Layered double hydroxide ceramic materials and its H₂S incorporation through topochemical reactions

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Oral malodor is produced by microbial putrefaction of food debris, resulting in the formation of volatile sulfur compounds (VSCs), such as hydrogen sulfide (H₂S) and methyl mercaptan, produced in the mouth. VSCs also have a bad influence on the periodontium and cause discoloration of dental alloy. Thus, an adsorbent that highly adsorbs VSCs would be useful for a healthy mouth and may prevent tooth decay. We investigated the possibility of adsorbing H₂S using heat-treated Magnesium aluminum hydrotalcite. We found that H₂S is adsorbed onto heat-treated hydrotalcite materials in an aqueous solution using gas chromatography with a flame photometric detector (FPD/GC), and the sulfide was found between the layers of the hydrotalcite structure by conducting a powder X-ray diffraction (XRD) analysis and using infrared spectroscopy (FT-IR). The amounts of adsorbed sulfide were higher for hydrotalcite heat-treated at 500 and 600°C for 30 min. The hydrotalcite material is expected to be an adsorbent material and useful for maintaining good oral hygiene.

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Key-words : Layered double hydroxide, Hydrotalcite, Heat-treatment, Volatile Sulfur Compounds, Adsorption

[Received May 31, 2013; Accepted July 7, 2013]

1. Introduction

Many people worldwide have noticed that they have frequent incidents of bad breath, halitosis, and malodor.¹⁾ In Japan, the percentage of persons having a VSC of 75 ppb or over, which is considered a socially acceptable level of oral malodor, ranges from 6–23%.²⁾ The odor emanating from the oral cavity is produced by microbial putrefaction of food debris, resulting in the formation of volatile sulfide compounds (VSCs), such as hydrogen sulfide (H₂S) methyl mercaptan (CH₃SH) and dimethyl sulfide [(CH₃)₂S], which are produced in the mouth.^{3,4)} The VSCs also have a bad influence on periodontal disease and cause discoloration of dental alloys such as the Au–Ag–Pd alloy. Thus, an adsorbent that highly adsorbs VSCs would be useful for maintaining good oral hygiene and may prevent tooth decay.

The adsorbent should be stable in the mouth. Ceramics are materials with excellent chemical and biological stability. Since VSCs are low molecular weight compounds, the pore sizes of microporous materials are sufficient for the encapsulation of low molecular weight compounds such as VSCs. We previously reported on the H₂S adsorptive properties of zeolite and Ag-zeolite materials.⁵⁾ The adsorption was reported by referring to the electronegativity.⁶⁾ Hydrotalcite (HT), whose composition is Mg_{1-x}Al_x(OH)₂A_{x/n}·mH₂O, where A is a univalent or bivalent atom, is a layer compound with a unique anion exchange behavior. HT is biocompatible system, and can be used in pharmaceutical and dental technologies and in medicine as drug supports or matrices.⁷⁾ The rehydration reactivity (topochemical reaction) of HT is also reported. HT is decomposed into a magnesium aluminum-oxide solid solution at 500–900°C and the oxide can rehydrate and incorporate anions in order to reconstruct the

original structure in an aqueous solution. When HT is heated above 900°C, the magnesium aluminum oxide solid solution decomposes to MgO and MgAl₂O₄, which showed no capacity to adsorb anions.⁸⁾ Some anions such as iodide ions, chloride ions and hydrogen phosphate ions^{9,10)} in an aqueous solution were reported to be absorbed into the heat-treated HT through a topochemical reaction, but the adsorption of the sulfur compounds in an aqueous solution was not reported. The aim of this study is to investigate the VSC adsorption capability of heat-treated HT for halitosis treatment. X-ray diffraction and FT-IR spectroscopy were used to analyze the H₂S-adsorbed HT samples.

2. Experimental procedure

2.1 Synthesis of Magnesium aluminum hydrotalcite

The magnesium aluminum hydrotalcite sample with a magnesium aluminum molar ratio equal to 2.0 ($x = 0.33$) was synthesized by using a co-precipitation method at a constant pH.¹¹⁾ All the chemicals used in this study were supplied by Wako Pure Chemical Industry, Ltd., and were used without further purification. Mg(NO₃)₂·6H₂O (0.019 mol) and Al(NO₃)₃·9H₂O (0.01 mol) were dissolved in 100 mL of Milli-Q water; 0.047 mol of Na₂CO₃ was also dissolved in 300 mL of Milli-Q water. The former was added to the latter while stirring and while maintaining the pH value at 10 at 70°C using a 0.5-M NaOH solution. The mixed solution was stirred at room temperature for 24 h to form precipitates. The precipitates were filtered, washed five times using Milli-Q water until the precipitate was free of extra sodium ions and then dried in air at 80°C for 12 h. These products are referred to as 'HT'. The HT sample was heated at 400, 500, 600 or 700°C for 30 min at a heating rate of 10°C/min. The products are thus referred to as 'HT-400', 'HT-500', 'HT-600', and 'HT-700'.

