

## Preparation of Ruthenium Incorporated Heterogeneous Catalysts Using Hydroxyapatite as Catalytic Supports for Aerobic Oxidation of Alcohols

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Three different kinds of hydroxyapatites (HAPs) having different sizes and compositions are prepared by hydrothermal and molten salt syntheses. Using the ion exchange reactions, ruthenium ions are incorporated on the surface of HAPs. The crystallinity, morphology and ruthenium contents are investigated by XRD, SEM, TEM and ICP. We found that smaller size of HAP having large amounts of ruthenium under ion exchange reaction shows higher catalytic activity for aerobic oxidation of alcohols.

**Key Words** : Aerobic oxidation, Heterogeneous catalysts, Hydroxyapatite, Surface

### Introduction

Transformation of various functional groups with clean and cost effective way has become a critical issue in synthetic chemistry. Particularly, the development of proper routes for alcohol oxidations into corresponding carbonyl compounds are one of the most important methodologies both academic and industrial aspects. Instead of the usage of stoichiometric amounts of expensive and harmful oxidizing reagents, recently many of researchers have focused on developing environmentally benign oxidation reactions by using molecular oxygen (O<sub>2</sub>) under mild conditions.<sup>1-3</sup>

Hydroxyapatite (HAP, Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>) is known as main inorganic component of mature mammalian bone and teeth.<sup>4</sup> Because of its biocompatibility, HAP has been used as the model compounds for the study of biominerals.<sup>5-7</sup> One important chemical characteristic of HAP is its high ion exchange capability. It is well known that various anions such as carbonate, fluoride and chloride ions can be incorporated onto HAP surface *via* anion exchange with hydroxyl group in aqueous solution.<sup>8</sup> Previously we microscopically investigated impact of chloride and fluoride deposit onto HAP surface on dissolution behavior of HAP through direct observation of HAP surface using AFM.<sup>9,10</sup> In addition to anions, the calcium cation of HAP can be replaced by various transition metal ions.<sup>11,12</sup> Because of this high cation exchange capability, HAP has been applied sorption materials for removal of heavy metal ions dissolved in water.<sup>13,14</sup>

The capability of incorporation of transition metal ions renders HAP to be applied for substrate of heterogeneous catalysts. Particularly, Kaneda and coworkers demonstrated that Pd and Ru supported HAP is a suitable heterogeneous catalysts for oxidation, aldol reaction, and Diels-Alder reac-

tions.<sup>15-17</sup> Compared to these wide range usages of HAP for the substrate of heterogeneous catalysts, the dependence of the chemical/physical nature of HAP on catalytic activities has been relatively less investigated. In this study, we prepared three kinds of HAPs, 1) single crystalline HAP (single-HAP), 2) amorphous HAP (amorph-HAP), 3) calcium deficient HAP (CD-HAP) having different chemical composition, shape, size and crystallinity, and utilized these HAPs for the substrates of ruthenium incorporated heterogeneous catalysts. We applied these catalysts to the aerobic oxidation of alcohols into corresponding carbonyl compounds to investigate effect of substrates on catalytic activities, and found that Ru supported on amorphous HAP has higher catalytic activity.

### Experimentals

**Preparation of Single Crystal HAP (single-HAP).** Single crystal HAP was prepared by molten salt synthesis.<sup>18,19</sup> Amorphous HAP (20.0 g) was thoroughly mixed with potassium sulfate (12.0 g). The mixture was put inside a furnace at ambient temperature and initially heated to 800 °C over a 3-hour period. The sample was then heated more slowly to a temperature of 1150 °C over a 3-h period at a heating rate of approximately 1.6 °C per minute, and it remained in incubation for an additional 3 h at this temperature. The sample was then slowly cooled to 800 °C over 3 h, and then the furnace power was turned off to allow the sample to gradually reach room temperature. Finally, the mixture was washed four times with boiling hot water and filtered to obtain single-crystal HAP.

**Preparation of Calcium Deficient HAP (CD-HAP).** Coprecipitation method was applied to the synthesis of CD-HAP. An aqueous calcium nitrate solution (0.09 M, 230 mL)

was added dropwise into the aqueous  $(\text{NH}_4)_2\text{HPO}_4$  solution (0.1 M, 230 mL) while stirring. The pH of solution was adjusted to 9.5 by adding concentrated ammonia solution. The solution was stirred for one hour at room temperature, and then it was refluxed for one hour. The white precipitate was filtered off, washed with boiling DI water three times, and dried in an oven at 70 °C.

