



Malodors adsorption behavior of metal cation incorporated hydroxyapatite



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ARTICLE INFO

Keywords:

Hydroxyapatite
Adsorption
Ammonia
Hydrogen sulfide
Metal cation

ABSTRACT

Several kinds of hydroxyapatites (HAp) prepared by modification of Ca^{2+} -HAp with transition metal (Fe^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+}) or aluminum (Al^{3+}) ions were evaluated via a gas bag-detection tube method whether they could be used as novel deodorant materials. The samples treated with divalent cation (Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+}) retained hydroxyapatite structure as well as Ca^{2+} -HAp, whereas those treated with trivalent cation (Al^{3+} and Fe^{3+}) showed lower crystallinity than Ca^{2+} -HAp. 5–8 wt% cation of the samples was introduced by modification with divalent metal cations, whereas about 40 wt% cation of the samples was introduced with relatively larger surface area and higher content of adsorbed water for trivalent cations. For NH_3 gas, modification of Ca^{2+} -HAp with a divalent metal cation enhanced its adsorption ability, and that with a trivalent metal cation resulted in considerable improvement of the ability. On the other hand, modification of Ca^{2+} -HAp with Cu^{2+} ion gave it remarkable H_2S gas adsorption ability in comparison to that with other metal cations. However, adsorption ability for H_2S of some polycrystalline powders including Cu^{2+} was not higher than that of Cu^{2+} -modified HAp. The effect of the incorporated cation on adsorption ability for NH_3 molecules may be based not only on a simple Lewis acid-base reaction but also on specific surface area and adsorbed water content, and the effect for H_2S molecules based on the specific local electron density around the cation present on/in the material.

1. Introduction

Hydroxyapatite (HAp; $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) is a representative calcium phosphate that has extensively been reported to act as an adsorbent for toxic inorganic species such as Pb^{2+} , Cd^{2+} , Hg^{2+} , AsO_4^{3-} , and CrO_4^{3-} from aqueous media through a facile ion exchange reaction of the cations or anions shown above with Ca^{2+} or PO_4^{3-} , respectively, in the HAp structure [1–5]. Moreover, HAp has been known to capture harmful organic compounds efficiently when it is prepared under a biomimetic condition [6] or its surface is modified with *O*-methylhydroxylamine [7]. These facts have attracted us to investigate the ability of HAp to adsorb inorganic stimulating odorants such as NH_3 and H_2S since these components make us feel unpleasant even when their concentrations are relatively low in ambient atmosphere. While concerning such an adsorbent for atmospheric application, activated charcoal, zeolite, and so on are very popular, there are few reports about the effects of HAp as an adsorbent for such odorants. In recent investigations aimed to remove simultaneously such unpleasant odors, activated carbon produced from petroleum coke with KOH [8], mixed metal (Zn–Al) oxide with microwave and ultrasound [9], manganese oxide nanoarchitectures derived from a sol-gel method [10], natural titanomagnetite against hot gas [11], for example, achieved high

performance for removal both of NH_3 and H_2S . Furthermore, the effect of metal dopants into CeO_2 on variations of acidic adsorption sites for NH_3 was experimentally and numerically investigated [12]. Referred to the previous literatures described above, transition metal and aluminum ions are expected to act as strong Lewis acids, thus modification of HAp with such cations may also lead to enhanced interaction with inorganic malodors. In the present study, the effect of incorporation of metal cation to HAp on the ability to adsorb NH_3 and H_2S gases was investigated at ambient temperature.

2. Materials and methods

2.1. Introduction of metal cation to hydroxyapatite

An incorporation of one of metal cations (M: Al^{3+} , Fe^{3+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} or Zn^{2+}) to calcium HAp (denoted as Ca^{2+} -HAp) was attempted by a simple immersion method. 1 g of Ca^{2+} -HAp powder (Sangi Co. Ltd., Japan) was added to 50 cm^3 of 0.1 $\text{mol} \cdot \text{dm}^{-3}$ M-nitrate (Wako Pure Chemical Industries Ltd., Japan; M: Al^{3+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} or Zn^{2+}) or Fe^{2+} -chloride (Wako Pure Chemical Industries Ltd., Japan, since $\text{Fe}(\text{NO}_3)_2$ was found not to be sold from any company as a pure reagent) aqueous solution and stirred at room temperature for

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86.4 ks. Then the solid phase was collected from the resultant slurry by centrifugation and washed with ultrapure water. After the obtained powder was dried at 333 K overnight, it was stored in a desiccator (RH: 7–10%).