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2.2 Characterization

X-ray diffraction (XRD) analysis was conducted using an X-ray diffractometer (RINT 2000, Rigaku Co., Japan) at 40 kV and at 30 mA for a Bragg-Brentano geometry using a Co K α radiation and a graphite monochromator. The data were obtained by scanning for 2θ values ranging from 10–80° of a scan speed of 2°/min. Identification of the crystal phases was achieved by comparing the diffraction patterns with the ICDD (JCPDS) standard patterns using MDI-JADE6 software (Rigaku Co., Japan). The peak angle corrections for the HT samples after soaking in an aqueous solution containing H₂S were carried out by scanning the relative to major peaks of a standard 4N silicon metal as an internal standard. The XRD data were obtained through scanning at a scan speed of 0.25°/min.

The fourier transform infrared (FT-IR) spectra were recorded on an FT-IR spectrometer (FT/IR-430, JASCO Co., Japan) within the wavelength range of 400–4000 cm⁻¹ at a 4-cm⁻¹ resolution using KBr.

2.3 H₂S adsorption in aqueous solution

The HT, HT400, HT500, HT600, and HT700 samples were dried in a vacuum at 150°C for 24 h to remove the adsorbed water. A Kitagawa gas detector tube system composed of an air sampling pump (AP-20) and a gas detector tube (H₂S No.120 SB) and a FPD/GC (GC-14B equipped with a Flame Photometric Detector, Shimadzu Co., Japan) were used to adjust the initial concentration and to measure the change in H₂S concentration. H₂S gas was introduced into Milli-Q water. The obtained water (H₂S water) was initially adjusted to 0.6 mg/L; 100 mg of the dry sample was placed in a 200-mL Erlenmeyer flask, equipped with a separating funnel and an injection port septum, into which 150 ml of H₂S water was placed. Two μ L of water and 30 mL of gas were removed through the port septum using a syringe, and the total H₂S concentration was measured by using FPD/GC at 1, 2, 3, 4, 5, 6, 12, and 18 h. The concentrations without a hydrotalcite sample were also measured to evaluate the amount of adsorption onto the glass flask wall.

3. Results and discussion

3.1 Materials

Figure 1 shows the X-ray diffraction patterns of HT and heat-treated HT samples. The XRD pattern of HT are identical to that

Fig. 1. X-ray diffraction patterns of HT (a), HT-400 (b), HT-500 (c), HT-600 (d), and HT-700 (e). The subscript of crystal plane means its crystal [i.e. (111)_{MgO} means the index (111) plane of MgO].

of the ICDD data (hydrotalcite, #22-0700). Those of the heat-treated HT samples (HT-400, HT-500, HT-600, and HT-700) are different from that of the HT. The peaks of the heat-treated HT samples were assigned to MgO (ICDD#45-0946), and broad peaks were also observed. When the HT samples were heated at 400°C or over, the hydrotalcite changed into a mixture of MgO and an amorphous phase (magnesium aluminum oxide solid solution).⁸⁾

3.2 H₂S adsorption into hydrotalcite materials in aqueous solution

3.2.1 H₂S adsorption

The changes in total H₂S concentration in the flask during the adsorption process are shown in Fig. 2. Little change in the H₂S concentration in the flask for the first 6 h was observed when the HT sample was used, while the H₂S concentration decreased when no sample was used. Both of these seemed to be almost the same for 12 h. This may indicate that a certain amount of H₂S gas is adsorbed onto the inner wall of the flask, and it might dissolve into the water due to the acid-base reaction,¹²⁾ when hydrotalcite is placed into the water. When HT-500 or HT-600 was used, the concentration fell to 50 or 30% in 6 h and 20% in 18 h. When HT-400 or HT-700 was used, the concentration fell to 75% in 6 h and 40% in 18 h.

3.2.2 H₂S adsorbed hydrotalcite materials

Figure 3 shows the X-ray diffraction patterns of the HT and heat-treated HT (HT-400, HT-500, HT-600, and HT-700) samples after soaking in H₂S water for 18 h. The XRD patterns were identical to that of the ICDD data (hydrotalcite, #22-0700) except for HT-700, so the reconstruction of the original hydrotalcite structure in an aqueous solution (topochemical reaction) was confirmed to occur through the rehydration and incorporation reaction. However, the HT heat-treated at a higher temperature

Fig. 2. Concentration of sulfide in flask as function of soaking time using no sample (a, $\square$, solid line), HT (b, $\blacksquare$, dotted line), HT-400 (c, $\diamond$, dashed line), HT-500 (d, $\blacklozenge$, chain line), HT-600 (e, $\triangle$, long dashed line), and HT-700 (f, $\blacktriangle$, long dashed double dotted line).