**Incorporation of Ruthenium on HAP Surface.** Two ruthenium concentration (10 mM and 50 mM) solutions were prepared by dissolving  $\text{RuCl}_3$  in DI water. To each of above solutions (20 mL), 1 g of three different HAPs (amorph-HAP, CD-HAP, single-HAP) is added respectively, followed by 5 min of sonication, and another 20 min of moderate mixing on a rocking platform at room temperature. The solution was filtered and washed three times using 100 mL of DI water. The resulting samples were dried overnight in a 70 °C oven prior to elemental analysis and catalytic reaction.

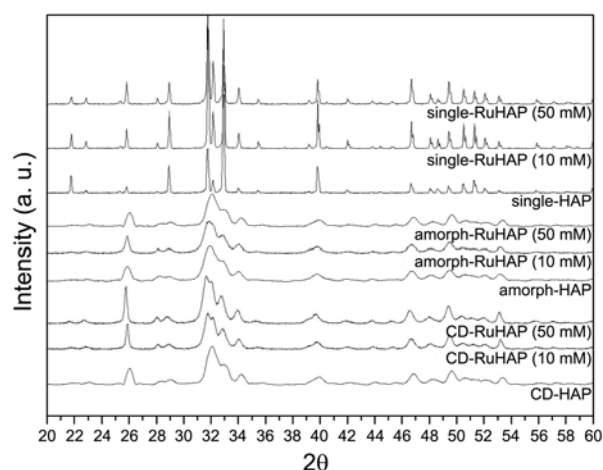
**Characterization of HAPs.** The crystalline phases of the HAPs and Ru incorporated HAPs were examined by powder XRD (3 kW Cu X-ray Diffractometer, D8 Advance, Bruker AXS Germany). The morphologies of the HAPs were identified by a scanning electron microscope (Jeol JSM-6380LV, Japan) and transmission electron microscope (Jeol 200 kV JEM-2010).

The amounts of Ru contents on HAP were characterized by inductively coupled plasma (ICP) spectrometer (OPTIMA 4300DV/5300DV, Perkin Elmer). Typical preparation of solution for ICP is as follow. 20 mg of ion-exchanged catalytic supports was dissolved in 3 mL of nitric acid followed by adjusting the volume of solution to 100 mL using volumetric flask by the addition of DI water.

**Catalytic Activity Measurements.** Given amount of alcohols (benzyl alcohol or 1-phenylethanol, 2.00 g) and catalysts (20 mg) were dissolved in toluene (20 mL) in 100 mL a round bottom flask (Table 2). All reactions were carried out at 90 °C at one atm pressure of  $\text{O}_2$  for given time. Yields are calculated by gas chromatography (Agilent 7890A).

## Results and Discussion

Figure 1 shows XRD patterns of three different kinds HAPs (single, amorphous, calcium deficient HAP) and their RuHAPs which are obtained after ion exchange. Single-

