Highly efficient oxidation of alcohols and aromatic compounds catalysed by the Ru-Co-Al hydrotalcite in the presence of molecular oxygen

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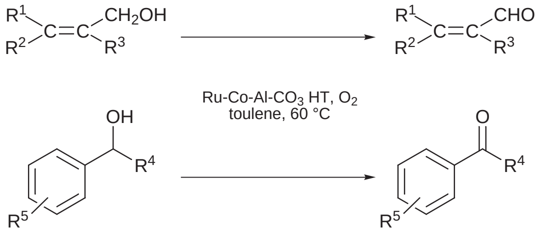
The ruthenium hydrotalcite having cobalt cations, Ru-Co-Al-CO_3 HT, is an effective heterogeneous catalyst for the oxidation of various kinds of alcohols in the presence of molecular oxygen.

From the standpoints of atom economy and environmental friendliness,[1,2] much attention has been paid to the development of selective oxidations catalysed by metal compounds using molecular oxygen as oxidant.[3–6] Hydrotalcites of layered mineral materials consist of cationic Brucite layers separated by layers of anionic species.[7] Changing the element ratios in the Brucite layer and selection of different anionic species enables tuning of the surface basicity.[8] Additionally, various metal elements can be introduced into the Brucite layer *via* the isomorphic substitution of Mg^{II} or Al^{III} cations at the octahedral sites, which are expected to be the active sites of the catalysts.[3] Thus, the interaction of introduced metal cations (M^1) with other cations (M^2) through M^1–O–M^2 bonds would lead to unique catalytic reactions using the functionalised hydrotalcites. Here, we have designed a highly active catalyst of the hydrotalcite containing Ru and Co cations for the oxidation of various alcohols and hydrocarbons in the presence of molecular oxygen. This heterogeneous catalyst has the advantages of using molecular oxygen and a simple work-up procedure over other homogeneous oxidizing reagents.[1] Furthermore, this hydrotalcite is reusable without appreciable loss of activity and selectivity for the above oxidation.

Various Ru hydrotalcites having divalent metal cations M^{II} in place of Mg^{II} (Ru : M^{II} : Al = 0.3 : 3.0 : 1.0) were prepared according to a modified version of a procedure in the literature.[7] A representative example is for the hydrotalcite having cobalt, aluminum, and ruthenium in the Brucite layer and CO_3 anions in the interlayer (Ru-Co-Al-CO_3 HT). A mixture of $RuCl_3\cdot3H_2O$ (1.53 mmol), $CoCl_2\cdot6H_2O$ (15.3 mmol) and $AlCl_3\cdot6H_2O$ (5.10 mmol) were dissolved in distilled water (10 ml). To an aqueous solution of Na_2CO_3 (13.3 mmol) and NaOH (46.4 mmol) was slowly added the above solution, and then the resulting mixture was heated at 65 °C for 18 h with stirring. The obtained slurry was cooled to room temperature and filtered, washed with distilled water and dried at 110 °C for 12 h, yielding 2.05 g of powder. The structure of the powder was confirmed by its X-ray diffraction pattern, and the basal spacing was estimated to be 7.9 Å, which is similar to that of the Ru–Mg–Al–CO_3 HT (7.92 Å); calc. for Ru-Co-Al-CO_3 HT (Ru : Co : Al = 0.3 : 3.0 : 1.0): Co, 20.1; Al, 7.4; Ru, 7.0%. Found: Co, 19.5; Al, 7.4; Ru, 7.3%. X-Ray photon spectroscopy (XPS) for the Ru-Co-Al-CO_3 HT: Co $2p_{3/2}$ = 780.6 eV, FWHM = 3.1 eV; Ru $3d_{5/2}$ = 282.7 eV, FWHM = 2.0 eV. XPS for the Ru-Mg-Al-CO_3 HT: Ru $3d_{5/2}$ = 281.7 eV, FWHM = 2.5 eV. The XPS peak positions are refered to Al_{1s} at 73.7 eV].

