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Creation of a Monomeric Ru Species on the Surface of Hydroxyapatite as an Efficient Heterogeneous Catalyst for Aerobic Alcohol Oxidation

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The oxidation of alcohols to carbonyl compounds is one of the most important functional transformations in organic synthesis,[1] and numerous oxidizing reagents are available to effect this selective transformation. These oxidizing reagents are, however, often used in stoichiometric amounts and are sometimes toxic. Recently, much attention has been paid for the development of metal catalysts for the alcohol oxidation using molecular oxygen,[2] and use of some homogeneous transition metal complexes has achieved high activity and selectivity,[3] but there are few excellent heterogeneous catalysts despite offering significant advantages from an environmental standpoint.[4]

Hydroxyapatites have been of considerable interest in many areas such as artificial bones and teeth, adsorbents, ion-exchangers, and catalysts because of their several unique characters.[5] Various kinds of transition metal cations, which have a high potentiality for the function as the catalytic active center, can be readily accommodated into the apatite framework based on their large cation exchange ability.[5] We found that monomeric Ru cation species could be uniformly fixed on the surface of the calcium hydroxyapatite and this Ru^{3+}-exchanged hydroxyapatite (RuHAP) acted as an effective heterogeneous catalyst for the oxidation of various alcohols using molecular oxygen. In this paper, we report a preparation of the RuHAP on the basis of the characterization using physicochemical methods and its unique catalysis for the alcohol oxidation.

A calcium hydroxyapatite of Ca/P = 1.67 (HAP), $Ca_{10}(PO_4)_6(OH)_2$, was synthesized according to the literature procedure.[5b] The HAP (1.0 g) was stirred with 75 mL of a 2.67×10^{-2} M aqueous $RuCl_3$ solution at 25 °C for 24 h. The obtained slurry was filtered, washed with deionized water, and dried overnight at 110 °C, yielding the RuHAP as a dark brown powder. The XRD peak positions of the RuHAP were similar to those of a parent HAP. From the elemental analysis, the (Ru+Ca)/P ratio of the RuHAP was estimated to 1.67 (Ru content: 17.1 wt %, 1.69 mmol·g^{-1}), which shows the occurrence of an equimolar substitution of Ru^{3+} for Ca^{2+} at the column of Ca and O atoms parallel to the hexagonal axis.[5] The presence of chlorine was confirmed by XPS and EDX analyses; the atomic ratio of Ru to Cl was 1:1. The Ru K-edge XANES of the RuHAP resembles that of $RuCl_3$.[6] In Fourier transform (FT) of k^3-weighted Ru K-edge EXAFS of the RuHAP, the lack of peaks around 3.5 Å indicates no Ru−Ru bond on the RuHAP in Figure 1a. The inverse FT of main peaks was well fitted by the use of three Ru−O and single Ru−Cl shells, as summarized in Figure 1b and Table 1.[7] Conclusively, the Ru species on the surface of the RuHAP exists as a monomeric Ru cation surrounded by oxygen and chlorine and a proposed surface structure of the RuHAP is represented in Figure 1c. *The present simple preparation method using the cation-exchange ability of HAP can allow a strong protocol to create a monomeric metal species on the solid surface as a hybrid heterogeneous catalyst.*

Table 1. Curve-Fitting Analysis for RuHAP Catalyst[a]

shell	coord. no.	interatomic dist., Å	Δσ,[b] Å
Ru−O(1)	4.1	1.97	0.0067
Ru−O(2)	2.1	2.28	0.0008
Ru−O(3)	1.7	2.62	−0.0054
Ru−Cl	1.2	2.32	0.0010

[a] The region of 0.8−2.8 Å was inversely Fourier transformed. [b] Δσ is the difference between the Debye−Waller factor of RuHAP and that of the reference sample.

