Oxidative decomposition of volatile organic compound on hydroxyapatite with oriented crystal structures

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Hydroxyapatite (HAp) exhibits superior biocompatibility, ion-exchange ability and high adsorption property which has attracted much attention as one of the most well-known ceramic functional materials. We have previously reported the efficient oxidative decomposition of volatile organic compounds (VOC) on commercial HAp powders which makes HAp a promising alternative material of precious metal nanoparticle catalyst for environmental purification. In this work, HAp with oriented crystal growth of a-plane and c-plane were synthesized via air-liquid interface precipitation in solution, and the influence of crystal orientation on VOC decomposition performance was systematically investigated. As a result, HAp with preferential growth of c-plane performs higher catalytic VOC decomposition activity, which can be attributed to the large number of active radicals generated on surface despite the relative smaller sufficient surface area. The results in this study highlight the important relation between crystal structure of HAp and the decomposition activity of VOC, which also provide useful information for the structure design of ceramic functional materials.

Key-words: Hydroxyapatite, Crystal orientation, Oxidative decomposition, Volatile organic compound

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NOTE

Hydroxyapatite (HAp) which has superior biocompatibility, ion-exchange ability, and high adsorption property, has attracted much attention as one of the most known ceramic functional materials. It has been widely used for various applications, such as artificial bone and tooth, filler of high-performance liquid chromatography.¹,² HAp with different chemical properties have been previously synthesized by numerous approaches, including precipitation in solution, sol–gel process, hydrothermal decomposition, microwave assisted method, combustion and pyrolysis method, etc. The precipitation in solution is the most facile synthesis approach with respect to easy control of size, morphology and crystallinity.³ Aizawa et al. previously reported the synthesis of crystal-oriented HAp via an air-liquid interface precipitation method. Needle-like and plate-like HAp were selectively synthesized with altered calcium (Ca) and phosphor (P) precursors, aging temperature and duration.⁴

We have previously reported the effective oxidative decomposition of volatile organic compound (VOC) on commercial HAp with thermally-activated surface. The mechanism of oxidative decomposition of VOC can be attributed to the generation of active oxygen radicals on HAp surface under thermal treatment.⁵ The comparable VOC decomposition efficiency with precious metal nanoparticle catalyst makes HAp as a promising alternative material for environmental purification. We previously investigated the influence of Ca/P molar ratio of HAp on the catalytic performance of VOC decomposition. However, other chemical properties of HAp, such as crystal structure, which may play an important role to VOC decomposition performance has not been clarified. Herein, two types of HAp with oriented crystal structures and preferential growth of a- and c-planes were synthesized via air-liquid interface precipitation in solution, and the influence of different crystal orientation of HAp on oxidative decomposition of VOC is systematically investigated.

Two types of oriented HAp crystals, needle-like (HAp-N) and plate-like (HAp-P) structures were synthesized using air-liquid interface precipitation in solution ⁵ with further optimized experimental conditions. For the synthesis of HAp-N, aqueous solution including 0.167 mol/L calcium nitrate tetrahydrate [Ca(NO₃)₂·4H₂O], 0.1 mol/L ammonium hydrogen phosphate [(NH₄)₂HPO₄], 0.5 mol/L urea [(NH₂)₂CO], and 0.1 mol/L nitric acid (HNO₃) was prepared, and was heated at 90°C for 96 h. In case of the HAp-P, solution containing 5.0 mmol/L calcium carbonate (CaCO₃), 3.0 mmol/L phosphoric acid (H₃PO₄), 1.0 mol/L urea, and aqueous nitric acid (60 wt %) as a pH adjuster (to pH = 3) was prepared. Then, 2.734 ml % of 0.1 mass % urease solution was added, followed by heating at 50°C for

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72 h. The precipitated solids were obtained by filtration and then heated at 600°C for 2 h.

The morphology of synthesized HAp was observed by scanning electron microscopy (SEM; SEM-7600F, JEOL). The crystallographic property of HAp was evaluated by X-ray diffraction (XRD) pattern (Rint 2000, Rigaku) with a Cu Kα line. The specific surface area (SSA) was measured by Brunauer–Emmett–Teller method on a commercial nitrogen adsorption–desorption system (BET, Belsorp mini, MicrotracBEL corp.). The evaluation of thermal-induced active oxygen radicals on HAp surface was confirmed by electron spin resonance (ESR) spectra recorded with JES-FE200 (JASCO) spectrometer.

The VOC decomposition performance was evaluated using in-situ Fourier transform infrared spectrometer (FTIR; FT-IR 6600, JASCO) characterization system. As illustrated in Scheme 1, HAp was loaded in sample cup in a closed reaction chamber equipped with gas flowing path and temperature controller. The diffuse reflectance FTIR spectra of HAp surface was recorded with in-situ continuous supplying of VOC (here ethyl acetate was used, which is mixed 1:1 with air) flow under different temperatures.

Fig. 1. SEM images of synthesized HAp-N (a, b) and HAp-P (c, d).

Scheme 1. Sample chamber with in-situ gas flowing and heating system used for diffuse reflectance FTIR measurement.

Fig. 2. (a) XRD pattern of synthesized HAp-N and HAp-P, (b) calculated peak intensity ratio of (300)/(002) planes.

