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Adsorption of Cl^- Ion with Pyrolysis Products of Yttrium Oxynitrate Hydrate, $Y_2(OH)_{6-x}(NO_3)_x \cdot nH_2O$

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We attempted adsorption of Cl^- ion in HCl and NaCl solutions with compounds which were prepared by heating yttrium oxynitrate hydrate, $Y_2(OH)_{6-x}(NO_3)_x \cdot H_2O$ up to 600 °C. The X-ray powder diffraction patterns of the compounds obtained by heating up to 200 °C was the same as that of $Y_2(OH)_{6-x}(NO_3)_x \cdot H_2O$; however, it changed to $YONO_3$ in the temperature range from 300 to 400 °C and finally changed to Y_2O_3 above 500 °C. In 0.1 M NaCl solution the starting compound and its pyrolysis products little incorporated Cl^- ion. On the contrary, in 0.1 M HCl solution the uptake of Cl^- ion increased with the treatment temperature, and the maximum value was 3.1 mequiv g^{-1} for samples heated above 500 °C.

It is well known that layered double hydroxide (LDH) with hydrotalcite-type structure is an inorganic anion ion exchanger;[1–3] however, there have been few reports of inorganic anion ion exchangers other than LDH.[4–9] Imai et al. reported that hydrated rare earth metal oxides had high selectivity of F^- ion adsorption in aqueous solution.[6] Hydrated bismuth oxides exhibited high adsorbability for Cl^- ion in aqueous solution.[7] These results indicated that trivalent metal oxides such as rare earth metals or bismuth had adsorbability for anion. As pyrolysis products of $Y_2(OH)_{6-x}(NO_3)_x \cdot H_2O$[10] had layer-type structure, it was expected that those had possibility of adsorption or ion exchange for anion. We attempted adsorption of Cl^- ion with compounds prepared by heating yttrium oxynitrate, $Y_2(OH)_{6-x}(NO_3)_x \cdot H_2O$.[10]

Yttrium oxynitrate, $Y_2(OH)_{6-x}(NO_3)_x \cdot H_2O$ was prepared by previously published method.[10] The adsorption of Cl^- ion was carried out by as follows: The compounds (0.40 g) obtained by heating yttrium oxynitrate, $Y_2(OH)_{6-x}(NO_3)_x \cdot H_2O$ at 100–600 °C were immersed in acid solution (0.1 M HCl 40 mL) or neutral solution (0.1 M NaCl 40 mL), and the containers were shaked at room temperature for 24 h. The solid and solution were separated by filtration and washed with distilled water. The amount of Cl^- ion in the solution was determined by titration using $AgNO_3$ solution. The products were identified by X-ray powder diffraction pattern using monochromated Cu Kα radiation. The phase change at elevated temperatures was investigated with high-temperature X-ray powder diffraction patterns. The thermal stability was investigated by TG-DTA with a heating rate of 10° min^{-1}. The gas species evolved during TG-DTA measurement were analyzed by Mass spectroscopy.

Figure 1 shows high-temperature X-ray powder diffraction patterns for $Y_2(OH)_{6-x}(NO_3)_x \cdot H_2O$. The X-ray powder diffraction patterns of the compounds obtained by heating up to 200 °C was the same as that of $Y_2(OH)_{6-x}(NO_3)_x \cdot H_2O$, and it changed to $YONO_3$ in the temperature range from 300 to 400 °C and finally changed to Y_2O_3 above 500 °C. These phase changes corresponded to the TG-DTA curves, and the mass spectroscopy of gas evolved during TG-DTA measurement as shown in Figure 2. Evolution of water and OH^- is observed up to 300 °C, and the subsequent mass loss is caused by evolution of NO_3^-. From this the chemical composition of this compound is determined to be $Y_2(OH)_{6-x}(NO_3)_x \cdot nH_2O$ ($x = 1.1$, $n = 2.2$).

