EFFECT OF CHEMICAL MODIFICATION OF HYDROXYAPATITE/ZEOLITE COMPOSITE ON MALODORS ADSORPTION BEHAVIOR

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Abstract: Hydroxyapatite (HAp)/zeolite composite (HZc) was prepared by a simple immersion method, and it was then modified with Cu\(^{2+}\) and 3-aminopropyltriethoxysilane (APES) to produce a novel adsorbent for unpleasant odors such as NH\(_3\), H\(_2\)S and CH\(_3\)CHO gases. The obtained materials were characterized by SEM-EDS, XRD, FT-IR, TG-DTA and ninhydrin reaction test. Nano-sized order HAp was observed distributed on zeolite for HZc, and modification of HZc with Cu\(^{2+}\) and APES maintained the original framework structure of HZc. Introduced amount of Cu\(^{2+}\) and APES after the modification was 3.6 mol\% and 12.6 mg g\(^{-1}\), respectively. The adsorption ability evaluated via a gas bag-detection tube method showed that Cu\(^{2+}\)-modified HZc increased NH\(_3\) and H\(_2\)S adsorption ability, and APES-modified HZc enhanced CH\(_3\)CHO adsorption ability in comparison to unmodified one, respectively. Sequential modification of HZc with Cu\(^{2+}\) and APES also maintained H\(_2\)S and NH\(_3\) adsorption ability, but decreased CH\(_3\)CHO adsorption ability. This suggests that adsorption sites for CH\(_3\)CHO were impeded in case of formation of Cu-N coordinate bond derived from direct interaction between Cu\(^{2+}\) and amino groups of APES. Therefore, use of HZc individually modified with Cu\(^{2+}\) and APES is recommended to capture multiple unpleasant odors.

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INTRODUCTION

Hydroxyapatite (HAp; Ca\(_{10}\)(PO\(_4\))\(_6\)(OH)\(_2\)) is a kind of calcium phosphate that has been used as biomaterials, adsorbents for chromatography to separate proteins, catalysts for dehydration, and so on.\(^{1,2}\) It is also useful as adsorbents for various metal cations from aqueous media through ion exchange reaction with Ca\(^{2+}\) in the HAp structure.\(^{2-7}\) Moreover, HAp has been known to eliminate HCHO efficiently when it is prepared under a biomimetic condition.\(^{8}\) In a previous research, we found that modification of HAp with metal cations gave it dramatically enhanced adsorption ability for inorganic stimulating odorants; especially Cu\(^{2+}\)-modified HAp for H\(_2\)S, and Al\(^{3+}\)- or Fe\(^{3+}\)-modified HAp for NH\(_3\).\(^{9}\) These odorants make us feel unpleasant in ambient atmosphere even their concentrations are relatively low. Furthermore, malodors such as fecal and garbage odors are composed of multiple components. Therefore, it is required for adsorbents to remove simultaneously such unpleasant odors. Some adsorbents having high efficiencies for removal of unpleasant odors, such as activated carbon, zeolite or other metal oxides, have been widely investigated.\(^{10-14}\) For example, zeolite, which is crystalline aluminosilicates minerals characterized by cage-like structure with high internal and surface areas, is well known to adsorb NH\(_3\),\(^{15,16}\) It is also useful as an efficient adsorbent to capture heavy metal cations from aqueous solution like HAp.\(^{17}\) According to these phenomena, HAp/zeolite composite (HZc) may become a potent adsorbent to simultaneous removal of unpleasant odorants because HZc may have advantageous characteristics of both HAp and zeolite.

On the other hand, inorganic materials which possess hydroxyl groups on their surfaces, can be modified with appropriate agents according to the purpose of use. For example, 3-aminopropyltriethoxysilane (APES) modified silica\(^{18}\) and O-methylhydroxylamine modified HAp\(^{19}\) were proven to exhibit good adsorption ability for CH\(_3\)CHO in ambient atmosphere. Therefore, HZc may be also able to adsorb CH\(_3\)CHO by modifying with such the agents. In the present study, HZc was prepared and modified with Cu\(^{2+}\) and APES, and then its ability to adsorb NH\(_3\), H\(_2\)S and CH\(_3\)CHO gases was investigated at an ambient temperature.
MATERIALS AND METHODS

Preparation of adsorbents

Natural zeolite was kindly supplied from Zeeklite Co., Ltd., Japan. (NH$_4$)$_2$HPO$_4$ and Ca(NO$_3$)$_2$·4H$_2$O were purchased from Wako Pure Chemical Industries Ltd., Japan. HAp was synthesized by adding 60 cm$^3$ of 2 mol·dm$^{-3}$ (NH$_4$)$_2$HPO$_4$ aqueous solution into 100 cm$^3$ of 2 mol·dm$^{-3}$ Ca(NO$_3$)$_2$ with Ca/P molar ratio of 1.67, and pH of the solution was adjusted to 10 using 28% ammonia solution (Nacalai Tesque inc., Japan). The resulting slurry was poured into a sealed vessel and shaken at 280 rpm for 72 h. After shaking, the solid was collected by filtration. Then, it was washed repeatedly with ultrapure water and dried in an oven at 333 K for 24 h. Finally, the dried solid was ground and sieved to obtain the geometric size less than 45 μm.