A typical example for the oxidation of alcohols is as follows (Scheme 1). Into a reaction vessel with a reflux condensor were placed cinnamyl alcohol (0.80 g, 6.0 mmol), the Ru-Co-Al-CO_3 HT (0.90 g) and toluene (15 ml). The resulting mixture was stirred at 60 °C under an O_2 atmosphere. After 40 min, the hydrotalcite was separated by filtration. GC analysis of the filtrate showed a quantitative yield of cinnamaldehyde. Removal of the solvent under reduced pressure was followed by column chromatography on silica to yield cinnamaldehyde (0.707 g, 89%). Isolated hydrotalcites were washed with aqueous 10% Na_2CO_3 (30 ml) and water, and could be reused without appreciable loss of activity for the above oxidation; the first, second and third runs of the experiment using the spent hydrotalcites gave cinnamaldehyde with > 92% GC yield.

Ru hydrotalcites having divalent metal cations in place of Mg^{II} were examined as catalysts for the oxidation of cinnamyl alcohol in the presence of molecular oxygen, as shown in Table 1. Generally, cinnamaldehyde is the main product under the



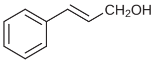
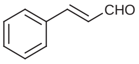
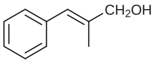
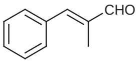
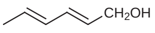
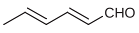
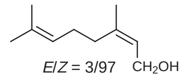
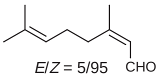
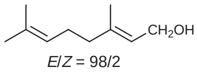
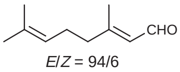
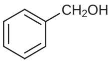
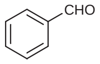
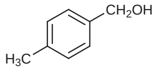
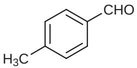
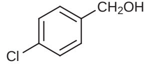
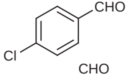
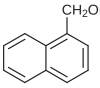
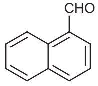
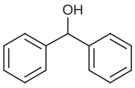
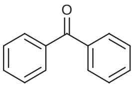
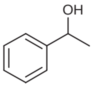
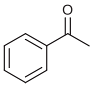
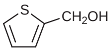
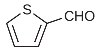
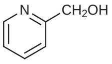
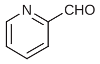
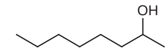
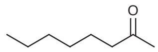
Scheme 1

Table 1 The oxidation of cinnamyl alcohol with various Ru hydrotalcites[a]

Entry	Catalyst	Time	Conversion (%)	Yield[b] (%)	Heat of adsorption[c]/ J g^{-1}
1	Ru-Co-Al-CO_3 HT	40 min	100	94	13.4
2	Ru-Mn-Al-CO_3 HT	40 min	99	92	13.3
3	Ru-Fe-Al-CO_3 HT	40 min	64	50	12.9
4	Ru-Zn-Al-CO_3 HT	40 min	23	23	6.6
5	Ru-Mg-Al-CO_3 HT	40 min	31	20	32.1
		8 h	100	95[d]	
6[e]	Co-Al-CO_3 HT + Ru-Mg-Al-CO_3 HT	40 min	33	22	

[a] Reaction conditions: cinnamyl alcohol (2.0 mmol), catalyst (0.30 g), toluene (5 ml), 60 °C, O_2 atmosphere. [b] Yields of cinnamaldehyde were determined by GC analysis using internal standards, based on cinnamyl alcohol. [c] The basicity of the hydrotalcites was estimated by calorimetric heats of benzoic acid adsorption (ref. 8). [d] Cited from ref. 3. [e] The physical mixture of the two catalysts which contained the same amounts of Ru and Co as entry 1 was used.

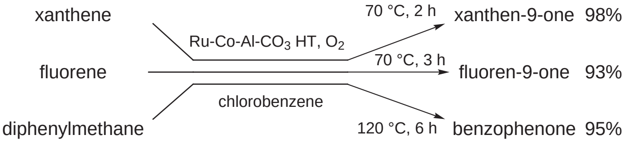
Table 2 The oxidation of various alcohols with Ru-Co-Al-CO_3 HT[a]

Entry	Substrate	Product	Time	Con-version (%)	Yield[b] (%)
1			40 min	100	94 (89)[c]
2			1.5 h	100	100
3			2 h	99	90
4	 *E*/*Z* = 3/97	 *E*/*Z* = 5/95	12 h	86	80
5	 *E*/*Z* = 98/2	 *E*/*Z* = 94/6	12 h	89	71
6			1 h	100	96
7			50 min	100	100
8			1.5 h	100	95
9			1 h	100	92
10			1 h	100	96 (98)
11			1.5 h	100	100
12			40 min	100	91
13			7 h	99	91
14			2 h	100	97 (82)

