Applied Clay Science 54 (2011) 274–280

Contents lists available at SciVerse ScienceDirect

Applied Clay Science

journal homepage: www.elsevier.com/locate/clay

Research paper

Characterization and boron adsorption of hydrothermally synthesised allophanes

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ARTICLE INFO

Article history:
Received 24 March 2011
Received in revised form 29 September 2011
Accepted 2 October 2011
Available online 4 November 2011

Keywords:
Allophane
Boron adsorption
Grafting
N-methyl-D-glucamine

ABSTRACT

Two hydrothermally synthesised allophanes (Si/Al = 0.5 and 1) were modified by heating at 400 °C. N-methyl-D-glucamine, a specific boron complexant, was grafted on the allophane material with Si/Al = 0.5. The surface and structural properties of the different materials were characterised by infrared spectroscopy and ^{29}Si CP MAS NMR spectroscopy. The porous characteristics of the different allophanes (specific surface area, pore size distribution) were determined by nitrogen adsorption at 77 K using the BET equation and the BJH model. The adsorption of boron, i.e. boric acid/borate, by the modified allophanes was studied in aqueous solutions with boron contents of 1 to 100 mg L^{-1}. The pH-dependence of boron adsorption of all the sorbents showed a maximum at a pH value close to the pKa value of boric acid (pKa $H_3BO_3/B(OH)_4^-$ = 9.26). The adsorption isotherms of boron by raw and modified allophanes were fitted with a double Langmuir equation, assuming the presence of two sets of adsorption sites. The grafting of N-methyl-D-glucamine did not improve the boron adsorption of the allophanes but the structural changes by heating at 400 °C increased the adsorption.

1. Introduction

Boron derivatives are used in many industrial processes. As a consequence, high amounts of boron are released in the environment. At high concentrations, boron is toxic for humans (Sah and Brown, 1997). The acceptable intake is 0.3 mg boron kg^{-1} day^{-1} which is well above the normal exposure levels (Murray, 1996). Boron is mainly present in water as undissociated H_3BO_3 boric acid and $B(OH)_4^-$ borate (Geffen et al., 2006). Many inorganic materials were already used for boron removal from water through precipitation (Remy et al., 2004), adsorption (Choi and Chen, 1979; Karahan et al., 2006; Su and Suarez, 1997) and complexation mechanisms (Inukai et al., 2005; Simonnot et al., 2000). These materials are mainly oxides (Del Mar de la Fuente García-Soto and Muñoz Camacho, 2006; Lemarchand et al., 2007; Peak et al., 2003; Seki et al., 2006) and clay minerals (Goldberg and Glaubig, 1986; Kehal et al., 2008; Keren and Talpaz, 1984; Palmer et al., 1987; Singh, 1971). The boron adsorption sites for clay materials are mainly the –OH groups present at the edges of the layers (Keren and Talpaz, 1984). To increase the efficiency of these materials, specific organic complexants with hydroxyl groups such as N-methyl-D-glucamine ($CH_3NHCH_2(CHOH)_4CH_2OH$:NMDG) were grafted on the surfaces of inorganic materials (Geffen et al., 2006). Polymer resins grafted with NMDG can selectively form complexes between their polyol groups and the borate ions (Inukai et al., 2005; Simonnot et al., 2000). The grafting of NMDG was also achieved with the silanol groups (Si–OH) of aluminosilicates, as for example a MCM41 mesoporous silica (Kaftan et al., 2005) and more recently a vermiculite clay (Kehal et al., 2008). The adsorption of boron by allophanes was reported as these materials both exhibit aluminol (Al–OH) and silanol groups on their surfaces (Son et al., 1998; Su and Suarez, 1997). However, so far as we know, the boron adsorption on NMDG grafted allophanes and heated allophanes was not reported in the literature survey.