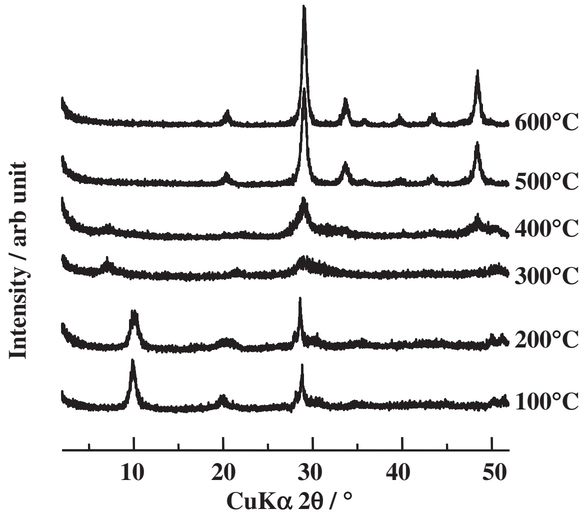

Figure 1. High-temperature X-ray powder diffraction patterns for $Y_2(OH)_{6-x}(NO_3)_x \cdot H_2O$.

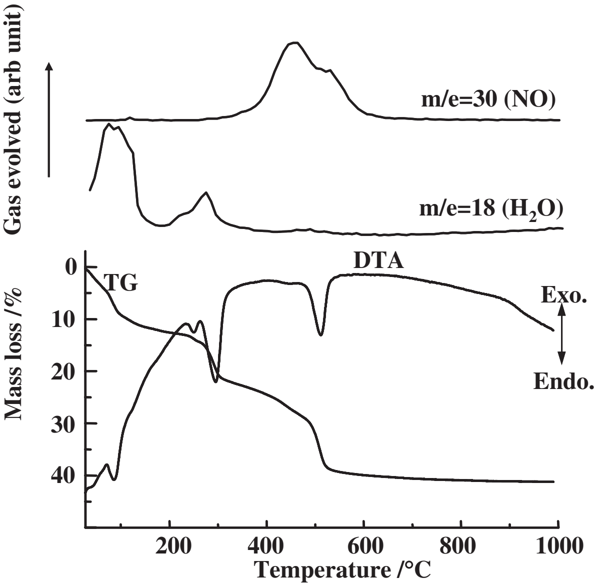

Figure 2. TG-DTA curves and gas evolution during TG-DTA curves of $Y_2(OH)_{6-x}(NO_3)_x \cdot nH_2O$.

Figure 3 shows the uptake amount of Cl^- ion with the pyrolysis products of $Y_2(OH)_{6-x}(NO_3)_x \cdot H_2O$. In 0.1 M HCl solution the

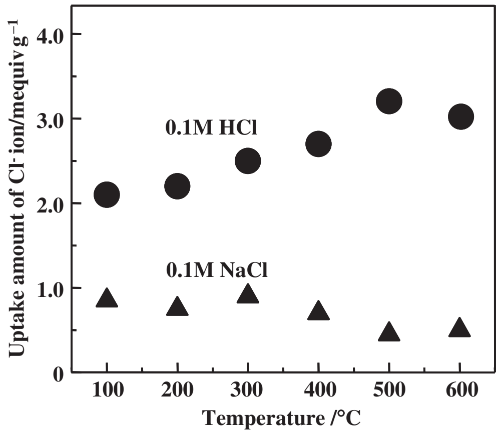

Figure 3. Uptake amount of Cl^- ion with the pyrolysis products of $Y_2(OH)_{6-x}(NO_3)_x \cdot nH_2O$.

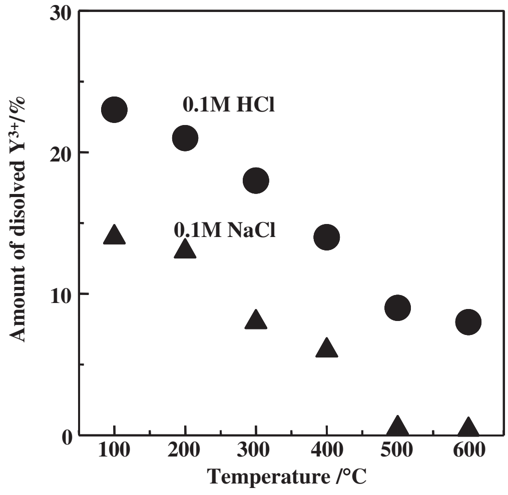

Figure 4. Degree of dissolution of pyrolysis products of $Y_2(OH)_{6-x}(NO_3)_x \cdot nH_2O$.