2.2. Characterization of metal cation incorporated hydroxyapatite

Crystalline phases and species of chemical bonds before and after introducing the alternative cations were analyzed by powder X-ray diffraction (XRD, UltimaIV, Rigaku, Japan) and Fourier-transform infrared spectroscopy (FT-IR, FT-710, Horiba, Japan), respectively. Particle size and morphology of the samples before and after introducing alternative cations were investigated by dynamic light scattering (DLS; Microtrac, Nikkiso Co. Ltd., Japan) and scanning electron microscopy (SEM; JSM-7600FA, Jeol, Japan), respectively. The amount of the metal cation incorporated in the samples was estimated by X-ray fluorescence analysis (XRF; EDXL300, Rigaku, Japan). Specific surface areas for the samples were calculated from BET method using N_2 adsorption (Monosorb; Quantachrome Instruments Japan Co. Ltd., Japan). Thermal behavior of the samples was monitored by thermogravimetry-differential thermal analysis (TG-DTA; Thermo plus TG8120, Rigaku, Japan) at the heating rate of 5 $K \cdot \text{min}^{-1}$ from R.T. to 573 K.

2.3. Adsorption test of malodor

The sample powder was introduced into a sampling bag, and then the entrance of the bag was sealed. Three liter of pure N_2 gas (99.999%) was sent into the bag, followed by introducing an appropriate volume of NH_3 or H_2S gas, which had been preliminarily generated in a bottle from 28% NH_3 aqueous solution or a reaction of granular FeS with HCl , respectively. After exposing the sample powder to the corresponding gas for a given period, the residual concentration of the gas was traced using a gas sampler and detecting tubes (GASTEC, Japan). The measurement value was determined by reading scale marks at the front of a coloring agent pre-loaded in the detecting tubes, which had changed its color by the reaction either with NH_3 or H_2S . When no change was observed in the coloring agent, the residual concentration was defined as below detection limit (NH_3 : < 0.20 ppm, H_2S : < 0.25 ppm). To make sure that cationic effect on the enhanced ability of HAp to adsorb malodors, specifically in the case of Cu^{2+} , commercial Cu^{2+} containing inorganic salts ($Cu(NO_3)_2 \cdot 3H_2O$, $CuCl_2 \cdot 2H_2O$, CuO and $Cu_3(PO_4)_2$, purchased from Wako Pure Chemical Industries Ltd., Japan) were used as adsorbents for H_2S by way of comparison.

3. Results and discussion

3.1. Characterization of metal cation incorporated hydroxyapatite

Fig. 1 shows powder XRD patterns of the samples before and after introducing the alternative cations. Diffraction peaks assigned only to hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, #09-0432) were detected for the samples treated with Fe^{2+} , Co^{2+} , Ni^{2+} and Cu^{2+} as well as for that before the treatment, whereas peaks attributed to zinc phosphate tetrahydrate ($Zn_3(PO_4)_2 \cdot 4H_2O$, #33-1474) were detected in addition to those of hydroxyapatite for the sample treated with Zn^{2+} . On the other hand, no distinct peaks were detected for the sample treated with Fe^{3+} , indicating that this sample is amorphous [13]. From now on, the samples treated with a certain kind of the metal cations is denoted as M-HAp, in spite that Fe^{3+} -HAp mainly consists of amorphous phase. Just for reference, XRD pattern of Al^{3+} -HAp prepared by treating Ca^{2+} -HAp with $Al(NO_3)_3$ showed that it consisted of hydroxyapatite structure in spite that the sample was treated with a trivalent cation as same as Fe^{3+} . However, each peak corresponding to hydroxyapatite was found to be broader for Al^{3+} -HAp than those for divalent M-HAp [14]. We found that the peak shift with respect to diffraction planes of HAp was hardly detected for the XRD pattern of each sample except for Fe^{3+} -

