Surface modification and dissolution behavior of Mg–Al hydrotalcite particles

Sheng Xu, Meng-Chen Liao, Hong-Yan Zeng*, Xiao-Jun Liu, Jin-Ze Du, Peng-Xuan Ding, Wei Zhang

College of Chemical Engineering, Xiangtan University, Xiangtan 411105, Hunan, China

ABSTRACT

The dissolution behavior of Mg–Al–CO_3^{2-} hydrotalcite (AHT) in aqueous solution was studied. The AHT dissolution strongly depended on pH and temperature, and the dissolution of AHT fitted the surface chemical reaction model well. The apparent activation energy during the dissolution process was 34.11 kJ/mol, which further confirmed that the dissolution was controlled by the surface chemical reaction. During the SO_4^{2-} modification, the exchange process between SO_4^{2-} and CO_3^{2-} in interlayer spaces of the AHT took place along with Mg^{2+} partial dissolution from edges of the brucite sheets. On the other hand, the modification mechanism of the AHT was discussed based on the dissolution–reprecipitation (D–R) mechanism. The modification process was suggested to occur on the solid/water interface, *i.e.*, dissolution of Al-ions and Mg^{2+}, adsorption and reprecipitation of the Al aqua ions on the surface of the solids.

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1. Introduction

Water pollution by heavy metals is considered to be a serious menace to the environment and especially to human health, which heavy metal ions are toxic even at a trace level [1,2]. Heavy metal compounds are considered cumulative poisons [3]. One effective way of removing heavy metal ions is the adsorption on various materials such as cation exchanger [4], zeolite [5] and hydrotalcites [6].

Hydrotalcites (LDHs) have found increasing interest as adsorbents by virtue of their properties, which made them attractive materials for adsorbing heavy metal ions and toxic anions [6,7]. The properties such as abundance in nature, low cost, high anion exchange capacity, good thermal stability, large surface area and regeneration ability make them suitable for wastewater purification [8,9]. However, LDHs are unfavorable for the removal of heavy metal cations. Surface modification of LDHs is crucial not only for the development and applications of hydrotalcite materials but also for changing their surface characteristics in order to make them available for the removal of heavy metal cations [10,11]. It is well demonstrated that the modification by $(NH_4)_2SO_4$ can improve the surface properties of metal oxides. Sulfate modification considerably increases the acid sites concentration of γ-Al_2O_3 by the impregnation method using an aqueous solution of $(NH_4)_2SO_4$ [12]. Both ZrO_2 and TiO_2 modified by $(NH_4)_2SO_4$ exhibit super acidic sites and are used as catalysts for the alkylation [13]. However, LDHs are unstable and dissoluble in acid solutions. The dissolution of LDHs is a very important process in applications of several areas such as releasing control of drugs and removing of pollutants, especially the removal of heavy metals from wastewater [14]. A detailed understanding of dissolution mechanism of LDHs should allow a deep insight on the modification methodologies of the material and further allow the properties of LDHs to be tailored to adsorb heavy metals. Until now, there are only a few reports on the dissolution of the Cu–Mg–Al–CO_3^{2-} and Mg–Al–Cl LDHs. They find that the dissolution is surface controlled and hydrotalcite solubility presented a strong dependence on pH [14,15]. However, some opinions in the literature were different and have not reached a uniform understanding.

The aim of the present work was to disclose the dissolution mechanism of the Mg–Al–CO_3^{2-} LDH in aqueous solutions, especially the modification mechanism by $(NH_4)_2SO_4$. The LDHs dissolution was discussed based on the characterization and analysis of the samples. We hoped that our detailed understanding of the dissolution and SO_4^{2-} modification process of the Mg–Al–CO_3^{2-} LDH would be available to develop further modification methodologies of LDHs and make LDHs tailored to specific applications.

