

## Local structure around non-crystallized transition metals incorporated in hydroxyapatites

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### Introduction

It is generally known that, in XRD of hydroxyapatite ( $M_{10}(PO_4)_6(OH)_2$ ; M = divalent cation) incorporated with transition metals, there are no information on the nature of the incorporated species. For example, XRD pattern of strontium hydroxyapatite (SrHAp, M=Sr) is essentially identical to that of SrHAp incorporated with  $Co^{2+}$  (Co-SrHAp) [1]. Based on the preparation procedure of Co-SrHAp, the following three situations for  $Co^{2+}$  may be suggested: (1) ion-exchanged type as  $Sr_{10}(PO_4)_6(OH)_2 + Co_{10}(PO_4)_6(OH)_2$  (CoHAp); (2) solid-solution type as  $Sr_{10-x}Co_x(PO_4)_6(OH)_2$ ; (3) Co-supported type as Co/Sr $_{10}(PO_4)_6(OH)_2$ . In this report, XAFS has been employed for the analysis of Co-SrHAp and possible structure of the Co-incorporated material is suggested.

### Experimentals

Strontium hydroxyapatite (SrHAp) was prepared from  $Sr(NO_3)_2$  and  $(NH_4)_2HPO_4$ . Into SrHAp, cobalt action was incorporated by stirring the solid and  $Co(NO_3)_2 \cdot 6H_2O$  in aqueous solution at 293 K [1]. Undoped SrHAp was treated in the same manner but without the addition of cobalt nitrate. After washing with distilled  $H_2O$  and drying 373 K overnight, the sample was calcined at 773 K for 3 h. The incorporated solids are denoted as Co $_{xx}$ SrHAp, with xx equal to 1000Co/Sr (atomic ratio), which is measured with ICP. In order to characterize those samples, XRD (Rigaku RINT-2500X), solid state  $^{31}P$  MAS NMR (Bruker Avance DSX300) and XPS (Shimadzu ESCA-1000AX) were employed together with XAFS. X-ray absorption spectroscopy (XAFS) were measured (2.5 GeV) with a storage ring current of 67 mA at the High Energy Research Organization. The X-rays were monochromatized with channel-cut Si(311) crystals at the BL-10B station for the measurement of XAFS near the Sr-K edge while those were monochromatized with Si(111) double monochromator and the higher order harmonics were eliminated by a focusing double mirror system at the BL-9A station for the measurement of XAFS near the Co-K edge. The absorption spectra were observed using ionization chamber in a transmittance mode. The photon energy was scanned in the range 7.4-8.8 and 15.8-17.1 keV for Co-K and Sr-K edges, respectively. Details of the calculation procedures on XAFS were described in our previous paper [2].

### Results and Discussion

XRD patterns of Co-SrHAp were essentially identical

to that of SrHAp and information from  $Co^{2+}$  in Co-SrHAp were not obtained at all, although ICP and XPS analyses showed that Co is certainly present in bulk and on surface of those samples, respectively. In the XPS spectra of those fresh hydroxyapatites, peaks attributed to Sr 3p $_{1/2}$ , O 1s, P 2s and Co 2p $_{3/2}$  (when present) were found at approximately 280, 531, 190 and 782 eV, regardless of the contents of incorporated cobalt. In order to characterize cobalt species in the cobalt-incorporated catalysts, XAFS and  $^{31}P$  MAS NMR have been employed. The X-ray absorption near-edge structure (XANES) spectra near the Co-K edge of Co55SrHAp and CoO showed that edge position of those samples near the Co-K edge was similar, indicating that the electronic configuration of cobalt-species in Co55SrHAp are not significantly different from that of  $Co^{2+}$  in CoO. However the shape of the spectra from those two samples was evidently different. Therefore the site symmetry of cobalt in those two samples was evidently different and Co species in Co55SrHAp was not CoO. Cobalt-oxygen distances obtained by EXAFS analyses of Co-SrHAp and CoO shows that the distances of Co-O in Co36SrHAp (0.204 nm) and Co55SrHAp (0.201 nm) are dissimilar to that in CoO (0.245 nm). Therefore Co species in Co-SrHAp is not Co-supported type as CoO/Sr $_{10}(PO_4)_6(OH)_2$ . It should be noted that the nearest distances of Sr-O in SrHAp (0.254 nm) and Co-SrHAp (0.252-0.255 nm) are longer than those of Co-O while XRD patterns of those catalysts were essentially identical. Based on these results and the structure of SrHAp, it may be suggested that  $Sr^{2+}$  in SrHAp is replaced by  $Co^{2+}$  to afford Co-SrHAp as solid-solution type of  $Sr_{10-x}Co_x(PO_4)_6(OH)_2$  while site-center of those cations may be rather different, resulting in the deviation from site symmetry of SrHAp, which can not be detected by XRD but detected by EXAFS.  $^{31}P$  MAS NMR spectra of SrHAp and Co-SrHAp revealed that the intensity of the side band was greater with increasing the content of  $Co^{2+}$  in Co-SrHAp, indicating that site symmetry around P species may fall into disorder due to site-positioning of  $Co^{2+}$ . Only one  $^{31}P$  MAS NMR peak from SrHAp and Co-SrHAp demonstrates that  $PO_4^{3-}$  ions in both unit cells have similar structural environment, suggesting the formation of solid-solution like  $Sr_{10-x}Co_x(PO_4)_6(OH)_2$ .

### References

- [1] S.Sugiyama et al., Appl. Catal. A., 211, 123 (2001).  
[2] S.Sugiyama et al., Bull. Chem. Soc. Jpn., 74, 187 (2001).

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