HAp/zeolite composite (HZC) was also prepared by a precipitation method. Suspension of natural zeolite (20 g) was added into 100 cm$^3$ of 2 mol·dm$^{-3}$ Ca(NO$_3$)$_2$ aqueous solution and stirred for 1 h. 60 cm$^3$ of 2 mol·dm$^{-3}$ (NH$_4$)$_2$HPO$_4$ and ammonia solution was dropped into the suspension above mentioned at a slow rate with stirring. After shaking for 72 h, the solid phase was filtered, rinsed, dried, ground and sieved to obtain the geometric size less than 45 μm.

Modification of adsorbents

Incorporation of Cu$^{2+}$ to the adsorbents was attempted by a simple immersion method. One gram of natural zeolite, HAp or HZC was added to 50 cm$^3$ of 0.1 mol·dm$^{-3}$ Cu(NO$_3$)$_2$ (Wako Pure Chemical Industries Ltd., Japan) aqueous solution and stirred at 278 ± 2 K for 1 h. Then the solid phase was collected by filtration and washed with ultrapure water. After the obtained powder was dried at 333 K overnight, it was stored in a desiccator (RH: 7-10 %).

Surface modification of the adsorbents with 3-aminopropyltriethoxysilane (APES) was also attempted by an immersion method. One gram of natural zeolite, HAp or HZC was added to a mixture of 50 cm$^3$ of 95 wt.% ethanol aqueous solution and 1 cm$^3$ of APES, degassed in advance for 10 min and stirred at room temperature for 1 h. Then the solid phase was collected by centrifugation, washed three times with 95 wt.% ethanol aqueous solution and dried in an oven overnight. Finally, the resultant powder was heated at 393 K for 3 h. In addition, HZC modified in order of Cu$^{2+}$ and APES was prepared and it was denoted as CA-HZC, whereas that of APES and Cu$^{2+}$ was AC-HZC. On the other hand, the mixture of Cu$^{2+}$- and APES-modified HZC was denoted as C/A-HZC.

Characterization of adsorbents

Morphology and elemental distribution of the prepared adsorbents was analyzed using a scanning electron microscope and energy dispersive X-ray spectroscopy (SEM-EDS: JSM-7600FA, JEOL, Japan). Identification of crystalline phase and chemical bonds was performed by powder X-ray diffraction (XRD; UltimaIV, Rigaku, Japan) and Fourier-transform infrared spectroscopy (FT-IR; FT-710, Horiba, Japan), respectively. The amount of Cu$^{2+}$ and APES included within the adsorbents was estimated by X-ray fluorescence analysis (XR; EDXL300, Rigaku, Japan) and thermogravimetric differential thermal analysis (TG-DTA; Thermo plus TG8120, Rigaku, Japan) at the heating rate of 5 K·min$^{-1}$ from room temperature to 873 K, respectively. Specific surface areas (SSA) of the samples obtained were measured using a BET surface area analyzer (Monosorb, Quantachrome Instruments Japan Co., Ltd.) by applying liquid N$_2$ with the aid of carrier gas of He and N$_2$ mixture. The ninhydrin test was employed to identify APES within the adsorbents before and after APES modification and heat treatment. Ten milligrams of the adsorbents and 2.5 mg of ninhydrin powder (Wako Pure Chemical Industries Ltd., Japan) were added to 5 cm$^3$ of acetone (Kanto Chemical Co., Inc., Japan), and then the suspension was heated in a warm bath. The solid phase was collected by centrifugation and dried at room temperature.

