99	0	1
11			6	>99	>99 (99[c])	>99	0	0

[a] Reaction conditions: substrate 3.0 mmol, H_2O 3.0 g, Ir–ReO_x/SiO_2-1 50 mg, T = 303 K, P_{H_2} = 0.8 MPa. [b] AL = aldehyde, SA = saturated alcohol. [c] Isolated yield. [d] Conjugated aldehyde (0.6%), unconjugated aldehyde (2.4%). [e] 3-Phenyl-1-propanol only. [f] 4-Isopropenylcyclohexane-1-methanol only. [g] 3,7-Dimethyl-1-octanol (0.2%), 3,7-dimethyl-6-octen-1-ol (2.8%).

Ir–ReO_x/SiO_2-1 provided the corresponding allyl alcohols with high selectivity at high aldehyde conversion (entries 1–7). Note that cinnamyl alcohol (entry 5), peril alcohol (entry 6) and a mixture of nerol and geraniol (entry 7), which are important components of fragrance and flavor compounds, were obtained in high yields. Unconjugated unsaturated aldehydes reacted to afford the corresponding esters with high selectivity (entries 8 and 9). Furfural and 5-hydroxymethyl furfural that are important intermediates from biomass were also hydrogenated to the corresponding furfuryl alcohols in excellent yields (entries 10 and 11). Therefore, the present catalytic system is practically promising in the production of important chemicals such as fragrance or flavor compounds.

To clarify the role of ReO_x species, the rate dependence on the substrate concentration was studied. The reaction order with respect to crotonaldehyde concentration was +0.03 and +0.59 for Ir–ReO_x/SiO_2-1 and Ir/SiO_2, respectively (Fig. S5, ESI†), indicating that the substrate is more strongly adsorbed on the surface of Ir–ReO_x/SiO_2-1 and this tendency is interpreted by ReO_x as the adsorption site of substrates. Probably the substrate was adsorbed on ReO_x sites at the oxygen atom of C=O. In addition, we reported that the Ir–ReO_x/SiO_2 catalyst can dissociate H_2 into H^+ and H^- on the interface between Ir metal and ReO_x species.[13] Considering that ionic hydrogen species are effective in hydrogenation of polarized double bonds,[3–5] the heterolytically dissociated hydrogen species on Ir–ReO_x/SiO_2 will be effective in the selective hydrogenation of crotonaldehyde. Therefore ReO_x is responsible for the promotion of substrate adsorption and the assistance of heterolytic dissociation of H_2 to H^+ and H^- species, leading to high activity and high selectivity, respectively.

In conclusion, Ir–ReO_x/SiO_2 showed high activity and selectivity in the hydrogenation of unsaturated aldehydes to unsaturated alcohols in water at a low H_2 pressure of 0.8 MPa and a low temperature of 303 K. The gram-scale experiment at 8 MPa H_2 pressure and 343 K with Ir–ReO_x/SiO_2 provided a record TON of 5500 and an initial TOF of up to 12 600 h^{-1} based on surface Ir without the loss of selectivity. Various unsaturated aldehydes can be converted to the corresponding unsaturated alcohols including useful chemicals in high yields. This catalyst system is generated by the synergy between Ir metal and ReO_x, which provides high selectivity while drastically raising the activity without sacrificing the activity of noble metals.

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