Allophanes are natural non-crystalline hydrated aluminosilicates of hollowed spherical shape (Lindner et al., 1998). The spherules are composed of a tetrahedral Si and an octahedral Al sheet (Parfitt, 1990). The resulting external diameter of the spherules ranges between 3.5 and 5 nm and the thickness of the wall between 0.7 and 1.0 nm. Due to the presence of defaults in the wall structure, allophanes present open pores of 0.35 nm diameter (Wilson et al., 1986) in which water molecules can penetrate. The molar Si/Al ratio of allophanes varies from 0.5, as for example for protoimogolites, to 1 for silicon rich compounds such as halloysite-type allophanes (Henmi and Wada, 1976). By hydrothermal synthesis using various aluminium and silicium precursors, a wide range of compositions were obtained (Lindner et al., 1998; Ohashi et al., 2002). Allophanes with Si/Al = 2 were also synthesised (Montarges-Pelletier et al., 2005). Synthetic allophanes usually exhibit higher specific BET

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doi:10.1016/j.clay.2011.10.002

surface areas and pore volumes compared to natural ones, which might extend their potential applications (Ohashi et al., 2002). Allophanes are well known as good adsorbents for polluting anions such as phosphates (Clark and McBride, 1984; Henmi and Huang, 1985), arsenates (Arai et al., 2005; Opiso et al., 2009), sulphates, molybdates, chromates and seleniates (Opiso et al., 2009). Furthermore, the silanol and aluminol groups on the allophane spherule surface give interesting adsorption properties towards boron (Clark and McBride, 1984).

The aim of this paper was to study and compare the boron adsorption of hydrothermally synthesised allophanes and of the calcined samples and samples grafted with N-methyl-D-glucamine.

2. Experimental

2.1. Synthesis of allophanes and calcination

The allophanes were synthesised according to a procedure previously described by Ohashi et al. (2002). A solution was prepared by rapid mixing of a sodium orthosilicate solution (Na_4SiO_4) and an aluminium chloride solution ($AlCl_3$) to obtain final products with Si/Al ratios of 0.5 and 1. After an ageing period of 1 h at room temperature, the sodium chloride by-product was removed from the gel by centrifugation. The gel was autoclaved and heated at 100 °C for 2 days. The allophanes were then recovered by filtration, washed with distilled water and dried at 40 °C.

The pristine allophanes were calcined at 400 °C for 2 h under air atmosphere. This temperature was chosen because boron adsorption measurements on allophanes annealed in the range of 200 °C–800 °C (not shown) pointed out that the highest uptakes were obtained after calcination at 400 °C.

2.2. Preparation of N-methyl-D-glucamine grafted allophane (Si/Al = 0.5)

In a first step, 3 g of pristine allophane (Si/Al = 0.5) were reacted under reflux with 50 mL of chloroform and 5 mL of (3-bromo-propyl)trimethoxysilane for 16 h at 120 °C under argon to obtain a propyl-bromide functionalized allophane. After filtration, the brominated allophane was washed under agitation with a 1:1 v/v diethylether:dichloromethane solution for 12 h. The solid was then filtered and vacuum dried at room temperature.

The second step consisted in a nucleophilic substitution of the brominated allophane by NMDG. The recovered dried allophane was reacted under reflux with 30 mL of an aqueous solution of NMDG (8 g L^{-1}) for 24 h at 70 °C, according to the procedure described by Kaftan et al. (2005). The obtained grafted material was washed at least three times with distilled water before being vacuum dried.

2.3. Determination of boron concentration in boron adsorption experiments

Uptake experiments were performed at 25 °C for 24 h using 1 g of sample and 100 mL of solution containing boron concentrations in the range of 1–100 mg L^{-1}. The initial pH was fixed at the pKa value of $H_3BO_3/B(OH)_4^-$, i.e. 9.26, by addition of a 0.1 mol L^{-1} NaOH solution. After adsorption, the dispersions were centrifuged at 4000 rpm, and the boron concentrations of the recovered solution were determined by UV–Visible spectrophotometry after complexation with curcumine (Rodier, 1978). A "20 Genesys" UV–Visible spectrophotometer from Spectronic Instruments with 1 cm glass cell was used for all measurements.

For pH dependent boron adsorption studies ([B] = 5 mg L^{-1}, $V_{solution}$ = 100 mL, $m_{adsorbent}$ = 1 g), the pH values of the allophane dispersions were adjusted by dropwise addition of 0.1 mol L^{-1} HCl (or 0.1 mol L^{-1} NaOH).