Adsorption test of malodors

Given amount of sample powder was introduced into a sampling bag to evaluate their adsorption abilities against three kinds of malodors, and then the entrance of the bag was sealed. Three liter of pure N$_2$ gas (≥ 99.9995% purity) was sent into the bag, followed by introducing an appropriate volume of NH$_3$, H$_2$S or CH$_3$CHO gas. NH$_3$ and CH$_3$CHO gases had been preliminarily generated in a glass bottle from 28% ammonia solution and in a sampling bag from 90% liquid CH$_3$CHO, respectively. H$_2$S gas was used by diluting commercial H$_2$S gas with pure N$_2$ gas. After exposing the samples to the gas mentioned above for 10 min, 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 coloring agent pre-loaded in the detecting tubes, which had changed its color by the reaction either with NH$_3$, H$_2$S or CH$_3$CHO. When no change was observed in the coloring agent, the residual
RESULTS AND DISCUSSION

FIGURE 1 shows XRD patterns of HZc, together with those of original zeolite and HAp. Natural zeolite consisted of clinoptilolite, mordenite and quartz. The main peaks at 2θ = 9.8°, 11.1°, 17.3°, 22.4°, 25.7°, and 30.0°, which were in agreement with the characteristic XRD peaks for the natural zeolite, were detected for the HZc. This indicates the presence of the natural zeolite in the HZc. In addition, comparatively broad diffraction peaks at 2θ = 25.8° and 31.8°, which were characteristic XRD peaks of HAp, were also found for the HZc. This indicates the presence of HAp in the HZc. It suggests that zeolite and HAp composite material was successfully synthesized. The positions of the main XRD peaks of Cu²⁺- modified HZc and APES-modified HZc were similar to those of HZc (data not shown). This indicates that the modification of HZc with Cu²⁺ and/or APES did not lead to significant structural change of the HZc.

FIGURE 1 XRD patterns of samples ((a) hydroxyapatite (HAp), (b) zeolite, (c) HAp/zeolite composite (HZc)).

FIGURE 2 shows SEM images of samples ((a) hydroxyapatite (HAp), (b) zeolite, (c) HAp/zeolite composite (HZc)).

FIGURE 3 SEM-EDS mapping of hydroxyapatite/zeolite composite (HZc).

SSA of HAp and HZc were calculated to be 116 and 114 m².g⁻¹, respectively. On the other hand, the SSA of natural zeolite was reported as 63 m².g⁻¹, which is about half compared to those of HAp and HZc.

TABLE 1 shows elemental composition of adsorbent materials before and after Cu²⁺ modification. In all of the samples after modification, copper was detected. Furthermore, HAp incorporated Cu²⁺ more than zeolite, which suggests that an ion exchange reaction for HAp occurred more easily than that for zeolite.

FIGURE 4 shows changes in (a) NH₃ and (b) H₂S concentrations before and after exposure of the samples to the corresponding gas for 10 min, as well as the data for a blank test, when the initial concentrations were adjusted to ca 390 ppm and 39 ppm, respectively. The concentration of NH₃ slightly decreased in the blank test, whereas the concentrations of residual NH₃ moderately and drastically decreased for the unmodified and Cu²⁺-modified samples.
Transmittance / a.u.

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-1090 and 1039 cm\(^{-1}\), and at 604 and 567 cm\(^{-1}\), respectively. A symmetric stretching mode (\(v_3\)) of the PO\(_4^{3-}\) was also found around 963 cm\(^{-1}\). On the other hand, peaks attributed to external TO\(_3\) (T=Si or Al) mode derived from zeolite were detected at 1390 and 1200 cm\(^{-1}\). A symmetric stretching mode of T-O was also detected at 789 cm\(^{-1}\). A broad band at 3400 cm\(^{-1}\) and a peak at 1645 cm\(^{-1}\) were relevant to stretching and bending modes of OH group for the adsorbed water, respectively. H\(_2\)O liberation mode was detected at 470 cm\(^{-1}\). In the spectra of APES-

**FIGURE 5** FT-IR spectra of hydroxypatite/zeolite composite (HZc) before and after 3-aminopropyltriethoxysilane (APES) modification.

**TABLE 1** Elemental distribution in samples before and after Cu\(^{2+}\) modification [mol%]

| Sample     | Ca   | P    | Si   | Al   | K    | Fe   | Cu   |
|------------|------|------|------|------|------|------|------|
| HAp        | 67.8 | 32.2 | -    | -    | -    | -    | -    |
| zeolite    | 1.2  | -    | -    | -    | -    | -    | -    |
| HZc        | 32.4 | 16.6 | 42.6 | 7.2  | 0.7  | 0.5  | -    |
| Cu-HAp     | 54.6 | 37.5 | -    | 39.1 | 7.9  | -    | -    |
| Cu-zeolite | 0.8  | -    | 79.1 | 14.0 | 3.4  | 0.9  | 1.8  |
| Cu-HZc     | 25.3 | 16.9 | 45.5 | 7.6  | 0.6  | 0.4  | 3.6  |

modified adsorbents, respectively. The concentration of H\(_2\)S did not decrease in the blank test and for the unmodified adsorbents, whereas the concentration of residual H\(_2\)S decreased relatively rapidly in the case of Cu\(^{2+}\)-modified zeolite. Moreover, the concentration of H\(_2\)S considerably decreased below the detection limit in the case of HAp and HZc after Cu\(^{2+}\) modification.