Figures 1(a) and 1(b) and Figs. 1(c) and 1(d) show the SEM images of synthesized HAp-N and HAp-P, respectively. Needle-like structure is observed in HAp-N [Figs. 1(a) and 1(b)], while HAp-P gives plate-like morphology [Figs. 1(c) and 1(d)]. The orientation of crystal structure of HAp-N and HAp-P were further confirmed by XRD, whose results are shown in Fig. 2(a). Characteristic peaks of HAp with hexagonal structure were confirmed, and any peaks corresponding to other phases were not detected. The peaks at 25.88 and 32.90° can be assigned as diffractions of (002) and (300) planes, respectively. The oriented crystal growth was evaluated by calculating the peak intensity ratio of (300)/(002) planes. As the results shown in Fig. 2(b), (300)/(002) ratios for HAp-N and HAp-P are 2.55 and 0.62, respectively. It indicates the as-synthesized HAp-N and HAp-P show preferential crystal growth of a-plane and c-plane, respectively, whose result is in good agreement with needle-like and plate-like crystal morphologies confirmed in SEM images of Fig. 1.
The results of in-situ FTIR spectra of HAp-N and HAp-P are shown as Figs. 3(a) and 3(b) and Figs. 3(c) and 3(d), respectively. The peak observed at 3570 cm\(^{-1}\) is assigned to the O–H stretching mode of apatite hydroxyl group, and peaks appear at 1950–2100 cm\(^{-1}\) correspond to the combination and overtone mode of PO\(_4^{3–}\)). The peaks at 1490, and 1545 cm\(^{-1}\) are attributed to CO\(_3^{2–}\) stretching vibration. Broad peak between 1750 to 1650 cm\(^{-1}\) is attributed to C=O band caused by adsorption of ethyl acetate. At room temperature (RT), such C=O band of each HAp was confirmed and it gradually decreased with increasing of temperature. It can be suggested that ethyl acetate was adsorbed on HAp surface and decomposed through heating process.

To confirm the VOC decomposition performance on HAp, the peak intensity ratio of C=O/PO\(_4^{3–}\) bands is calculated as a function of temperature, whose results are shown in Fig. 3(e). Here, PO\(_4^{3–}\) peak was chosen as reference since it is known that PO\(_4^{3–}\) is thermally stable until the heating temperature at 900°C. As results shown in Fig. 3(e), initial adsorption ratio of ethyl acetate on HAp-N is much less than HAp-P. The adsorption of ethyl acetate on HAp should be attributed to the formation of hydrogen bond between carbonyl group in ethyl acetate and -OH in HAp. According to the hexagonal crystal structure of HAp (space group: P6\(_3\)/m), -OH exists in the channel along c-axis. Thus, HAp-P with more c-plane surface must possess more -OH groups on its surface, which can also adsorb more ethyl acetate. The C=O/PO\(_4^{3–}\) ratio of each sample is reduced with increase of heating temperature, which illustrates that adsorbed ethyl acetate on surface of HAp was decomposed. Based on the result in Fig. 3(e), the VOC decomposition rate is further estimated and summarized in Fig. 3(f). The peak intensity ratio of C=O/PO\(_4^{3–}\) at 100°C was used as a criterion for the calculation of decomposition rate. The VOC decomposition rate for HAp-N at 400°C is 97.8%, whose value is 48.4% for HAp-P, which demonstrates HAp-P exhibits superior catalytic activity of VOC decomposition than HAp-N.

We have previously reported that the decomposition mechanism of VOC on HAp is attributed to the generation of active oxygen radical during heating process. Such active radical is formed by the recombination of oxygen molecular and electron trapped on HAp, which is produced by the dehydration of -OH on c-plane of HAp. In order to clarify the difference in VOC decomposition performance between HAp-N and HAp-P, the oxygen radical generated on each HAp was confirmed by ESR spectra. As results shown in Fig. 4, signal originated from active oxygen radicals was observed at 323 mT (g = 2.003), whose...
peak intensity of HAp-P is higher than that of HAp-N. It demonstrates that large number of active radicals are generated on HAp-P, which can be attributed to the harvested -OH groups exist on c-plane of HAp-P.

It has been known that SSA may also play an important role on VOC decomposition performance,\textsuperscript{11)} the SSA of our synthesized HAp was analyzed. As a result, SSA of HAp-N and HAp-P are 21.0 and 17.8 m\textsuperscript{2}/g, respectively, which indicates HAp-N may exhibit higher VOC decomposition performance based on larger SSA. However, HAp-P show superior VOC decomposition performance than HAp-N, which suggests that difference of oriented crystal structures on surface is the main factor for the VOC decomposition performance regardless of a different SSA.

In summary, two types of crystal-oriented HAp, HAp-N and HAp-P, which has needle-like and plate-like structures are synthesized via air-liquid interface precipitation in solution. The morphology of as-synthesized HAp is confirmed by SEM images and crystal structures is analyzed by XRD. The orientation of crystal structure is investigated by calculating the diffraction peak intensity ratio of (300)/(002) planes. The VOC decomposition performance is evaluated by an in-situ FT-IR system, whose results demonstrate that HAp-P exhibits higher VOC decomposition activity than HAp-N. The reason is clarified by confirmation of active oxygen radicals via ESR, which reveals that a harvested c-plane with large amount of -OH groups in plate-like HAp (HAp-P) can generate more active radicals and higher catalytic activity for VOC decomposition. The results in this study may provide useful information on the design and development of new precious metal-free catalyst for environmental purification.

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