Oxidation of various alcohols using the RuHAP catalyst at 80 °C under O_2 atmosphere efficiently proceeded to give the corresponding carbonyl compounds, as summarized in Table 2. Especially, benzylic and allylic compounds showed high reactivity for the oxidative dehydrogenation (entries 1−13). A 100 mmol scale oxidation of benzyl alcohol was also performed to give 98% yield of benzaldehyde; the turnover number approached 290 after 24 h. It is notable that a *primary* aliphatic alcohol of 1-octanol was smoothly oxidized to afford 1-octanal without any formation of the corresponding carboxylic acid and ester (entry 14).[8] Moreover, this catalyst system was applicable for the oxidation of heterocyclic alcohols including nitrogen and sulfur atoms. For example, 2-pyridinemethanol and 2-thiophenemethanol gave the corresponding aldehydes in high yields (entries 17 and 18). Even under air conditions in place of pure O_2, the above oxidations proceeded smoothly; a quantitative yield of benzaldehyde was obtained within 3 h (entry 2). Furthermore, *the RuHAP catalyst could be reused with a retention of its high catalytic activity and selectivity*; the yield of benzaldehyde in the case of benzyl alcohol could be kept over 93% during three recycling experiments. The Ru content between fresh and spent RuHAP catalysts did not change and no Ru leaching in the filtrate was observed during the above recycles by the ICP method whose detection limit is 24 ppb.

In the oxidation of para-substituted benzyl alcohols, the Hammett ρ value was −0.429, which is close to that with a stoichiometric reagent of a monomeric $RuCl_2(PPh_3)_3$ complex, $\rho = -0.431$. When an equimolar mixture of 1-octanol and 4-octanol was used as substrate, 95% 1-octanal was selectively obtained

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[6] X-ray adsorption spectra were recorded at the beam line 01B1 station attached to the Si(311) monochromator at SPring-8 of JASRI, Harima, Japan (prop. No. 2000A0278-NX-np). The detailed procedures for data analysis are described elsewhere: Tanaka, T.; Yamashita, H.; Tsuchitani, R.; Funabiki, T.; Yoshida, S. *J. Chem. Soc., Faraday Trans.* **1988**, *84*, 2987.

[7] The distance from Ru to the nearest four oxygen atoms, Ru−O(1), in the RuHAP is consistent with the value for RuO_2 (R = 1.96 Å), and the Ru−Cl distance of 2.32 Å is close to that found in monochlororuthenium complexes: Joslin, F. L.; Mague, J. T.; Roundhill, D. M. *Organometallics* **1991**, *10*, 521.

[8] When the reaction temperature was raised from 60 to 80 °C, 1-octanoic acid was obtained in 82% yield for 6 h without formation of the corresponding aldehyde.

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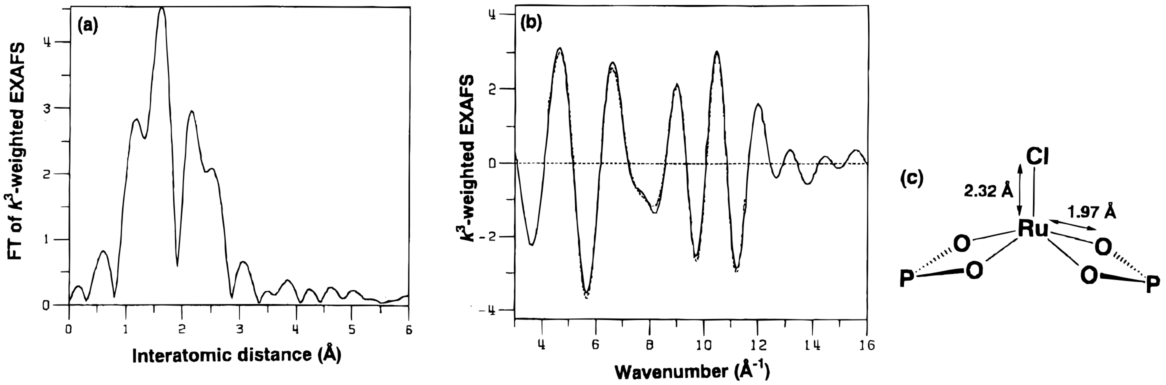
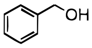
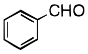
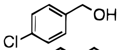
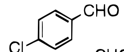
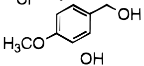
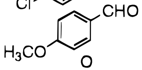
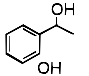
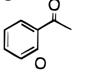
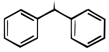
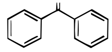
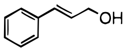
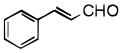
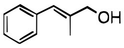
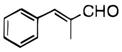
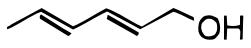
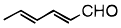
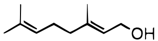
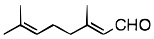
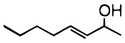
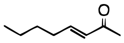
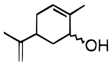
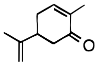
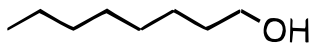
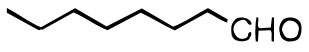
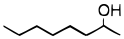
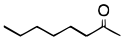
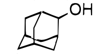
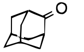
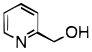
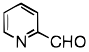
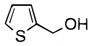
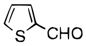


Figure 1. (a) FT magnitude of k^3-weighted EXAFS of RuHAP, (b) inverse FT of the peaks with the $0.8 < R/\text{Å} < 2.8$ range in part a, and (c) a proposed surface around Ru^{3+} of RuHAP catalyst. The nearest oxygens around Ru^{3+} are shown. The dotted line in part b shows the result of a curve-fitting analysis using three Ru−O and a single Ru−Cl shell parameters in the range 4−12 Å^{-1}.