**FIGURE 4** Residual concentrations of various unpleasant odors exposed to Cu\(^{2+}\)-modified samples. (a) NH\(_3\), adsorbent weight: 100 mg. (b) H\(_2\)S, adsorbent weight: 10 mg, dotted pattern; 0 min, slanting line pattern; 10 min

**FIGURE 5** shows representative FT-IR spectra of the adsorbents before and after APES modification. Adsorption bands attributed to asymmetrical stretching (\(v_3\)) and bending (\(v_2\)) modes of PO\(_4^{3-}\) were detected at 1090 and 1039 cm\(^{-1}\), and at 604 and 567 cm\(^{-1}\), respectively. A symmetric stretching mode (\(v_3\)) of the PO\(_4^{3-}\) was also found around 963 cm\(^{-1}\). On the other hand, peaks attributed to external TO\(_3\) (T=Si or Al) mode derived from zeolite were detected at 1390 and 1200 cm\(^{-1}\). A symmetric stretching mode of T-O was also detected at 789 cm\(^{-1}\). A broad band at 3400 cm\(^{-1}\) and a peak at 1645 cm\(^{-1}\) were relevant to stretching and bending modes of OH group for the adsorbed water, respectively. H\(_2\)O liberation mode was detected at 470 cm\(^{-1}\). In the spectra of APES-

**FIGURE 6** shows TG-DTA curves of HZc before and after APES modification. Compared with the adsorbent before APES modification, an exothermic peak was detected at the range from 473 K to 723 K, which might be derived from decomposition of APES for APES-modified HZc. To confirm the existence of APES, the sample was reacted with ninhydrin. Ninhydrin is known as a chemical reagent used to detect ammonia, primary amine and secondary one. Especially, when reacting with primary amine, Ruhemann’s purple is produced. Figure 7 shows the images of HZc before and after APES modification. As a result, APES-modified HZc changed in color from white to purple (FIGURE 7(a), (c)). Then, for the HZc heated at 423 K, the color change was confirmed as well as the non-heated one (FIGURE7(b), (f)). Contrary, for 573 and 773 K heated samples, colors did not change before and
ninhydrin reaction (FIGURE 7(c), (d), (g)). On the other hand, the sample’s color heated at 573 K was darker than non-heated and 773 K heated samples before ninhydrin reaction (FIGURE 7(c), (d)). It might be derived from the presence of soot due to insufficient combustion of APES. From these results, the amount of modified APES onto the adsorbents could be calculated by weight loss ratio in the range from 423 K to 773 K.

FIGURE 7 Color changes of samples before and after ninhydrin reaction of APES-modified hydroxyapatite/zeolite composite (APES-HZc). (Upper section; before ninhydrin reaction, lower section; after ninhydrin reaction, (a)(e) non-heated, heated at (b)(f) 423 K, (c)(g) 573 K, (d)(h) 773 K)

FIGURE 8 shows CH₃CHO concentration before and after exposure of the samples to the gas for 10 min, as well as the data for a blank test, when its initial concentration was adjusted to ca 18 ppm, in company with the samples modified with APES. The concentration of CH₃CHO barely decreased in the blank test, whereas the concentration of residual CH₃CHO decreased using HAp after APES modification. Moreover, the concentration of CH₃CHO decreased significantly using zeolite and HZc after APES modification. These results suggest that removal of CH₃CHO occurs due to nucleophilic reaction between aldehyde group and primary amine.

TABLE 2 shows elemental composition and the amount of modified APES of the adsorbent materials before and after Cu²⁺ and APES modification. For all of the samples after the modification, Cu²⁺ and APES were certainly detected.

