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Influence of thermal treatment on the structure and adsorption properties of layered zinc hydroxychloride

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ABSTRACT

Layered zinc hydroxychloride ($Zn_5(OH)_8Cl_2{\cdot}H_2O$) synthesized by hydrolyzing the ZnO particles in aqueous $ZnCl_2$ solutions at 100 °C for 48 h was outgassed at different temperatures ranging from 100 to 250 °C for 2 h and the structure and adsorption properties of the products were examined by various means. Outgassing at 100–150 °C eliminated the H_2O molecules in interlayer of zinc hydroxychloride. The layered structure of zinc hydroxychloride was disintegrated at 175 °C by breaking the OH···Cl hydrogen-bond in interlayer to form curled thin films composed of poorly crystallized β-Zn(OH)Cl and ZnO, leading to the increment of the specific surface area from 4 to 39 m^2/g. The β-Zn(OH)Cl was decomposed at 225 °C to form ZnO. The crystallinity of ZnO was increased on elevating the outgassing temperature, giving rise to the UV absorption property. The H_2O and CO_2 adsorption measurements revealed that the zinc hydroxychloride outgassed at 100–150 °C possessed a high H_2O and CO_2 adsorption selectivity, and the selectivity diminished by the formation of thin films of ZnO above 175 °C.

1. Introduction

Recently, two-dimensional (2D) nano-structured material such as nano-sheet is of great interest for preparation of high surface area catalyst, self-consistent film and so forth. There are many studies reported about the synthesis of nano-sheet by exfoliation of layered materials, *e.g.*, layered double hydroxide (LDH) [1–6], MnO_2 [7], graphite [8–10], niobate (HNb_3O_4, $K_4Nb_6O_{17}$ and $H_2K_2Nb_6O_{17}$) [11–13], metal phosphate [14–20], titanate [21,22] and so on.

Layered zinc hydroxychloride ($Zn_5(OH)_8Cl_2{\cdot}H_2O$:ZHC), which is one of the basic zinc salts, possesses the basal nano-sheets mainly composed of Zn(II) octahedron and tetrahedron [23]. The Cl atoms are located in each top corner of the Zn(II) tetrahedron [23] and are replaced with various anions [24]. While, the H_2O molecules exist in the layer [23]. Hence, the ZHC has received attention in applications such as catalyst, anion exchanger, and adsorbent. Furthermore, basal nano-sheets of ZHC are bounded by weak hydrogen-bonds of OH···Cl [23]. It can be inferred, therefore, that the layered structure of ZHC is exfoliated by thermal treatment. Moreover, it has been reported that the ZHC is thermally transformed to ZnO [25], which is widely used in industrial field as pigment, varistor, catalyst and so on. Zhang and Yanagisawa prepared a large-sized single crystal ZHC by hydrothermal process and indicated that the ZHC is transformed to polycrystalline ZnO by calcination at 500 °C for 5 h in air [25]. Although, exfoliation of the layered ZHC is not detected during calcination. Also, Ishikawa et al. have synthesized the Al-substituted ZHC from a mixture of $ZnCl_2$ and $AlCl_3$ solutions at 50 °C and revealed that the exfoliation of Al(III)-substituted ZHC took place by outgassing at 125 °C [24]. Nonetheless, Zn(II) atoms in the synthetic ZHC were partly replaced with Al(III) and the thermal decomposition mechanism of this material was not fully clarified. To corroborate the detailed information about thermal transformation mechanism of ZHC and characterization of thermal decomposition products, synthesis of ZHC freed from Al(III) is required. In our previous study, the ZHC freed from Al(III) was prepared by hydrolyzing the ZnO in aqueous $ZnCl_2$ solutions at 6–140 °C for 48 h [26].