uptake of Cl^- ion increased with pyrolysis temperature, and Y_2O_3 obtained at 500 °C exhibited the maximum value (3.1 mequiv g^{-1}) among the pyrolysis products. On the other hand, the uptake of Cl^- ion in 0.1 M NaCl solution was very small (0.5–0.9 mequiv g^{-1}) when compared with that in 0.1 M HCl and decreased slightly with pyrolysis temperature. The X-ray powder patterns of the samples after immersing in acid and neutral solution were identical to that before treatment. This suggests that Cl^- ion could not be incorporated into the crystal structure but was adsorbed on the surface of the pyrolysis products or that an amorphous phase was produced by reaction with Cl^- ion. The maximum value (3.1 mequiv g^{-1}) of the uptake of Cl^- ion was comparable to 3.4 mequiv g^{-1} for bismuth hydroxide[7] and higher than the 2.1 mequiv g^{-1} anion-exchange capacity of hydrotalcite.[2] No metal oxides other than these compounds have been reported as an adsorbent or ion exchanger of Cl^- ion.

The pyrolysis products of $Y_2(OH)_{6-x}(NO_3)_x \cdot nH_2O$ were partially dissolved in acid and neutral solutions as shown in Figure 4. The degree of dissolution in 0.1 M HCl solution was larger than that in 0.1 M NaCl solution and decreased with pyrolysis temperature. No dissolution in 0.1 M NaCl solution was observed for the pyrolysis products heated at above 500 °C. This indicates that $Y_2(OH)_{6-x}(NO_3)_x$ and $YONO_3$ obtained from pyrolysis of $Y_2(OH)_{6-x}(NO_3)_x \cdot nH_2O$ was dissolved partially in aqueous solution. The specific surface area of pyrolysis products of $Y_2(OH)_{6-x}(NO_3)_x \cdot nH_2O$ increased with pyrolysis temperature, and the maximum value was 52 $m^2 g^{-1}$ for the pyrolysis product at 50 °C. This tendency corresponds to the uptake amount of Cl^- ion with pyrolysis products in 0.1 M HCl solution. XPS spectra were measured in order to confirm existence of Cl atom in the sample after the adsorption treatment in 0.1 M HCl solution. Figure 5 shows XPS spectra of samples before and after 0.1 M HCl solution treatment for pyrolysis product at 600 °C of $Y_2(OH)_{6-x}(NO_3)_x \cdot nH_2O$. For pyrolysis product at 600 °C of $Y_2(OH)_{6-x}(NO_3)_x \cdot nH_2O$ Cl 2p binding energy (198 eV)[11] was observed after the adsorption treatment; however, no spectra were observed before the starting compounds. Similar XPS spectra was observed for hydrotalcite ($Mg_{0.75}Al_{0.25}(OH)_2(CO_3)_{0.13} \cdot nH_2O$) under the same experimental conditions. In hydrotalcite anion can be incorporated into the crystal structure unlike pyrolysis products of $Y_2(OH)_{6-x}(NO_3)_x \cdot nH_2O$. From these results there are two possibilities for reaction of pyrolysis products of $Y_2(OH)_{6-x}(NO_3)_x \cdot nH_2O$ with Cl^- ion in solution; it could adsorb Cl^- ion by ion exchange with OH^- on the surface or form an amorphous phase containing Cl^- ion on the surface. By taking into account of higher dissolution of pyrolysis products and higher uptake of Cl^- ion in acid solution, the adsorption of Cl^- ion may be governed by formation of an amorphous phase containing Cl^- ion by dissolution–precipitation mechanism. We propose for the first time that an yttrium oxide is a promising candidate for adsorption of Cl^- ion in aqueous solution.

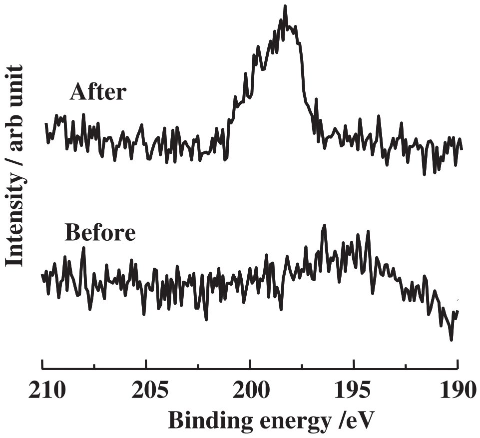

Figure 5. XPS spectra of samples before and after 0.1 M HCl solution treatment for pyrolysis product at 600 °C of $Y_2(OH)_{6-x}(NO_3)_x \cdot nH_2O$.

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