Fig. 3. X-ray diffraction patterns of heat treated HT [HT-400 (a), HT-500 (b), HT-600 (c), and HT-700 (d)] after soaking in H₂S water for 18 h.

Fig. 4. X-ray diffraction patterns of HT before soaking in aqueous solution (a), and heat-treated HT [HT-400 (b), HT-500 (c)] after soaking in H₂S water for 18 h, and silicon metal as internal standard.

did not reconstruct the original structure in an aqueous solution, which indicated the low capacity for taking up an anions in aqueous solution. The peaks assigned to MgO remain in the XRD pattern of HT-700 after soaking in H₂S water for 18 h. The MgO and the amorphous phase of the heat-treated HT changed into the hydrotalcite structure through rehydration in H₂S water.

The X-ray diffraction patterns of HT, HT-400 and HT-500 after soaking for 18 h in H₂S water are shown in Fig. 4. The internal standard, high purity metallic Silicon, was used as a reference for making corrections in the peak position. The peaks of the HT-400 and HT-500 slightly shifted after soaking in H₂S water, and so,

Fig. 5. FT-IR spectrometry of HT before soaking in aqueous solution (a), and heat-treated HT [HT-400 (b), HT-500 (c), HT-500 (d), and HT-500 (e)] after soaking in H₂S water for 18 h.

the sulfide in H₂S water may be included into the hydrotalcite structure during immersion in H₂S water. The diffraction patterns show the peak shifts of the (003) and (006) plane to a lower angle that may be caused by a partial exchange of carbonate ions with the hydrogen sulfide ions, which may happen between the layers of the hydrotalcite structure. In contrast, the peak position of the (110) plane of HT-500 after soaking for 18 h in H₂S water is almost the same as that of HT, which may suggest no change in the constitution of the hydrotalcite layers.

Figure 5 shows the infrared spectroscopy results for HT before soaking in H₂S water, and HT-400, 500, 600, and 700 after soaking in H₂S water for 18 h. The absorption peaks can be identified at around 3400–3600 cm⁻¹ as the stretching band and 950–1000 cm⁻¹ as the bending band of hydroxide. The absorption peaks of molecular water were also observed at around 1650 cm⁻¹.¹³⁾ The carbonate anion vibrations can be identified. The absorption peak at around 860 cm⁻¹ was identified as carbonate anion vibration (ν_2), that at 1355 cm⁻¹ as ν_3 , and that at 670 cm⁻¹ as ν_4 .¹²⁾ In the 200–1000 cm⁻¹ region, there were some bands related to the vibrations of the anions, and some related to cation-oxygen vibration.¹³⁾ The absorption peak at 2580 cm⁻¹ identified as vibration of a mercapto molecule (-SH) was not found in HT-400, 500, 600, or 700 after soaking in H₂S water for 18 h. The peak profile around 1000–1350 cm⁻¹ in HT is different from that of HT-400, 500, and 600 after soaking in H₂S water for 18 h. An absorption peak assigned to the sulfoxide group (S=O) was observed in the latter, which may indicate H₂S adsorption in the latter. The absorption peaks at 800 and 1600 cm⁻¹ respectively attributed to the bending and librational modes of molecular H₂O were not observed in HT-700 after soaking in H₂S water for 18 h. However, the absorption peaks at 860 and 1415 cm⁻¹ were attributed to the reduction of the carbonate anion in HT-400, 500, and 600 after soaking in H₂S water for 18 h.

4. Conclusion

The VSC adsorption on/in heat-treated hydrotalcite in an aqueous medium was studied by using FPD/GC. The hydrotalcite materials were hydrothermally synthesized and identified by using powder X-ray diffraction. The concentrations of H₂S were decreased to 20% in 18 h when the hydrotalcite heated at 500 or 600°C was used, fell in 18 h to 75% when the hydrotalcite heated at 400°C was used, and to 40% in 18 h when the hydrotalcite was heated at 700°C. XRD and FT-IR analyses

revealed that the sulfides moved into or out of the hydrotalcite structure through topochemical reactions.

Acknowledgements The Authors are grateful to Dr. T. Inamura for carrying out the BJH pore size distribution measurement at Technology Research Institute of Osaka Prefecture and to Prof. Y. Doi, Prof. M. Hotta, and Dr. K. Fujii of Asahi University for their receiving instruction about halitosis and discoloration of dental alloys.

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