Synthesis of Hydroxyapatite–Zeolite Composite Material from Disposed Steel Slag and Investigation of Its Structural and Physicochemical Characteristics

Yasutaka Kuwahara, Tetsutaro Ohmichi, Takashi Kamegawa, Kohsuke Mori, and Hiromi Yamashita*
Divisions of Materials and Manufacturing Science, Graduate School of Engineering,
Osaka University, 2-1 Yamada-oka, Suita, Osaka 565-0871

(Received April 9, 2009; CL-090358; E-mail: yamashita@mat.eng.osaka-u.ac.jp)

Steel slag is a commercial waste material mainly containing SiO_2, Al_2O_3, and CaO which are the chemical components of zeolite and hydroxyapatite (HAP), respectively. From the steel slag, a hydroxyapatite–zeolite composite material (HAP–ZE) was successfully synthesized in a one batch system by adding H_3PO_4 and NaOH. The structural characteristics of HAP–ZE were investigated by XRD, SEM, and N_2 adsorption. From the adsorption of VOCs, HAP–ZE was found to have adsorption properties comparable to those of pure zeolite and HAP.

Steel slag is a waste material generated in steel production and contains SiO_2, Al_2O_3, CaO, and MgO as its main chemical components. Among several kinds of steel slags, over 80% is produced as water-granulated slag, and its production in 2008 in Japan reached to over 20 million tons.[1] The water-granulated slag is mostly recycled as cement, concrete aggregate, and a material for roadbed in civil engineering work. However, the amount of reusable steel slag tends to be saturated as the production of steel slag has increased annually. It is, therefore, essential to develop new recycling techniques exploiting the nature of steel slag.

Recently, the conversion of the steel slag into zeolites using it as a Si and Al source has been largely investigated.[2–4] Zeolite is an aluminosilicate microporous material with large surface area (more than $500\,m^2\,g^{-1}$) and exchangeable cations in its structure. Owing to its unique characteristics, it has been widely used in industry as an adsorbent, a molecular sieve, an acid solid catalyst, and also a support material for various catalysts.[5] However, in order to convert steel slag into the zeolites, some specific pretreatments or synthetic methods as follows has been required, since steel slag contains relatively high Ca content which inhibits the nucleation of zeolite crystals, generating calcium silicate ($CaSiO_3$); 1) elimination of unnecessary chemical components such as Ca and Fe by acid-leaching prior to synthesis, 2) synthesis with additives to compensate the shortage of chemical components or to attenuate the Ca content, 3) synthesis using hydrothermal treatment.[2–4] These synthetic methods requiring complex preparation steps or waste of a large amount of Ca component are not economic from the aspect of resources utilization.

In this study, hydroxyapatite (HAP) and zeolite composite material (HAP–ZE) was synthesized from steel slag by coprecipition of Si, Al, and Ca components as zeolite and hydroxyapatite, respectively. HAP ($Ca_{10}(PO_4)_6(OH)_2$) is a main constituent of bone tissues, and it is well known to have biocompatibility, anion-exchange properties, and great adsorption properties.[6] Both zeolite and HAP are generally synthesized by precipitation under high pH. The structural characteristics of HAP–ZE were investigated by XRD, SEM, and N_2 adsorption. Furthermore, the adsorption properties of HAP–ZE were evaluated by VOCs (volatile organic compounds) adsorption.

The chemical composition of the water-granulated slag used in this study (raw-slag) was, CaO: 41.5, SiO_2: 35.8, Al_2O_3: 15.3, MgO: 5.48, Fe_2O_3: 1.58, MnO: 0.28 (wt %). The raw-slag mainly consists of amorphous phase CaO, SiO_2, and Al_2O_3 with a molar ratio of $SiO_2/Al_2O_3 = 4$, which is fairly common in water-granulated slags. This SiO_2/Al_2O_3 ratio is suitable for the generation of Y-type zeolite (generally synthesized with a molar ratio of $3.5 < SiO_2/Al_2O_3 < 6$). Prior to synthesis, the raw-slag was ball milled at 650 rpm and screened using a 45-μm mesh to facilitate dissolution. The synthesis of HAP–ZE was performed as follows: First, 5.0 g of the ball-milled slag was dissolved into 22 mL of 1 M aqueous H_3PO_4 solution at ambient temperature for 2 h. Phosphoric acid was added as a solvent and also as a phosphorous source of HAP. Then, 50 mL of 3 M aqueous NaOH solution was added dropwise to obtain a grayish suspension. Sodium hydrate was added as a base and also as a cation source of zeolite. The molar ratio of the gel was approximately adjusted as follows according to the refs 6 and 7; $10Na_2O{:}1Al_2O_3{:}4SiO_2{:}5CaO{:}1.5P_2O_5{:}550H_2O$ (stoichiometric composition for generation of Na–X zeolite with $Si/Al = 2$ and HAP with $Ca/P = 1.67$). The obtained suspension was heated at 353 K for 3 h using a water bath under vigorous stirring, subsequently sealed into a Teflon bottle, and aged at 363 K for 2 days in an electric oven to carry out crystallization. The obtained material was filtered off, washed with water, and dried at 383 K overnight.

