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Heterogeneous Oxidation of Allylic and Benzylic Alcohols Catalyzed by Ru−Al−Mg Hydrotalcites in the Presence of Molecular Oxygen

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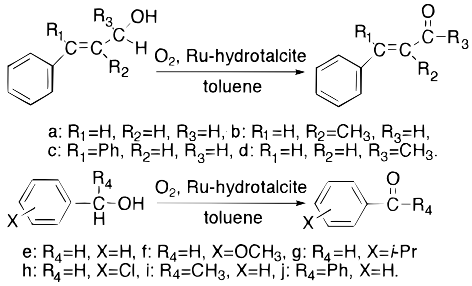
Selective oxidation of alcohols using various kinds of reagents has been widely studied because the functional transformation to aldehydes and ketones plays an important role in many organic syntheses.[1] But even at present, stoichiometric reagents such as Cr and Mn have been used for the above selective transformation. From the standpoints of atom economy and environmental demand for chemical reactions,[2] much attention has been paid to development of the metal catalyst systems using molecular oxygen as an oxidant.[3] Hydrotalcites of layered materials consist of a cationic Brucite layer and anionic compounds in the interlayer.[4] Various kinds of metal elements, which are expected to act as active sites of catalysts, can be introduced in the Brucite layer. In this paper, we report that the hydrotalcites having Ru in the Brucite layer showed high catalytic activity for oxidation of allylic and benzylic alcohols in the presence of molecular oxygen.[5] This heterogeneous catalyst has the advantages of not only the use of molecular oxygen but also of a simple workup procedure than other homogeneous oxidizing reagents. Furthermore, this catalyst is reusable without an appreciable loss of the activity and selectivity for the oxidation.



a: R_1=H, R_2=H, R_3=H, b: R_1=H, R_2=CH_3, R_3=H,
c: R_1=Ph, R_2=H, R_3=H, d: R_1=H, R_2=H, R_3=CH_3.

e: R_4=H, X=H, f: R_4=H, X=OCH_3, g: R_4=H, X=*i*-Pr
h: R_4=H, X=Cl, i: R_4=CH_3, X=H, j: R_4=Ph, X=H.

Various hydrotalcites were prepared according to a modified procedure in the literature.[4] A representative example is for the hydrotalcite having ruthenium in the Brucite layer and CO_3 anion in the interlayer, $Mg_6Al_2Ru_{0.5}(OH)_{16}CO_3$. A mixture of $RuCl_3{\cdot}3H_2O$ (4.3 mmol),[6] $MgCl_2{\cdot}6H_2O$ (43.2 mmol), and $AlCl_3{\cdot}H_2O$ (14.4 mmol) was dissolved in distilled water (30 mL). To an aqueous solution of Na_2CO_3 (74.7 mmol) and NaOH (0.13 mol) was slowly added the above solution, and then the resulting solution was heated at 65 °C for 18 h with stirring. The obtained slurry was cooled to room temperature and filtered, followed by washing with distilled water and drying at 110 °C for 12 h (5.25 g). The structure of hydrotalcite was confirmed by its XRD pattern, and the basal spacing was estimated to be 7.9 Å. [Anal. Calcd for $Mg_6Al_2Ru_{0.5}(OH)_{16}CO_3{\cdot}nH_2O$ (n = 8): Mg, 20.1; Al, 7.4; Ru, 7.0. Found: Mg, 19.5; Al, 7.4; Ru, 7.3. XPS: Ru $3d_{5/2}$ = 281.0 eV,[7] FWHM = 2.5 eV.] A typical example for the oxidation of alcohols is as follows. Into a reaction vessel with a reflux condensor were placed cinnamyl alcohol (0.80 g, 6.0 mmol), $Mg_6Al_2Ru_{0.5}(OH)_{16}CO_3$ (0.90 g), and toluene (15 mL). The resulting mixture was stirred at 60 °C under an O_2 atmosphere. After 24 h, hydrotalcite was separated by filtration. GC analysis of the filtrate showed a quantitative yield of cinnamaldehyde. Removal of the solvent under reduced pressure followed by column chromatography on silica yielded the product of cinnamaldehyde (0.734 g, 92%). Isolated hydrotalcites were washed with 10 wt % Na_2CO_3 (aq) solution (30 mL) and water, which could be reused as a catalyst without an appreciable loss of activity for the above oxidation; the first, second, and third runs of the reuse experiments gave cinnamaldehyde over 95% GC yields.