**TABLE 2 Table 2 Elemental distribution [mol%] and amount of APES [mg·g⁻¹] for modified HZc**

| Sample | Ca  | P   | Si  | Al  | K   | Fe  | Cu | APES |
|--------|-----|-----|-----|-----|-----|-----|----|------|
| HZc    | 32.4| 16.6| 42.6| 7.2 | 0.7 | 0.5 | –  | –    |
| CA-HZc | 22.4| 14.2| 50.7| 8.3 | 0.5 | 0.4 | 3.4| 10.4 |
| AC-HZc | 25.8| 15.7| 47.3| 8.0 | 0.6 | 0.4 | 2.2| 1.6  |
| C/A-HZc| 26.4| 16.8| 46.2| 7.7 | 0.6 | 0.4 | 1.9| 6.8  |

FIGURE 9 shows changes in NH₃, H₂S and CH₃CHO concentrations before and after exposure of the samples to the corresponding gas for 10 min, when the initial concentrations were adjusted to ca 29 ppm, 27 ppm and 11 ppm, respectively. The concentrations of NH₃ and H₂S rapidly decreased regardless of the adsorbents used, whereas the concentration of residual CH₃CHO was relatively lower using C/A-HZc than those using CA-HZc and AC-HZc. In other words, APES-modified samples adsorbed CH₃CHO more than the samples free from APES, but the adsorption ability of the sample modified binarily with Cu²⁺ and APES were lower than that of the sample modified singly with APES.
Although the changes of odor gases concentrations should be standardized by the SSA of the adsorbent used, the tendency of their adsorption properties may not significantly be different from that without the standardization. Thus, the adsorption properties of the adsorbents obtained in the present study are continued to discuss on the basis of the result shown in FIGURES 4, 8 and 9.

FIGURE 10 shows ESR spectra measured for adsorbents modified with Cu$^{2+}$. In all the ESR spectra, the characteristic patterns attributed to hyperfine structure derived from planar 4-coordinated Cu$^{2+}$ complexes were observed. The ESR signal for Cu-HZc was observed at $g_{\parallel} = 2.396$ and $A_{\parallel} = 0.135$ cm$^{-1}$, and those for CA-HZc and AC-HZc were observed at $g_{\parallel} = 2.392$ and $A_{\parallel} = 0.137$ cm$^{-1}$. These signals are corresponding to planar CuO$_4$ coordinated structure. Furthermore, the ESR signals for CA-HZc and AC-HZc were observed at $g_{\perp} = 2.349$ and 2.347 and $A_{\perp} = 0.163$ cm$^{-1}$, respectively. The relation between each ESR parameter was seemed to be attributed to translation from planar CuO$_4$ to CuN$_4$ coordination.$^{22-25}$ Consequently, it suggests that new coordination states appeared in the binarily modified samples, caused by a direct interaction between Cu$^{2+}$ and amino groups terminated in APES.

In the present study, the odor gas concentrations were measured using a gas sampler and detecting tubes. Their detection limits were higher than the allowable concentrations given by the Offensive Odor Control Law. To evaluate whether the adsorbents examined in this study show the efficiencies for removal of the unpleasant odors, it is necessary to consider regulations applied to daily or work environment, that is, to investigate the adsorption abilities of the adsorbents for malodors at lower gas concentrations by such as an olfactory sensing method.

Furthermore, it is known that the lower Si/Al ratio zeolites have, the higher cation exchangeable capacities they can show. On the other hand, the Si/Al ratio of the natural zeolite used in this study is relatively high. So, it is worth evaluating the adsorption capability for NH$_3$ by using a zeolite at low Si/Al ratio such as ZSM-5 in our future study since such a zeolite is expected to uptake Cu$^{2+}$ more and thus to adsorb NH$_3$ more efficiently.

CONCLUSIONS

HAp/zeolite composite (HZc) was modified with Cu$^{2+}$ and/or APES by a simple immersion method and it maintained NH$_3$ gas adsorption ability. Modification of HZc with Cu$^{2+}$ kept framework structure and morphology of the HZc, allowed it to dope Cu$^{2+}$ in the HZc effectively. And Cu$^{2+}$-modified HZc led to dramatic improvement both of H$_2$S and NH$_3$ gases adsorption ability in comparison to unmodified one. This suggests that Cu$^{2+}$ acted as Lewis acid to interact with such inorganic gases. Modification of HZc with APES also kept framework structure and morphology of the HZc, and newly provided amino groups derived from APES. Consequently, APES-modified HZc showed enhanced CH$_3$CHO adsorption ability in comparison to unmodified one. The adsorption of CH$_3$CHO on APES-HZc may be achieved via a formation of Schiff’s base involving nucleophilic addition reaction and dehydration. On the other hand, sequential
modification of HZc with Cu$^{2+}$ and APES maintained H$_2$S and NH$_3$ gases adsorption ability, but decreased CH$_3$CHO gas adsorption ability. This suggests that Cu$^{2+}$ interacted directly with amino groups, thus adsorption sites for CH$_3$CHO were impeded. The results obtained in this work indicate that mixture of HZc individually modified with Cu$^{2+}$ and APES can enhance simultaneous adsorption ability of HZc for H$_2$S, NH$_3$ and CH$_3$CHO gases in ambient atmosphere.

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