Ruthenium-Incorporated Hydroxyapatites for the Oxidation of Alcohols and Amines Using Molecular Oxygen as an Oxidant

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Oxidation of alcohols and amines into the corresponding carbonyl and nitrile compounds in an environmentally benign and cost-effective way has been an important topic in synthetic chemistry. Particularly, as a replacement for the treatment of stoichiometric amounts of expensive and toxic oxidizing reagents, recently there have been intensive efforts on the development of novel oxidation reactions by using molecular oxygen as an oxidant under mild conditions.[1–3]

Hydroxyapatite (HAP, $Ca_{10}(PO_4)_6(OH)_2$)[4] is known to be a major inorganic constituent of mammalian bone and teeth. In particular, it is reported that various kinds of transition metals having catalytic activities can be readily incorporated into hydroxyapatite by a cation exchange reaction. In particular, the Kaneda group reported that HAPs containing Pd and Ru can be applied for various reactions.[5,6] Recently, we reported the aerobic oxidation of alcohols using ruthenium-incorporated HAP (RuHAP) in which the HAP used as catalytic support was (1) a single crystal prepared by molten salt synthesis, (2) an amorphous HAP, or (3) a calcium-deficient HAP.[7] In this study, we have synthesized seven calcium phosphates that were prepared under seven different NaOH concentrations. We have utilized these calcium phosphates as catalytic supports for ruthenium, and applied RuHAP for the oxidation of alcohols and amines using O_2 as oxidant. We found that RuHAPs prepared under NaOH concentration ranging from 2 to 5 M exhibited high catalytic property.

The synthesis of calcium phosphates was reported previously.[7,8] RuHAP was prepared by soaking each HAP (0.5 g) into 20 mM of $RuCl_3$ solution (20 mL). The solution was filtered and washed three times using 100 mL of deionized (DI) water, followed by drying overnight in an oven at 70 °C temperature.

Figure 1 shows the X-ray diffraction (XRD) data of calcium phosphates prepared under different NaOH concentrations (0, 2, 4, 5, 10, 15, and 20 M). We find that monetite ($CaHPO_4$, dicalcium phosphate anhydrous, DCP) is synthesized at 0 M NaOH concentration (JCPDS card number 70-1425). With NaOH concentration >2 M, HAPs are synthesized without the presence of other crystal phases. In general, monetite is prepared under acidic conditions.[9]

Figure 2 presents the morphological changes of calcium phosphates as a function of the NaOH concentration. Figure 2(a) shows the morphology of dicalcium phosphate in which the crystallites exhibit an elongated rod shape with a few micrometers in size. At higher NaOH concentrations (Figure 2(b)–(g)), nanocrystalline HAPs present as elongated hexagonal rods. Particularly, as the NaOH concentration increases, the aspect ratio seems to decrease. Figure 2(h) shows the transmission electron microscopy (TEM) image of HAP-4M NaOH after ion exchange under 50 mM $RuCl_3$ solution (RuHAP (4 M)). Ruthenium clusters (< ~2 nm) are dispersed evenly on the surface of HAP after the ion-exchange reaction.

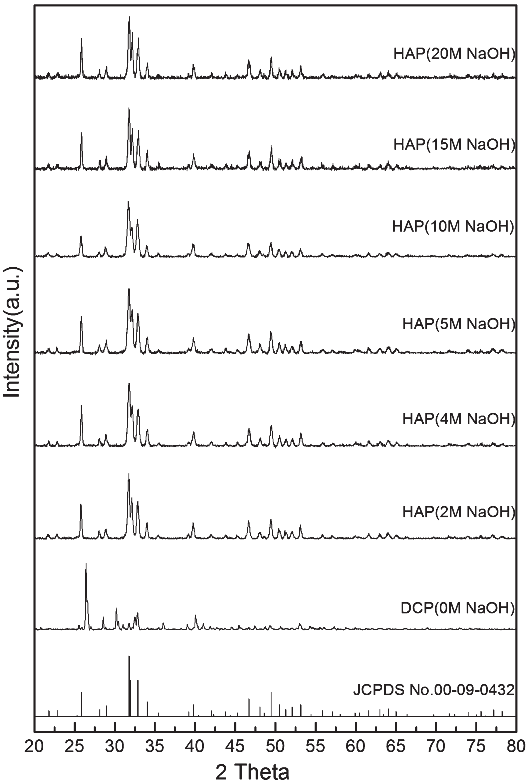

Figure 1. XRD patterns of calcium phosphates synthesized under different NaOH concentrations.

