Layered double hydroxide ceramic materials and its H$_2$S 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 (H$_2$S) and methyl mercaptan, produced in the mouth. VSCs also have a bad influence on periodontal disease and cause discoloration of dental alloy. Thus, an adsorbent that highly adsorbs VSCs would be useful for maintaining good oral hygiene and may prevent tooth decay. We investigated the possibility of adsorbing H$_2$S using heat-treated Magnesium aluminum hydrotalcite. We found that H$_2$S 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.

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

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 (H$_2$S) methyl mercaptan (CH$_3$SH) and dimethyl sulfide [(CH$_3$)$_2$S], 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 H$_2$S adsorptive properties of zeolite and Ashton materials.5) The adsorption was reported by referring to the electronegativity.6) Hydrotalcite (HT), whose composition is Mg$_{x}$Al$_{y}$O$_{z}$(OH)$_{2}$-nH$_2$O, where A is a univalent or bivalent atom, is a layer compound with a unique anion exchange behavior. HT is biocompatible, and can be used in pharmaceutical and dental technologies and in medicine as drug supports or matrices.7) The hydration reactivity (topochemical reaction) of HT is also reported. HT decomposes 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 MgAl$_2$O$_4$, which showed no capacity to adsorb anions.8) Some anions such as iodide ions, chloride ions and hydrogen phosphate ions 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 H$_2$S-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.9) All the chemicals used in this study were supplied by Wako Pure Chemical Industry, Ltd., and were used without further purification. Mg(NO$_3$)$_2$·6H$_2$O (0.019 mol) and Al(NO$_3$)$_3$·9H$_2$O (0.01 mol) were dissolved in 100 mL of Milli-Q water; 0.047 mol of Na$_2$CO$_3$ 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 Kα radiation and a graphite monochromator. The data were obtained by scanning for 2θ values ranging from 10° to 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 μL 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 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).

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, 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...
did not reconstruct the original structure in an aqueous solution, which indicated the low capacity for taking up anions in aqueous solution. The MgO and the amorphous phase of the heat-treated HT changed into the hydrotalcite structure through rehydration in H$_2$S water. In contrast, the peak position of the (110) plane of HT-500 after soaking for 18 h in H$_2$S 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 H$_2$S water, and HT-400, 500, 600, and 700 after soaking in H$_2$S 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$^{-1}$. The carbonate anion vibrations can be identified. The absorption peak at around 860 cm$^{-1}$ was identified as carbonate anion vibration ($\bar{v}_2$), that at 1355 cm$^{-1}$ as $\bar{v}_3$, and that at 670 cm$^{-1}$ as $\bar{v}_4$. In the 1000–1350 cm$^{-1}$ region, there were some bands related to the vibrations of the anions, and some related to cation-oxygen vibration. 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 H$_2$S water. The peak profile around 800–1350 cm$^{-1}$ in HT is different from that of HT-400, 500, and 600 after soaking in H$_2$S water for 18 h. An absorption peak assigned to the sulfoxide group (S=O) was observed in the latter, which may indicate H$_2$S adsorption in the latter. 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 H$_2$S 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 H$_2$S 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 H$_2$S 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.

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References