Standard boron solutions were prepared by dissolving 0.229 g of 99% boric acid in 1 L of Ultra High Quality grade water (UHQ:18.2 MΩ cm) to obtain an initial solution of 40 mg L^{-1} of boron. Working solutions were prepared by appropriate dilution of this initial solution with water.

The complexant solution was prepared by mixing 3 mL of a curcumine solution (prepared by dissolving 0.125 g of curcumine in 100 mL of 99.5% acetic acid) with 3 mL of an acid reagent (1.5 mL of 18 mol L^{-1} H_2SO_4 and 1.5 mL of 99.5% acetic acid). 0.2 mL of a boron solution were added to the complexant solution, homogenised and left to settle for 45 min before the addition of 15 mL of a buffer solution (1 L of buffer solution was prepared by dissolving 250 g of 99.5% ammonium acetate and 100 mL of 99.5% acetic acid in UHQ water). After standing for 30 min, the absorbance of the rosocyanin complex formed was measured at 550 nm against a blank. The concentration of boron was interpolated from a calibration curve obtained with standard boron solutions in the range of 0–5 mg L^{-1}, using the same procedure, with an accuracy of ± 0.05 mg L^{-1}.

2.4. Physico-chemical characterizations

The N_2 adsorption–desorption isotherms of the allophanes were measured using an automatic adsorption instrument (ASAP 2020, Micromeritics) at 77 K. Prior to the measurements, the samples were slowly degassed under vacuum (10^{-3} mbar) at 75 °C for 2 h and then 110 °C for 12 h. The specific surface areas (S_{BET}) were calculated using the BET (Brunauer–Emmett–Teller) equation by assuming the area of the nitrogen molecule to be 0.162 nm^2. The microporous volumes were estimated by the t-plot method (Rouquerol et al., 1999). The total pore volumes were estimated as the liquid volume of adsorbate adsorbed (N_2) at a relative pressure of 0.99. In addition, the pore size distribution was determined by using the Barrett–Joyner–Halenda (BJH) method applied on the adsorption/desorption hysteresis loop assuming a model of cylindrical pores (Barrett et al., 1951).

Mid-infrared transmittance measurements (400–4000 cm^{-1}) were carried out on a Bruker IFS 66 V spectrometer equipped with an N_2-cooled MCT detector, a black body source and a KBr beam splitter. The spectral resolution was 2 cm^{-1}, and 64 scans were taken for each spectrum. Spectra were obtained at room temperature (300 K ± 1 K). Pellets (pressed under 370 MPa) were made of a mixture of 1.5 mg of allophane and 300 mg of dried KBr. The spectra were not smoothed, and no baseline correction was performed. The given frequency corresponds to the peak maxima.

^{29}Si nuclear magnetic resonance experiments under $^{29}Si-^{1}H$ Hartmann–Hahn cross-polarisation with magic angle spinning were performed on a Varian spectrometer. All spectra were recorded on a 9.4 T wide bore magnet corresponding to a Larmor frequency of 79.49 MHz and referenced to tetramethylsilane (TMS). A solid state CP MAS NMR probe, a rotor of 7.5 mm in diameter spinning at 5 kHz and a last delay of 5 s were used to investigate all the samples.

Thermogravimetric analyses (TGA) were performed on a TGA 2050CE analyzer from TA Instruments under an air flow (90 mL min^{-1}) with a heating rate of 20 °C min^{-1}.

3. Results and discussion

3.1. Characterization of the allophanes

3.1.1. N_2 adsorption–desorption and porosity

The adsorption–desorption isotherms of raw and modified allophanes showed type IV behaviour with H_2 type hysteresis loop, characteristic of mesoporous samples (Fig. 1).

The specific surface areas of the raw samples (S_{BET}) were typical of synthetic allophanes (Montarges-Pelletier et al., 2005; Ohashi et al., 2002), as the S_{BET} values increased from 291 m^2 g^{-1} for the Si/Al = 1