2. Experimental

2.1. Materials

All the reagents/reactants used were analytical grade. All solutions were prepared with deionized water. 0.1 mol/L NaOH and HCl

* Corresponding author. Tel.: +86 731 58298175; fax: +86 731 58298167.
E-mail address: hongyanzeng99@hotmail.com, hyzeng@xtu.edu.cn (H.-Y. Zeng).

solutions were used for pH adjustment. A pH electrode for high temperature (Mettler Toledo) was used for pH measurements.

2.2. Preparation of hydrotalcites

The hydrotalcites with Mg/Al molar ratio of 3.0 was prepared by urea method (urea/NO_3^- molar ratio of 4.0) [16]. An aqueous solution containing $Mg(NO_3)_2 \cdot 6H_2O$ (0.12 mol/L) and $Al(NO_3)_3 \cdot 9H_2O$ (0.04 mol/L) was placed into a three-neck flask. The solution was maintained at 105 °C for 12 h under stirring (300 rpm), and then aged statically at the same temperature for 18 h at about pH 9.0. The formed solid was collected by filtration and washed to neutral using deionized water, and subsequently dried at 100 °C for 18 h. The filtered material was heated at 200 °C for 6 h, and then cooled to 30 °C, which was denoted as AHT.

2.3. AHT modification process

A $(NH_4)_2SO_4$ solution (18 wt%) was obtained by dissolving $(NH_4)_2SO_4$ in deionized water, which the pH in the $(NH_4)_2SO_4$ solution was measured to be 5.4. In our preliminary work, the most optimum modification time was 4 h (see detailed information in Fig. S1). A 400-mL $(NH_4)_2SO_4$ solution was added to a reactor and preheated to 60 °C, and then 2.5-g AHT was placed into the reactor, shaking continuously at 60 °C and 200 rpm for 4 h. The amount of Mg and Al in the reaction solution was monitored by atomic absorption spectrophotometer at regular intervals at pH 5.4. After the reaction, the mixture was cooled to room temperature and centrifuged at 7000 rpm for 20 min, washed three times with deionized water. The initial and subsequently washed supernatants of the modification were stored for the determination of Mg and Al amounts. The precipitate was dried at 200 °C for 6 h, which was denoted as MHT.

2.4. Dissolution and kinetic data measurement

The dissolution of AHT was carried out in aqueous solution at pH 1.0–11.0. Buffer solutions were used due to instable pH in aqueous solution, and the buffer that could form stable complexes of Al-ion and/or Mg^{2+} had to be avoided. On this account, pH was kept constant by adding small amounts of HCl or NaOH solutions during the whole dissolution process. AHT sample immersed in aqueous solution with a constant pH 5.4 for 72 h was aimed for further characterization analyses, denoted as c-pH-AHT.

A 0.50-g sample was suspended in 200-mL solution at 25 °C, mixed for at least 5 min, adjusted to the desired pH, and stored in a shaker with 200 rpm at 25 °C. The pH in the solution had to be determined during the entire process, whereas the addition of small amounts of HCl or NaOH solutions was necessary at times. A little mixed solution was withdrawn at defined time intervals in order to acquire the kinetic data. When the reaction was over, the mixed dissolved solutions were cooled down and centrifuged, and then the amount of Mg and Al in the supernatant was analyzed. Each dissolution experiment was carried out twice in order to test the reproducibility of results. The dissolved fraction (X) was calculated from the leaching of Mg^{2+}/or Al-ion.

$$X(\%) = \frac{[Mg^{2+}]_t}{[Mg^{2+}]_{max}} \times 100 \text{ or } = \frac{[Al]_t}{[Mg^{2+}]_{max}} \times 100$$

where $[Mg^{2+}]_t$ and $[Al]_t$ are the Mg and Al amounts at any time t, respectively, and $[Mg^{2+}]_{max}$ is the Mg amount after the complete dissolution of the sample.