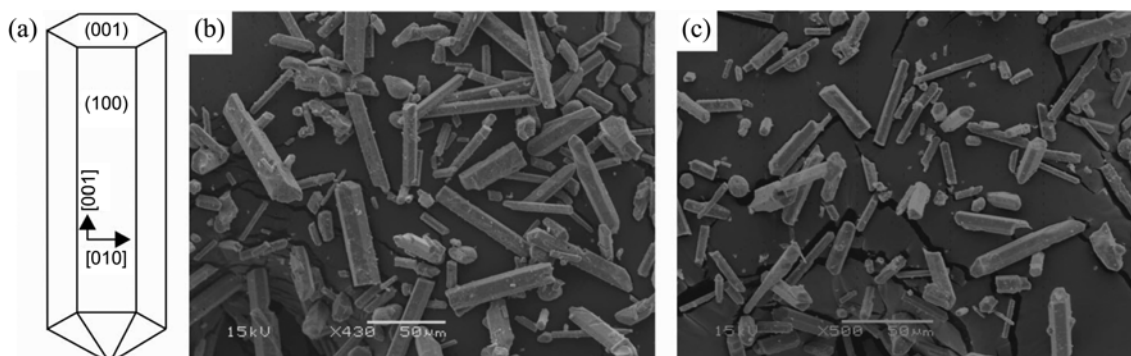


**Figure 1.** XRD patterns of HAP and RuHAP.

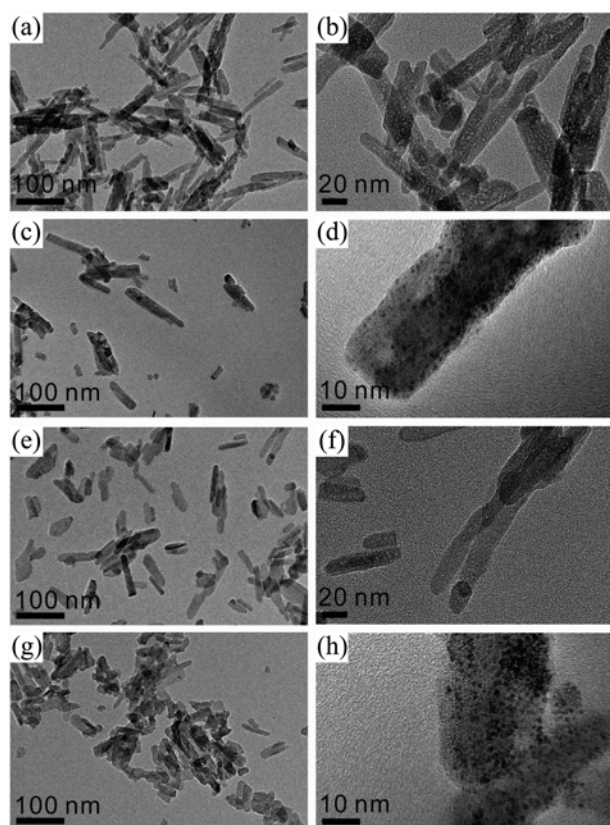
HAP prepared at high temperature (1150 °C) *via* molten salt synthesis exhibits relatively sharp XRD pattern. Amorphous and calcium deficient HAPs represent smooth XRD pattern compare to the XRD pattern of single-HAP, however, the 2-theta values are almost same for all three sample. All XRD data are consistent with prior typical HAP patterns.<sup>7</sup> In addition, careful analysis of XRD patterns confirms that single-HAP does not contain  $\alpha$ -tricalcium phosphate ( $\text{Ca}_3(\text{PO}_4)_2$ ), a thermal decomposition byproduct of HAP, which is commonly found when overheating occurs during HAP synthesis. Particularly, regardless of the type of HAPs, the XRD patterns after ion exchange are almost same to the XRD patterns previous to ion exchange. Therefore, the bulk crystallinity of HAPs is not affected by the treatment of Ru ion in aqueous solution.

Figure 2(a) shows the model of single crystal HAP in which crystallographic axis and facets are indicated. Figures 2(b) and 2(c) represent SEM image of single-HAPs and their Ru incorporated ones (single-RuHAP-50 mM). Single crystal HAPs prepared by molten salt synthesis represent typical [001]-direction elongated hexagonal rod shape (Fig. 2(b)). The length of single HAPs along the [001] direction is 30-80 nm. There is no notable morphological change after ion exchange (comparison of Figs. 2(b) and 2(c)).

Figures 3(a) and 3(b) show TEM images of amorph-HAP prepared by a hydrothermal method. amorph-HAPs exhibit



**Figure 2.** Model of HAP (a), SEM image of single-HAP (b), and single-RuHAP-50 mM (c).



**Figure 3.** TEM images, (a and b) amorph-HAP, (c and d) amorph-RuHAP, (e and f) CD-HAP, (g and h) CD-RuHAP.

elongated rod which is similar to the shape of single-HAP. We assume that the elongated direction of amorph-HAP corresponds to [001] direction of the single-HAP. However, the specific crystallographic facets are no longer observed in the amorph-HAP. The average size along the elongation direction is approximately 110 nm which is approximately much smaller than the size of single-HAP. Figures 3(c) and 3(d) represent TEM images of amorphous HAP after ion exchange under 50 mM  $\text{RuCl}_3$  solution (amorph-RuHAP-50 mM). After ion exchange, elongated morphology is not changed considerably. Compared to the sample before ion exchange (Fig. 3(a)), however, precipitates having smaller size (less than  $\sim 10$  nm) are appeared (Fig. 3(c)). Existence of these small precipitates might be caused by dissolution-precipitation mechanism under acidic solution.<sup>20,21</sup> Figure 3(d) shows high resolution TEM image of RuHAP-50mM where ruthenium cluster (less than  $\sim 2$  nm) are distributed homogeneously on the surface of amorphous HAP. Previously Kaneda and coworker group investigated the ion exchange properties of HAPs with various cations.<sup>22-24</sup> They reported that ruthenium exists in monomeric cation instead of cluster under ion exchange reaction under aqueous solution.<sup>16</sup> They also reported incorporation of monomeric Pd and Pd cluster on HAP where water and organic solvent are used for the preparation of monomeric Pd and Pd cluster, respectively.<sup>15</sup> Considering preferential existence of monomeric Ru in aqueous solution, we suppose that both monomeric Ru and Ru

cluster form can be possible in our sample. The morphology of CD-HAP prepared by a hydrothermal reaction shows an elongated rod, which is similar to the shape of amorph-HAP (Figs. 3(e) and 3(f)). In addition, Ru clusters are also observed on the surface of CD-HAP after ion exchange reaction.