The XRD patterns of the synthesized HAP–ZE, together with those of the common HAP and Na–Y zeolite with $SiO_2/Al_2O_3 = 5$ (NaY(5)) as reference samples, are shown in Figure 1. The peaks attributable to faujasite-type (FAU) zeolite phase and HAP phase were clearly observed in HAP–ZE, suggesting that the X-zeolite and HAP composite material was successfully and simultaneously synthesized from the slag. The Ca/Si ratio of HAP–ZE determined by XRF was 6. Considering the intensity of diffraction peaks and composition ratio, it is indicated that well-crystallized HAP was formed, while the crystallinity of zeolite phase was rather low. Additionally, any peaks attributable to Mg, Fe, and Mn compounds were not observed.

The SEM images of HAP–ZE are depicted in Figure 2. The image of HAP–ZE shows that the two morphologically different crystals are blended in microorder. Considering the crystal sizes and the morphologic features, it is thought that the octahedral crystals might be FAU-type zeolite (Figure 2b)[8] and that other roundish crystals might be HAP, most of which is crystallized as huge HAP grains (Figure 2c), and part of which is uniformly dispersed onto the zeolite crystals.

Figure 3 shows the N_2 adsorption–desorption isotherms of the synthesized HAP–ZE, HAP, NaY(5), and raw-slag. The

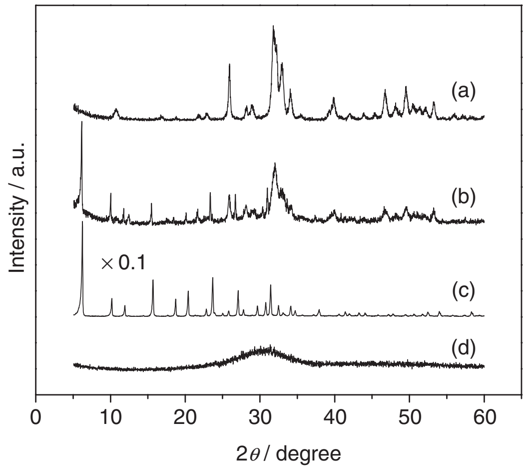

Figure 1. XRD patterns of (a) HAP, (b) HAP–ZE, (c) NaY(5), and (d) raw-slag.

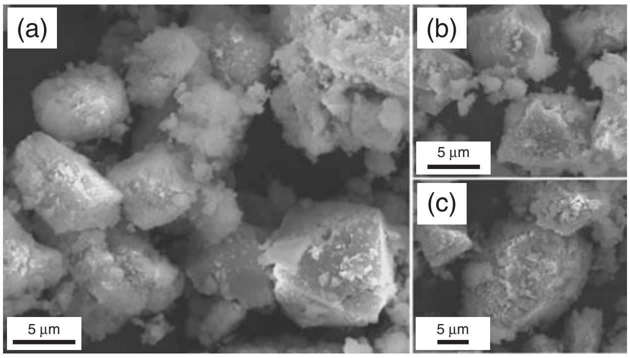

Figure 2. SEM images of (a) HAP–ZE (b) zeolite crystals, and (c) HAP crystals.

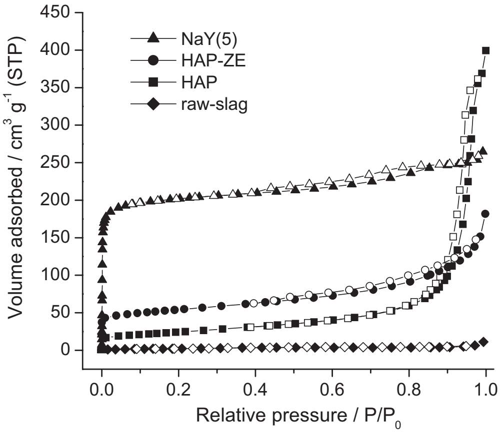

Figure 3. N_2 adsorption–desorption isotherms at 77 K.