The aim of this study was to exfoliate the layered structure of ZHC by thermal treatment *in vacuo* and to characterize the thermal decomposition products. Hence, we treated the synthetic ZHC *in vacuo* at different temperatures ranging from 100 to 250 °C for 2 h. The products thus obtained were characterized by a variety of conventional techniques. The exfoliation and thermal decomposition mechanisms of the ZHC are discussed in this article based on the results obtained.

2. Experimental

2.1. Preparation of ZnO

An aqueous solution (1.0 dm^3) of 50.0 $mmol/dm^3$ $ZnCl_2$ was prepared and the solution pH was adjusted to 9.0 by adding a 28%

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NH_3 solution under stirring condition. The resultants were aged at 50 °C for 24 h in a sealed polypropylene vessel without stirring. After aging, the resulting precipitates were filtered off, thoroughly washed with deionized-distilled water and finally dried at 50 °C in an air oven for a over night.

2.2. Preparation of ZHC

The layered ZHC particles were prepared by the following method [26]. The synthetic ZnO particles (16.0 mmol) were added into 50.0 ml of 2.0 mol/dm^3 aqueous $ZnCl_2$ solutions in a sealed polypropylene vessel and they were aged at 100 °C for 48 h without stirring. The precipitates generated were filtered off, washed with acetone and finally dried *in vacuo* at 50 °C for 24 h. All the chemicals used in this study were reagent grade and used without further purification. The Zn and Cl contents of the synthetic ZHC, estimated from ICP and ion-chromatograph, were 9.12 and 3.60 mmol/g, respectively, almost corresponding to theoretical Zn (9.06 mmol/g) and Cl contents (3.62 mmol/g) calculated from the chemical formula of this material.

2.3. Characterization

The materials thus obtained were characterized by a variety of conventional techniques. Powder X-ray diffraction (XRD) patterns were taken on a Rigaku diffractometer with a Ni-filtered Cu Kα radiation (30 kV, 16 mA). Particle morphology was observed by a TOPCON transmission electron microscope (TEM). Transmission IR spectra were recorded with a resolution of 4 cm^{-1} using a KBr method by a JASCO Fourier transform infrared (FTIR) spectrometer. Diffuse reflectance UV–vis spectra were recorded by a Shimadzu UV–vis spectrometer and an integrating sphere. For the measurements, the samples of 100.0 mg were fully mixed with $BaSO_4$ of 3.325 g used as a diluent. Specific surface area was obtained by fitting the BET equation to the N_2 adsorption isotherms measured by a Quantachrome volumetric apparatus at the boiling temperature of liquid nitrogen. Adsorption isotherms of H_2O were determined by a gravimetric technique at 25.0 °C. Adsorption isotherms of CO_2 were measured at 25.0 °C with an automatic volumetric apparatus assembled in our laboratory. Prior to the adsorption measurements, the samples were treated at different temperatures ranging from 100 to 250 °C under 10^{-5} Torr for 2 h.

3. Results and discussion

3.1. Influence of thermal treatment on the structure and morphology of ZHC

The synthetic layered ZHC was treated at various outgassing temperatures ranging from 100 to 250 °C for 2 h and the XRD patterns were traced. The results are shown in Fig. 1. Pattern ‘a’ of the synthetic ZHC possesses no diffraction peaks of ZnO used as a raw material of ZHC and the peaks due to ZHC (JCPDS card no. 7-195) mainly develop at $2\theta = 11.2°$, 22.5°, 28.1° and 46.0°, which respectively correspond to the reflection from (0 0 3), (0 0 6), (1 1 0) and (0 0 12) planes of the crystal. No remarkable difference in XRD patterns of ZHC outgassed at 100 and 125 °C was recognized (patterns not shown here). When the ZHC is outgassed at 150 °C, diffraction intensity of the (0 0 3) peak increases, while no new peaks are detected (pattern b), revealing the improvement of crystallinity of the layered structure. At 175 °C, the ZHC peaks suddenly disappear and some weak peaks are seen at $2\theta = 15.6°$, 31.7°, 34.4° and 36.2° (pattern c). This indicates that the ZHC is transformed to poorly crystallized ZnO (no. 89-1397) and β-Zn(OH)Cl (no. 72-525). The diffraction intensity of β-Zn(OH)Cl is increased at 200 °C and reaches to zero at 225 °C (patterns d and e). On the other hand, the ZnO peaks gradually intensify on elevating the outgassing temperature (patterns c–f). These facts allow us to infer that the ZHC is thermally transformed to ZnO.