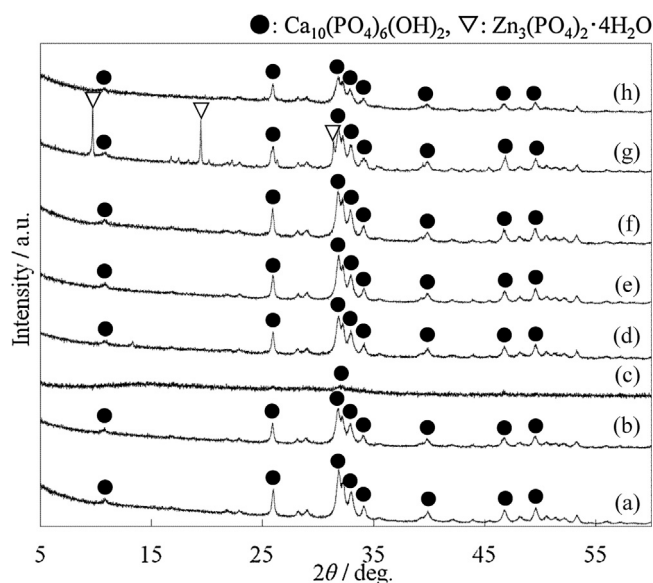


Fig. 1. XRD patterns of M-HAp. ((a) Ca-, (b) Fe(II)-, (c) Fe(III)-, (d) Co-, (e) Ni-, (f) Cu-, (g) Zn-, (h) Al-HAp).

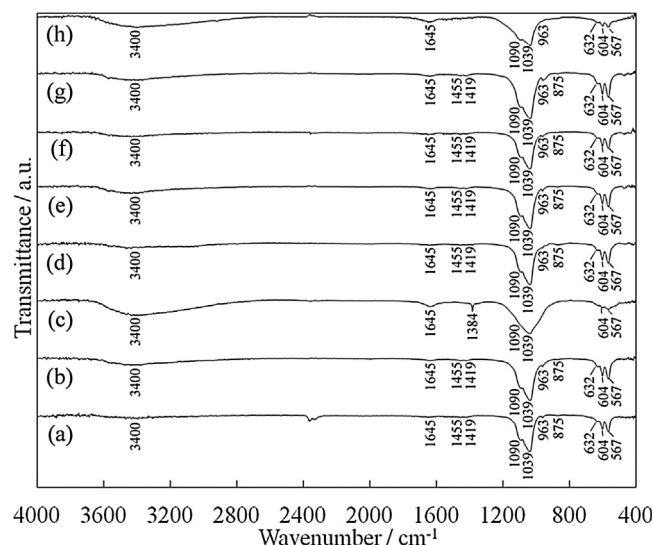


Fig. 2. FT-IR spectra of M-HAp. ((a) Ca-, (b) Fe(II)-, (c) Fe(III)-, (d) Co-, (e) Ni-, (f) Cu-, (g) Zn-, (h) Al-HAp).

HAp, which indicates that metal ions incorporated in samples are present mostly not in crystal lattice but on surface.

Fig. 2 shows FT-IR spectra of M-HAp together with Ca^{2+} -HAp. Absorption bands attributed to asymmetrical stretching (ν_3) and bending (ν_4) modes of PO_4^{3-} ions were detected 1090 and 1039 cm^{-1} , and 604 and 567 cm^{-1} , respectively. Symmetric stretching modes (ν_1) of the PO_4^{3-} ions were also found around 963 cm^{-1} . The peaks at 632 cm^{-1} , and 1455 and 1419 cm^{-1} are attributed to liberation modes of OH^- ions hosted by HAp framework and partial substitutions of CO_3^{2-} ions with PO_4^{3-} sites in the structure of HAp, respectively [15,16]. The broad band at 3400 cm^{-1} and the peak at 1645 cm^{-1} are relevant to stretching and bending modes of OH^- group for the adsorbed water, respectively. It might also be noted that there was a small band around 875 cm^{-1} , which attests the presence of HPO_4^{2-} . Almost all the adsorption bands described above were detected for Ca^{2+} -, Fe^{2+} -, Co^{2+} -, Ni^{2+} -, Cu^{2+} - and Zn^{2+} -HAp, but a part of them attributed to PO_4^{3-} -, CO_3^{2-} - and OH^- ions derived from apatite were absent for Fe^{3+} - and Al^{3+} -HAp. Especially for Fe^{3+} - and Al^{3+} -HAp, the adsorption intensities for OH^- group from the adsorbed water were

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