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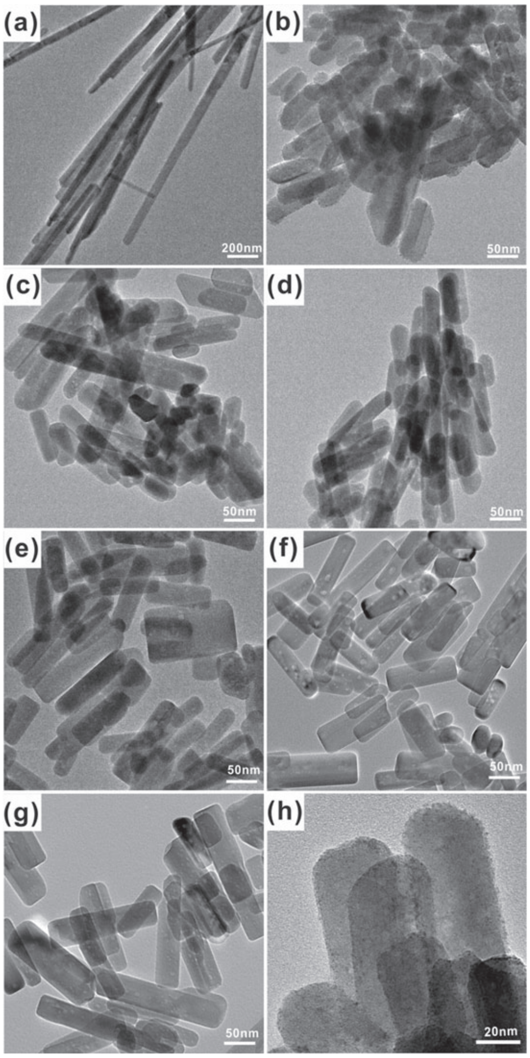
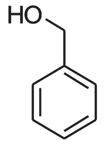
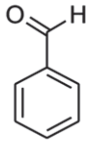
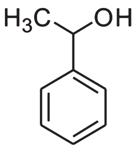
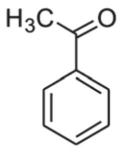
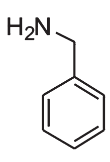
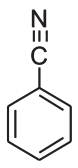


Figure 2. (a–g) TEM images of calcium phosphate prepared by different NaOH concentrations. (a) 0 M, (b) 2 M, (c) 4 M, (d) 5 M, (e) 10 M, (f) 15 M, and (g) 20 M. (h) TEM image of RuHAP (4 M).

Table 1 shows the catalytic property of our solid catalysts for oxidation of alcohols and amines into the corresponding carbonyl and nitrile compounds using O_2 (under 1 atm) as oxidant. We find that RuHAPs prepared under NaOH concentration ranging from 2 to 5 M exhibit higher catalytic ability for the oxidation of all three compounds (benzyl amine, 1-phenyl ethanol, and benzalhehyde). As shown in Figure 2, the sizes of HAP crystallites prepared under NaOH concentration between 2 and 5 M are small compared to those prepared under other concentrations. Therefore, surface area might be playing an important role in the catalytic activity. We plan to investigate the relation between the catalytic property and the structure of HAPs.

In summary, we prepared calcium phosphates under seven different NaOH concentrations. When these HAPs were tested as catalytic supports of Ru for alcohol and amine oxidation, we found that RuHAPs prepared under NaOH concentration ranging from 2 to 5 M exhibited high catalytic activity.

Table 1. Oxidation of benzyl alcohol, 1-phenyl ethanol, and benzyl amine catalyzed by RuHAP using O_2.

Catalyst	Substrate	Product	Time (min)	Conversion (%)
RuHAP(0 M)			30	17
RuHAP(2 M)			30	91
RuHAP(4 M)			30	88
RuHAP(5 M)			30	85
RuHAP(10 M)			30	53
RuHAP(15 M)			30	70
RuHAP(20 M)			30	43
RuHAP(0 M)			120	40
RuHAP(2 M)			120	90
RuHAP(4 M)			120	98
RuHAP(5 M)			120	49
RuHAP(10 M)			120	65
RuHAP(15 M)			120	83
RuHAP(20 M)			120	72
RuHAP(0 M)			60	8
RuHAP(2 M)			60	64
RuHAP(4 M)			60	54
RuHAP(5 M)			60	46
RuHAP(10 M)			60	42
RuHAP(15 M)			60	43
RuHAP(20 M)			60	49

Reaction conditions: catalyst 50 mg, benzyl alcohol (50 mM), 1-phenyl ethanol (50 mM), benzyl amine (10 mM) in 2 mL toluene at 105 °C.

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References

1. V. V. Costa, M. J. Jacinto, L. M. Rossi, R. Landers, E. V. Gusevskaya, *J. Catal.* **2011**, *282*, 209.
2. Z. Opre, D. Ferri, F. Krumeich, T. Mallat, A. Baiker, *J. Catal.* **2006**, *241*, 287.
3. K. Yamaguchi, N. Mizuno, *Angew. Chem. Int. Ed.* **2003**, *42*, 1480.
4. M. I. Kay, R. A. Young, A. S. Posner, *Nature* **1964**, *204*, 1050.
5. K. Mori, T. Hara, T. Mizugaki, K. Ebitani, K. Kaneda, *J. Am. Chem. Soc.* **2003**, *125*, 11460.
6. K. Mori, M. Tano, T. Mizugaki, K. Ebitani, K. Kaneda, *New J. Chem.* **2002**, *26*, 1536.
7. Y. Kim, D. Kim, S. Lee, D. Woo, J. Byun, K.-Y. Kwon, *Bull. Korean Chem. Soc.* **2014**, *35*, 2241.
8. S. Kim, J. H. Jung, D. H. Kim, D. K. Woo, J. B. Park, M. Y. Choi, K. Y. Kwon, *Bull. Korean Chem. Soc.* **2013**, *34*, 221.
9. B. Jokić, M. Mitrić, V. Radmilović, S. Drmanić, R. Petrović, D. Janaćković, *Ceram. Int.* **2011**, *37*, 167.

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