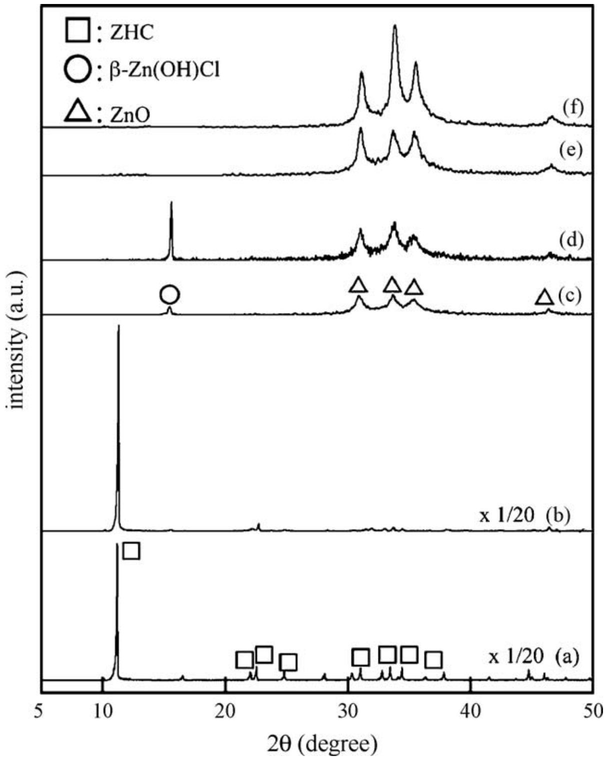

Fig. 1. XRD patterns of (a) synthetic ZHC and (b–f) ZHC outgassed at different temperatures. Outgassing temperature (°C): (b) 150, (c) 175, (d) 200, (e) 225, and (f) 250.

Fig. 2 plots the mass value of the samples as a function of outgassing temperature. A mass loss of 3.31 wt% is found at 25–150 °C, of which the value almost coincides with the mass of H_2O molecules of 3.30 wt% in ZHC layer calculated from the chemical formula. Therefore, the mass loss between 25 and 150 °C can be assigned to the release of H_2O molecules in interlayer of ZHC. The mass is steeply reduced at 150–175 °C and is further slightly

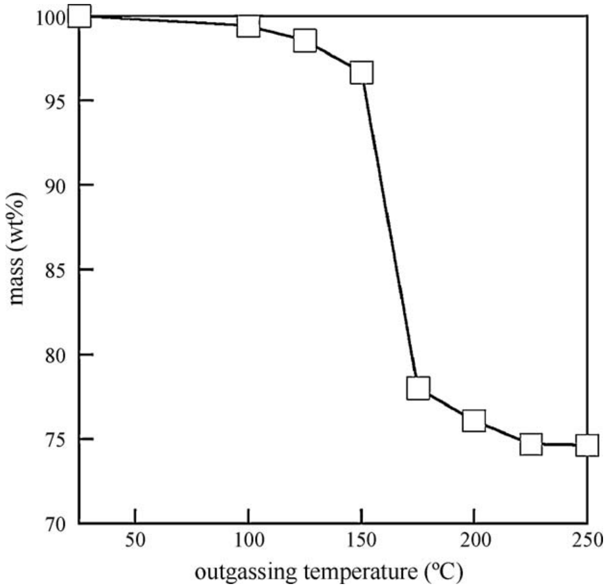

Fig. 2. Plots of mass as a function of outgassing temperature.