Ion exchange of ruthenium in the presence of each of HAPs revealed the amount of ruthenium that could be incorporated onto the catalytic supports is related to size and Ca composition of HAPs. In order to identify the Ru content of the catalytic supports after ion exchange, ICP elemental analysis was performed on each of HAPs (single, amorphous, and CD-HAP) in two different ruthenium concentrations (10 mM and 50 mM). We identified that the ruthenium amount of single-RuHAP is much smaller than that of amorph-RuHAP (or CD-RuHAP) under both 10 and 50 mM concentration (Table 1). Small Ru contents of single-RuHAP may originate from smaller surface area of single-HAP attributable to the larger crystal size of single-HAP. It is noteworthy to point out that highest Ru content of samples is 0.571 mmol of Ru per gram of CD-RuHAP-50 mM. The amount of 0.571 mmol of Ru/gram of catalytic support indicates that less than 6% of calcium ions are exchanged with ruthenium (The lowest amounts of 0.073 mmol of Ru per gram of single-RuHAP-10 mM mmol corresponds to approximately 0.7% of ion exchange). Therefore, we believe that ion exchange takes place dominantly on the surface of HAP instead of the calcium ion in the bulk. Consequently, the patterns of XRD after ion exchange are almost same to the XRD patterns

**Table 1.** Contents of ruthenium in RuHAP

Catalyst	Ru (mmol)/Cat. (g)
single-RuHAP (50 mM)	0.089
amorph-RuHAP (50 mM)	0.549
CD-RuHAP (50 mM)	0.571
single-RuHAP (10 mM)	0.073
amorph-RuHAP (10 mM)	0.126
CD-RuHAP (10 mM)	0.149

**Table 2.** Oxidation of benzyl alcohol and 1-phenyl ethanol catalyzed by RuHAP using  $\text{O}_2$

Catalyst	Substrate	Product	Time (h)	Yield (%)
single-RuHAP (50 mM)			24	20
amorph-RuHAP (50 mM)			3	> 99
CD-RuHAP (50 mM)	<chem>c1ccc(cc1)CO</chem>	<chem>c1ccc(cc1)C=O</chem>	3.5	> 99
single-RuHAP (10 mM)	<chem>c1ccc(cc1)CO</chem>	<chem>c1ccc(cc1)C=O</chem>	24	13
amorph-RuHAP (10 mM)			20	99
CD-RuHAP (10 mM)			20	> 99
single-RuHAP (50 mM)			24	43
amorph-RuHAP (50 mM)			3.5	98
CD-RuHAP (50 mM)	<chem>c1ccc(cc1)C(O)C</chem>	<chem>c1ccc(cc1)C(=O)C</chem>	4	97
single-RuHAP (10 mM)	<chem>c1ccc(cc1)C(O)C</chem>	<chem>c1ccc(cc1)C(=O)C</chem>	24	14
amorph-RuHAP (10 mM)			24	94
CD-RuHAP (10 mM)			24	89

before ion exchange. CD-RuHAP contains slightly higher Ru content than amorph-RuHAP under both 10 and 50 mM Ru solutions. We suppose that by lowering the Ca composition during synthesis of the HAP crystals, ruthenium can incorporate on HAP supports by adsorption on the calcium deficient sites as well as ion exchange with calcium ions.

Oxidation of benzyl alcohol and 1-phenyl ethanol using three different kind of RuHAP catalysts at 90 °C under 1 atm pressure of O<sub>2</sub> proceeded to provide the corresponding carbonyl compounds, as summarized in Table 2. The catalytic activities of amorph-RuHAP and CD-RuHAP are better than that of single-RuHAP. We think that this difference is mainly caused by the amount of Ru incorporated on the surface of catalytic supports. Therefore amorph-RuHAP and CD-RuHAP shows similar catalytic activity.

In conclusion, we prepared ruthenium incorporated heterogeneous catalysts using three different kind of HAP as catalytic supports. Ruthenium is introduced on the surface of HAP in which monomeric ruthenium and cluster can be formed. amorpho- and CD-RuHAP containing higher Ru contents shows better catalytic activity than single-RuHAP. We believe that this ion exchange capability of HAP can be applied a wide range of functional transformations in synthetic chemistry.

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