In the oxidation of cinnamyl alcohol, various hydrotalcites were examined as a catalyst in the presence of molecular oxygen, which is shown in Table 1. Generally, cinnamyl alcohol was oxidized to give cinnamaldehyde as a main product under the above reaction conditions. We found that hydrotalcites containing ruthenium in the Brucite-like layer showed the highest catalytic activity for the oxidation among the hydrotalcites with many transition metals, e.g., Fe, Ni, Mn, V, and Cr. The most effective anion in the interlayer of Ru-hydrotalcites is carbonate ion (Table 1, run 1).[8]

With respect to solvents, toluene, chlorobenzene, and benzene were good solvents, giving 95, 93, and 92% yields of cinnamaldehyde for 8 h, respectively. Reactions in *n*-hexane, acetonitrile, 1,2-dichloroethane, and cyclohexane solvents led to 70−86% of cinnamaldehyde, while use of methanol resulted in a 27% yield. The oxidation at 80 °C gave the highest yield of cinnamaldehyde; the increase of the reaction temperature over 100 °C resulted in low selectivity, whereas cinnamyl alcohol was perfectly consumed.

Oxidation of various kinds of allylic and benzylic alcohols using $Mg_6Al_2Ru_{0.5}(OH)_{16}CO_3$ in a toluene solvent was carried out at 80 °C under an oxygen atmosphere. The hydrotalcite showed high catalytic activities for many allylic and benzylic alcohols, while saturated and nonallylic alcohols such as cyclohexylmethanol and 2-octanol had low reactivity for the oxidation. Typical examples for the oxidation of allylic and benzylic alcohols are summarized in Table 2. Cinnamyl alcohol and its derivatives can be easily oxidized to give corresponding α,β-unsaturated aldehydes in almost quan-

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[1] (a) Parshall, G. W.; Ittel, S. D. *Homogeneous Catalysis*, 2nd ed.; John Wiley & Sons, Inc.: New York, 1992. (b) Hill, C. L. *Advances in Oxygenated Processes*; Baumstark, A. L., Ed.; JAI Press, Inc.: London, 1988; Vol. 1, p 1. (c) Hudlucky, M. *Oxidations in Organic Chemistry*; ACS Monograph Series; American Chemical Society: Washington, DC, 1990. (d) Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidations of Organic Compounds*; Academic Press: London, 1981.

[2] Trost, B. M. *Science* **1991**, *254*, 1471; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 259.

[3] (a) Kaneda, K.; Fujii, M.; Morioka, K. *J. Org. Chem.* **1996**, *61*, 4503. (b) Kaneda, K.; Fujie, Y.; Ebitani, K. *Tetrahedron Lett.* **1997**, *38*, 9023.

[4] Cavani, F.; Trifiro, F.; Vaccari, A. *Catal. Today* **1991**, *11*, 173.

[5] (a) Kaneda, K.; Ueno, S.; Imanaka, T. *J. Chem. Soc., Chem. Commun.* **1994**, 797. (b) Kaneda, K.; Ueno, S.; Imanaka, T. *J. Mol. Catal. A: Chem.* **1995**, *102,* 135. (c) Kaneda, K.; Ueno, S. *Heterogeneous Hydrocarbon Oxidation*; Warren, B. K., Oyama, S. T., Eds.; ACS Symposium Series No. 638; American Chemical Society: Washington, DC, 1996; Chapter 22, p 300.

[6] Purchased from N. E. Chemcat. Co. Ltd.

[7] This Ru $3d_{2/5}$ XPS peak position is assigned to an oxidized ruthenium. X-ray absorption measurements on the Ru K-edge also showed the state of Ru in the hydrotalcite is a cationic form. Therefore, the Ru element in the hydrotalcite is present in an oxidized state and a possibility of metallic Ru in the hydrotalcite can be excluded.

[8] The order of the d-spacing of the Ru-hydrotalcite with various interlayer anions is as follows: DS (26.0 Å) > TA (14.1 Å) > ND (8.6 Å) > SA (8.1 Å) > Cl (7.95 Å) ≈ AcO (7.94 Å) ≈ CO_3 (7.92 Å) ≈ SO_4 (7.92 Å). The d-spacing of the Ru-hydrotalcite is not related to the oxidation activity. Most of the active basic sites are probably located on the outer surface of the Ru-hydrotalcite.