2.5. Analytical methods of Mg and Al

The amounts of mononuclear dissolved Al (free Al^{3+}) were determined by solvent extraction and spectrophotometry of aluminum 8-hydroxyquinoline described in the literature [17]. 5-mL supernatant was transferred to a extraction vessel with 1 mL NH_4Ac–$NH_3 \cdot H_2O$ buffer (1 mol/L, pH 6.8), followed by adding 0.6 mL 2% 8-hydroxyquinoline sodium acetate solution, and then adjusted pH to 8.5 by adding 6-mol/L ammonia solution. The vessel was quickly swirled to blend the mixed solution for 3 s, and 10-mL toluene was then added. The vessel was closed immediately and shaken vigorously to extract the free Al^{3+} into the toluene phase for 10 s. The mixture was filtered, and the filtrate was diluted to 10 mL. The mononuclear Al was determined at 390 nm using a Shimadzu UV-2450 spectroscopy at room temperature. The solution for analyses of Al-ions and Mg^{2+} was prepared by adjusting the supernatant to pH 1.0 using 0.1-mol/L HCl solution. The Mg and Al-ions contents were analyzed by atomic absorption spectrophotometer (Hitachi, Z-8000).

2.6. Characterization of hydrotalcites

X-ray diffraction (XRD) patterns were collected on a Japan Rigaku D/max 2550PC (λ = 1.5405 Å) with CuKα radiation. The scan step was 0.02° (2θ) with a filament intensity of 30 mA and a voltage of 40 kV. FT-IR spectra were recorded in the range 400–4000 cm^{-1} on PE Spectrum One B FT-IR spectrometer. Scanning electron micrograph (SEM) was obtained with a JEOL JSM-6700F instrument and energy dispersive x-ray spectroscopy (EDS) analysis was performed by a Noran SystemSix instrument. EDS was used to determine the contents of C, O, S, Mg and Al elements in the samples. Surface areas of samples were determined by N_2 adsorption-desorption at −196 °C, using the surface area analysis method, with a NOVA 1000e (Quantachrome, USA) instrument.

2.7. pH point of zero charge

The determination of the pH point of zero charge (pHzpc) of the AHT and MHT was carried out using the potentiometric titration (PT) method described by Li et al. [18]. The pH at pHzpc was determined in NaCl solutions (inert electrolytes) with different concentrations. The experiments were carried out in a shaker at 150 rpm and 25 °C for 200 min. After the experiments, the pH in the solution was measured while a 0.1-mol/L NaOH solution was being added. The adsorption amount of H$^+$ (Γ_{H+}) and OH$^-$ (Γ_{OH-}) was calculated. Finally, PT curves were obtained by plotting ($\Gamma_{OH^-} - \Gamma_{H^+}$) versus pH in NaCl solutions with different concentrations, and the crossover point of ($\Gamma_{OH^-} - \Gamma_{H^+}$) $\sim$ pHzpc curves was pHzpc which was electrically neutral.

3. Results and discussion

3.1. Characterization of AHT and MHT samples

3.1.1. XRD characterization

Powder XRD patterns for the AHT, MHT and c-pH-AHT are shown in Fig. 1. The samples had the typical layered double hydroxide structures of Mg–Al–LDHs with sharp and intense (003), (006), (009), (110) and (113) reflections and broadened (015) and (018) reflections. Further analyses of the XRD patterns revealed some differences in the cell parameters among the samples. For the SO_4^{2-} intercalated hydrotalcite, the interlayer space distance d_{003}-value was supposed to be in the range 0.858–0.880 nm, and for the CO_3^{2-}, it was in the range 0.760–0.780 nm [19,20]. The distances of the AHT and c-pH-AHT were 0.778 and 0.763 nm, respectively, expecting the intercalated anions were CO_3^{2-}. The distances of the MHT increased to 0.859, possibly due to the intercalation of SO_4^{2-} anions. For the AHT, no other crystalline phases were observed, indicating that the sample was a highly crystalline hydroxide structure. X-ray diffraction patterns of the MHT and c-pH-AHT showed the presence of $Al(OH)_3$ as an impure phase. The parameter a, average cation–cation distance in the brucite sheet, was calculated from the (110) XRD reflection. There was a value of