[a] Reaction conditions: substrate (2 mmol), Ru-Co-Al-CO_3HT (0.3 g), toluene (5 ml), 60 °C, O_2 atmosphere. [b] Yields of aldehydes and ketones were determined by GC analysis using internal standards, based on alcohols. [c] Values in parentheses are isolated yields. In the case of the product isolation experiments, the reaction scale was three times as much as that given in footnote (*a*).

above conditions. The hydrotalcite with Ru cations in the Brucite layer, Ru-Mg-Al-CO_3 HT, has been previously found to be a good catalyst (entry 5).[3] Substitution of Mg ions with Co ions in the Brucite layer of the above Ru-Mg-Al-CO_3 HT drastically enhanced the catalytic activity (entries 1 and 5). The Ru-Mn-Al-CO_3 HT was also an effective catalyst, while the introduction of Fe and Zn cations resulted in low yields of cinnamaldehyde.

Oxidation of various kinds of alcohols using the Ru-Co-Al-CO_3 HT in toluene was carried out at 60 °C. Typical results for the oxidation of aromatic and aliphatic alcohols were summarized in Table 2. Cinnamyl alcohol and its derivative gave α,β-unsaturated aldehydes in almost quantitative yield (entries 1 and 2). In the cases of benzylic alcohols, the corresponding aldehydes were obtained in high yield (entries 6–11). It is notable that benzoic acids (over-oxidation products) were barely detected under the above conditions. Further, the hydrotalcite catalyst is applicable for the oxidation of aliphatic allylic alcohols (entries 3–5) and heterocyclic alcohols including sulfur and nitrogen species in spite of slow reaction rates (entries 12 and 13).† A secondary saturated alcohol, octan-2-ol, was smoothly converted into the corresponding ketone (entry 14), while primary saturated alcohols such as octan-1-ol showed extremely low reactivity for this oxidation. Interestingly, the hydrotalcite could also efficiently oxygenate the benzylic positions of aromatic compounds, *i.e.* xanthene, fluorene and diphenylmethane, to give the corresponding ketones (Scheme 2).



Scheme 2

The hydrotalcite catalyst was easily separated from the reaction mixture and was reusable without an appreciable loss of activity and selectivity for the above oxidations.

In the oxidation of cinnamyl alcohol, the Co-Al-CO_3 HT (Co : Al = 3 : 1) barely catalysed the oxidation, and the activity of Ru-Co-Al-CO_3 HT was much higher than that of a physical mixture of Co-Al-CO_3 HT and Ru-Mg-Al-CO_3 HT (Table 1, entry 6). These results indicate that it is the synergism derived from interaction of Co and Ru cations in the Ru-Co-Al-CO_3 HT that enhances the catalytic activity. The XPS results show that the oxidation state of the Ru cations of Ru-Co-Al-CO_3 HT was higher than that of Ru-Mg-Al-CO_3 HT; the Ru $3d_{5/2}$ electron binding energy of Ru-Co-Al-CO_3 HT was similar to that of RuO_3.[9] Presumably, the Ru cation species with higher oxidation states, *i.e.* Ru^{IV} to Ru^{VI}, induced by the introduction of Co cations are responsible for high catalytic activity in the above oxidation.[5] From Table 1, the basicity of hydrotalcites is not correlated with the catalytic activity for the oxidation.[3] At present, we think that substitution of Mg cations with divalent Co cations in the Brucite layer might lead to generation of an active species having a high oxidation state for the Ru ions, *e.g.* Ru=O species.[10]

In conclusion, the ruthenium hydrotalcite having Co cations was found to be an effective heterogeneous catalyst for the oxidation of various kinds of alcohols in the presence of molecular oxygen. This heterogeneous oxidation can be regarded as an environmentally benign chemical process because of the use of molecular oxygen, the simple work-up procedure and the reusability of the hydrotalcite catalyst.

Notes and references

† The oxidations of aliphatic allylic alcohols and 2-pyridylmethanol hardly proceeded in the presence of the Ru-Mg-Al-CO_3 HT under these reaction conditions.

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