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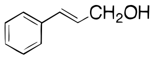
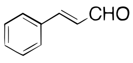
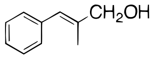
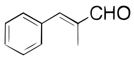
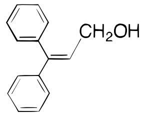
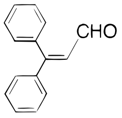
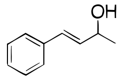
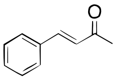
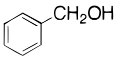
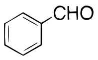
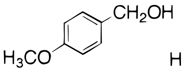
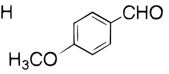
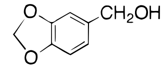
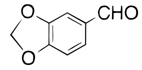
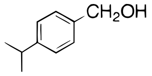
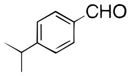
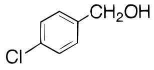
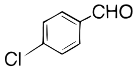
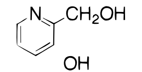
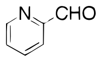
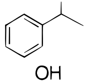
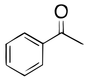
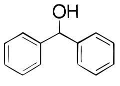
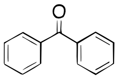
Table 1. Oxidation of Cinnamyl Alcohol Using Various Hydrotalcites[a]

run	catalyst	conversion (%)	yield of cinnamaldehyde (%)	heat of adsorption[b] (J/g)
1	$Mg_6Al_2Ru_{0.5}(OH)_{16}CO_3$	73	68	32.1
2	$Mg_6Al_2Ru_{0.5}(OH)_{16}Cl$	50	47	28.8
3	$Mg_6Al_2Ru_{0.5}(OH)_{16}AcO$	45	36	10.2
4	$Mg_6Al_2Ru_{0.5}(OH)_{16}SO_4$	29	26	1.7
5	$Mg_6Al_2Ru_{0.5}(OH)_{16}TA$[c]	18	15	
6	$Mg_6Al_2Ru_{0.5}(OH)_{16}ND$[d]	18	15	
7	$Mg_6Al_2Ru_{0.5}(OH)_{16}DS$[e]	30	9	
8	$Mg_6Al_2Ru_{0.5}(OH)_{16}SA$[f]	4	4	0
9	$Mg_6Al_2(OH)_{16}CO_3$	5	2	

[a] Reaction conditions: cinnamyl alcohol, 2.0 mmol; catalyst, 0.3 g; toluene, 5 mL; 60 °C, 5 h, O_2 atmosphere. [b] Calorimetric heat of adsorption of benzoic acid. [c] TA = terephthalic acid. [d] ND = 1,5-naphthalenedisulfonic acid. [e] DS = dodecylsulfuric acid. [f] SA = sebacic acid.

Table 2. Oxidation of Various Allylic and Benzylic Alcohols using $Mg_6Al_2Ru_{0.5}(OH)_{16}CO_3$ Hydrotalcite[a]

Entry	Substrate	Product	Time (h)	Conv. (%)	Yield [b] (%)
1			8	98	95(92)
2			5	100	97
3			5	100	quantitative (96)
4			24	95	95
5			8	98	95
6			8	95	91(76)
7			8	100	quantitative (92)
8			8	100	quantitative
9			8	64	61
10			24	66	50
11			18	100	quantitative (90)
12			8	100	quantitative (91)

[a] Reaction conditions: substrate, 2 mmol; catalyst, 0.3 g; toluene, 5 mL; 60 °C, O_2 atmosphere. [b] Yields were determined by GLC analysis. Values in parentheses are isolated yields. In the case of the product isolation experiments, the reaction scale was three times as much as that of reaction conditions (a).

titative yields (Table 2, runs 1−3). 4-Phenyl-3-buten-2-ol showed lower reactivity than the above allylic alcohols, but prolonging the reaction time to 24 h attained 95% yield of 4-phenyl-3-buten-2-one (Table 2, run 4). In the cases of benzylic alcohols, the corresponding benzyl aldehydes could be obtained in high yields for 8 h (Table 2, runs 5−8) except for *p*-chlorobenzyl alcohol (Table 2, run 9). It is notable that benzoic acids as overoxidation products could not be detected under the reaction conditions. In this oxidation system, *primary* alcohols were generally oxidized faster than *secondary* alcohols; 1-phenylethanol took 18 h to attain a high yield of acetophenone (Table 2, run 11).