Table 2. Oxidation of Various Alcohols Catalyzed by RuHAP Using Molecular Oxygen[a]

entry	substrate	product	time (h)	convn[b] (%)	yield[b] (%)
1			3	100	>99
2[c]			3	100	95
3[d]			48	20	17
4			3	100	>99
5			3	100	92
6			2	100	98
7			2	100	>99
8			1	100	99
9			2	100	95
10			4	99	99
11			3	90	85
12			5	93	91
13			6	83	80
14[e]			16	95	94
15			6	96	96
16[f]			4	100	95
17			10	100	>99
18			2	100	94

[a] Alcohol (2 mmol), RuHAP (0.2 g), toluene (5 mL), 80 °C, O_2 atmosphere. [b] Determined by GC using an internal standard technique. [c] Under 1 atm of air instead of pure O_2. [d] N_2 atmosphere. [e] The reaction temperature was lowered to 60 °C [f] Alcohol (1 mmol), RuHAP (0.1 g), toluene (5 mL), 80 °C, O_2 atmosphere.

together with 5% 4-octanone.[3e,f,9] In the intramolecular competitive oxidation of 1,7-octanediol, the RuHAP catalyst gave chemoselectively 7-hydroxyoctanal in 80% yield. The above high chemoselectivity for primary hydroxyl functions is not similar to that of bulk Ru catalysts such as RuO_2 and Ru/Al_2O_3,[10] but to that of a monomeric $RuCl_2(PPh_3)_3$ complex. We think that this catalytic behavior may be attributed to monomeric Ru cation species on the RuHAP surface. In consideration of the reaction mechanism for monomeric Ru complexes, we here propose a possible catalytic cycle of this alcohol oxidation using the RuHAP. The oxidation is initiated by a ligand exchange between an alcohol and a Cl species of the RuHAP to give a Ru-alcoholate species,[11] which undergoes the β-hydride elimination to produce the corresponding carbonyl compound and a Ru-hydride species. Reaction of the hydride species with O_2 affords a Ru-hydroperoxide species, followed by the ligand exchange to regenerate the Ru-alcoholate species together with the formation of O_2 and H_2O.[12] In the case of $RuCl_2(PPh_3)_3$, the catalytic cycle was not completed without hydroquinone[3d] or 2,2′,6,6′-tetramethylpiperidine *N*-oxyl.[3e] It is notable that our RuHAP catalyst does not need the above additives for the catalytic aerobic oxidation. Further, the above mechanism can be well evidenced by the following experiments of benzyl alcohol: (i) Addition of a radical trap, 2,6-di-*tert*-butyl-*p*-cresol, to the reaction medium hardly influenced the oxidation. (ii) One mole of H_2O was produced for every mole of benzaldehyde formation. (iii) In monitoring the O_2 uptake, 2 mol of benzaldehyde were equivalent to 1 mol of O_2 consumption. (iv) Under N_2 atmosphere, benzaldehyde was obtained only in a stoichiometric amount to Ru on the RuHAP catalyst (Table 2, entry 3). Kinetics data of this alcohol oxidation could be well accommodated with a rate equation based on the Michaelis−Menten type model for the above proposed mechanism.[13] The β-elimination is a rate-determining step in the overall oxidation process because the k_H/k_D value of 7.0 was observed in the competitive oxidation of benzyl alcohol and benzyl-d_7 alcohol ($C_6D_5CD_2OH$).[13]

In conclusion, the RuHAP is an effective heterogeneous catalyst for the oxidation of various alcohols, which is dominated by the formation of a monomeric Ru species as the phosphate complex on the RuHAP surface. No Ru leaching was observed during oxidations and then the Ru catalyst was recyclable. We believe that this design strategy for HAP-bound transition metal catalysts can be further applied to a wide range of functional transformations in organic synthesis.

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Supporting Information Available: Experimental procedures and kinetics (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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