N_2 adsorption–desorption isotherm of HAP–ZE showed a rapid increase in the amount of N_2 at the very low pressure ($P/P_0 < 0.01$) and a slight hysteresis loop in the range of $P/P_0 > 0.4$. Such characteristics should be attributable to those of zeolite with micropores. Furthermore, the N_2 adsorption–desorption isotherm of HAP–ZE showed a gradual increase again in the range of $P/P_0 > 0.8$, reflecting the presence of HAP. From the result of pore distribution, it was confirmed that the HAP–ZE has as small micropores ($d = 0.8$ nm) as zeolite ($d = 0.74$ nm). However, the BET surface area of HAP–ZE, HAP, NaY(5), and raw-slag was estimated to be 194.1, 85.5, 816.3 and 8.1 $m^2 \cdot g^{-1}$, respectively. The surface area of HAP–ZE was substantially smaller than that of original zeolite but larger than that of HAP. These results indicate that the zeolite micropores should be partly covered or filled by HAP crystals as confirmed from SEM analysis, accordingly resulting in the low intensity in XRD and small surface area.

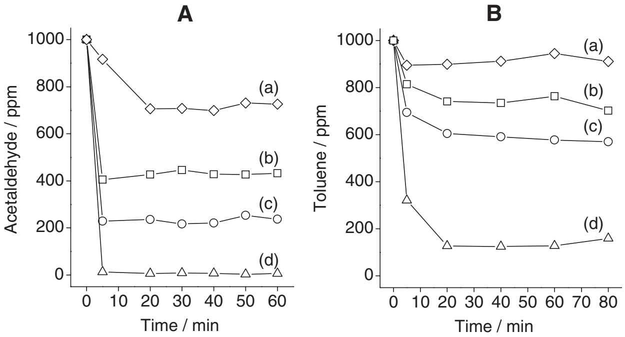

Figure 4. Adsorption of (A) acetaldehyde and (B) toluene in air (1000 ppm); (a) raw-slag, (b) HAP, (c) HAP–ZE, and (d) NaY(5).

The adsorption property of HAP–ZE was evaluated by the adsorption test of VOCs (acetaldehyde and toluene) diluted in air (shown in Figure 4). On HAP, HAP–ZE, and NaY(5), the adsorption of VOCs immediately took place within the first 5–20 min and then reached equilibrium. HAP–ZE showed stronger adsorption properties compared to pure HAP and raw-slag without porous structure, while it is rather weaker than that of pure zeolite. Similarly, the high water adsorption properties were demonstrated from the TG measurement as well. From the enhancement in adsorption, it is also presumable that the HAP–ZE should have both physicochemical characteristics of HAP and zeolite.

In conclusion, a hydroxyapatite–zeolite composite material, whose HAP and zeolite phases were physically blended in micro-scale, was successfully synthesized from steel slag via a convenient route, utilizing its chemical composition. It was practically demonstrated that the synthesized material has a great adsorption performance against VOCs, which is applicable enough for practical use as an adsorbent. This conversion process from waste material to valuable material is beneficial from the view point of effective use of resources.

References and Notes

1 The Japan Iron and Steel Federation, Nippon Slag Association, *The Annual Report of Statistics of Iron and Steel Slag* **2008**, see the Web site, http://www.slg.jp.
2 Y. Kuwahara, T. Ohmichi, K. Mori, I. Katayama, H. Yamashita, *J. Mater. Sci.* **2008**, *43*, 2407.
3 Y. Sugano, R. Sahara, T. Murakami, T. Narushima, Y. Iguchi, C. Ouchi, *ISIJ Int.* **2005**, *45*, 937.
4 R. Anuwattana, K. J. Balkus, Jr., S. Asavapisit, P. Khummongkol, *Microporous Mesoporous Mater.* **2008**, *111*, 260.
5 H. Yamashita, K. Mori, *Chem. Lett.* **2007**, *36*, 348.
6 T. Tsuchida, J. Kubo, T. Yoshioka, S. Sakuma, T. Takeguchi, W. Ueda, *J. Catal.* **2008**, *259*, 183.
7 H. Lechert, *Zeolites* **1996**, *17*, 473.
8 H. Tanaka, H. Eguchi, S. Fujimoto, R. Hino, *Fuel* **2006**, *85*, 1329.