We think that active sites of $Mg_6Al_2Ru_{0.5}(OH)_{16}CO_3$ might be derived from hydroxyl groups associated to the ruthenium cations.[9] Alcohol attacks on a hydroxyl group on the ruthenium, and then a ligand-exchange reaction between the hydroxyl and alcohol gives a Ru-alkoxide species, which further undergoes β-elimination to afford an aldehyde product.[10] Molecular oxygen reacts with remaining a Ru-hydride species to generate the Ru-hydroxyl species on the hydrotalcite.[11] Presumably, the hydroxyl groups (OH^-) with strong bacisity promote the ligand exchange between alcohol and hydroxyl; a basic hydroxyl group abstracts a proton from alcohol to form a water molecule and a Ru-alkoxide species. In our separated experiments, we found that Ru-hydrotalcites having high heat of adsorption of benzoic acid, viz. strong basicity, showed high yields of the aldehydes in the above oxidations, as shown in Table 1.[12]

In conclusion, oxidation of various kinds of allylic and benzylic alcohols is efficiently catalyzed by the ruthenium-hydrotalcite having a carbonate anion to give the corresponding carbonyl compounds in the presence of molecular oxygen. Aromatic allylic alcohols, especially, show much higher reactivity toward the above oxidation than aliphatic allylic ones.[13] This heterogeneous hydrotalcite catalyst system does not stress the environment because of the use molecular oxygen as an oxidant and of its strikingly simple workup; the hydrotalcite is easily separated from the reaction mixture and is reusable without an appreciable loss of activity.

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[9] The addition of 2,6-di-*tert*-butyl-*p*-cresol as a radical scavenger to the reaction mixture did not strongly affect the yield of cinnamaldehyde.

[10] (a) Almeida, M. L. S.; Beller, M.; Wang, G.-Z.; Bäckvall, J. E. *Chem. Eur. J.* **1996**, *2*, 1553. (b) Karlsson, U.; Wang, G.-Z.; Bäckvall, J. E. *J. Org. Chem.* **1994**, *59*, 1196. (c) Graauw, C. F.; Peters, J. A.; Bekkum, H.; Huskens, J. H. *Synthesis* **1994**, 1007.

[11] In the absence of molecular oxygen, oxidation of cinnamyl alcohol using $Mg_6Al_2Ru_{0.5}(OH)_{16}CO_3$ gave an extremely low yield (5%) of cinnamaldehyde.

[12] The basicity of the various hydrotalcites was estimated by measurement of calorimetric heats of benzoic acid adsorption using a micro differential scanning calorimetry. (a) Miyata, S. *Clays. Clay Miner.* **1983**, *31*, 305. (b) Ueno, S.; Ebitani, K.; Okubo, A.; Kaneda, K. *Appl. Surf. Sci.* **1997**, *121/122*, 366.

[13] The oxidation of aliphatic allylic alcohols such as 2-hexen-1-ol, 3-octen-2-ol, perillyl alcohol, and myrtenal hardly occurred on $Mg_6Al_2Ru_{0.5}(OH)_{16}CO_3$ under the above reaction conditions. In many oxidation systems, the reactivities of aliphatic and aromatic allylic alcohols are comparable. There are few reagents having higher activity for aromatic allylic alcohols than aliphatic ones. For examples, see the following. Alkoxymagnesium bromide/*N*-chlorosuccinimide/*t*-BuOLi: Mukaiyama, T.; Tsunoda, M.; Saigo, K. *Chem. Lett.* **1975**, 691. Notably, Ru/Al_2O_3 catalyst (Ru content: 5 wt %[6]) efficiently oxidized both the aromatic and aliphatic allylic alcohols under our reaction conditions. The different phenomena between the above two Ru catalysts may arise from the differences of the Ru oxidation state and/or of a dispersion of the Ru species. The origin of the unique catalytic behavior of the Ru-hydrotalcite will be discussed in a full paper based on the characterization of the Ru cations in the Brucite layer by means of XAFS together with the catalyst preparation method.