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Reaction of acid activated montmorillonites with hexadecyl trimethylammonium bromide solution

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ABSTRACT

Acid-activated montmorillonites (AMt) prepared at different acid\montmorillonite ratios were reacted with hexadecyl trimethylammonium (C16TMA) bromide solution. The acid treated Mt incorporated smaller amounts of the surfactants than the parent Mt, due to the reduction of the cation exchange capacity after acid-treatment. The powder X-ray diffraction patterns exhibited a similar basal spacing of 3.80 nm but with less ordered structure at higher acid\montmorillonite ratios. A certain degree of conformational heterogeneity was observed by ^{13}C CP\NMR spectroscopy due to the different local environment of C16TMA^{+} ions in the interlayer space. The *in-situ* PXRD patterns showed an increase of the basal spacing of organo acid-activated montmorillonites when heated at intermediate temperatures (100–200 °C), while the basal spacing was almost constant in this range of temperature for the organomontmorillonite. Generally, the stability of the surfactant decreased when intercalated into the montmorillonites compared to the pure C16TMABr. This fact implies that the interlayer space influences the decomposition steps.

1. Introduction

The treatment of clay minerals, mainly swelling ones, with inorganic acids of high concentration and at elevated temperatures, referred to as “acid activation” or “acid dissolution” (Komadel and Madejová, 2006) is commonly used for production of relatively inexpensive adsorbents or catalysts used in industry or environmental protection (Mokaya et al., 1994; Ravichandran and Sivasankar, 1997; Bergaya and Lagaly, 2001; Komadel and Madejová, 2006). During the acid treatment, many changes occurred in the aluminosilicate structure due to dissolution of structural ions and rearrangement of the structure (Komadel and Madejová, 2006). The acid treatment firstly renders the surface of clay acidic. It leaches metal ions from the clay mineral lattice (Komadel and Madejová, 2006). It also increases the external specific surface area of the clay and introduces permanent mesoporosity (Hart and Brown, 2004; Kooli and Jones, 1997). The proton exchanged clay minerals are not stable. Autotransformation results in gradual dissolution of metal ions, mainly Al^{3+} (Janek et al., 1997).

When the exchangeable inorganic cations are replaced by organic cations, the clay mineral surface properties are greatly modified (Lagaly et al., 2006). As a result, the organoclay becomes an excellent adsorbent for poorly water-soluble organic species. The commonly used types of organic cations for the exchange reaction are tetramethylammonium (TMA^{+}) and its long-chain alkyl trimethylammonium homologues such as trimethyl phenylammonium (TMPA^{+}), and benzyl trimethylammonium cation (BTMA^{+}) (Brixie and Boyd, 1994; Kwolek et al., 2003; Lagaly et al., 2006). The quaternary ammonium is adsorbed on the clay mineral surface and the attached long carbon chain renders the interlayer space organophilic, swelling in water is minimized but swelling in organic solvents or organic fluids is greatly enhanced.

The combination of acid-activation with alkylammonium intercalation provides a potential enhancement of the clay mineral properties. The clay mineral presents a proton rich environment when mixed to organic molecules. On the other hand, the catalytic abilities can be improved by providing organic cations in the interlamellar space, which enable the access to/and interact effectively with organic molecules. The catalytic properties in these systems are enhanced, the effect of different acid-treatments on organoclays formed from clay minerals of different initial composition was studied by evaluating the resistance of these organocations to acid leaching (Breen et al., 1997). These catalysts were also tested in the isomerization of α-pinene to camphene and limonene (Breen et al., 1997).

The ammonium salt used for the most organoclay preparations has been hexadecyl trimethylammonium (C16TMA) from its bromide or chloride forms (Jaynes and Boyd, 1991; Dentel et al., 1995; Guangyao et al., 1996; Zhao et al., 1996; Boyd and Mortland, 1998). Recently, the effect of the counteranion was studied on the intercalation properties of C16TMA into clay minerals and layered silicates such as magadiite (Kooli et al., 2006a,b). The effect of acid activation on the intercalation of

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C16TMA$^+$ with different anions was also investigated using bromide and hydroxide solutions (Kooli and Magussin, 2005; Kooli et al., 2005). The acid-activation process affected the amount of intercalated C16TMA$^+$ from its hydroxide form on acid-activated clay minerals and magadiites (Kooli et al., 2005, 2006b). However, there was not a systematic or detailed study on the intercalation of these cations from their bromide form using acid activated clay minerals treated at different ratios. Few studies were reported on the intercalation of C16TMA$^+$ cations into acid activated clay minerals at different given acid\clay mineral ratios, although they were often used as an intermediate stage to prepare mesoporous or porous clay heterostructures (Pichowicz and Mokaya, 2001; Linssen et al., 2002; Kooli et al., 2006c). In this study, we report a study on the acid treatment effect of a selected montmorillonite at different acid\montmorillonite ratios on the intercalation properties of C16TMA$^+$ from its bromide solution. The thermal properties will be also reported using *in-situ* X-ray diffraction at increasing temperatures.

2. Experimental

2.1. Materials

A Ca^{2+}-montmorillonite (STx-1, with CEC of 0.92 meq/g) was obtained from the Source Clays repository, Purdue University (USA) and used as received. The method of acid-activation has been described in detail elsewhere (Kooli and Jones, 1998). Acid activation was accomplished by mixing the Mt with aqueous sulfuric acid (maintaining an acid/Mt ratio of 20 mL g^{-1}) at 90 °C for overnight. This w\w ratio calculated by using the dry mass of montmorillonite and H_2SO_4 (98%) was varied between 0.1 and 0.5. These acid-activated montmorillonites (AMt) were repeatedly washed with distilled water until free SO_4^{2-} ions, as tested by $BaCl_2$. The samples (noted 0.1, 0.2, 0.3, 0.4 and 0.5AMt) were dried at room temperature.

2.2. Preparation of organo acid-activated clays

Amounts of 1 g of AMt was dispersed in a solution containing 0.3 g of C16TMABr in 25 g of deionized water. The suspension was stirred for overnight at room temperature. The material was collected by filtration, washed with deionized water until free of Br$^-$ ions, as tested by $AgNO_3$, and dried at room temperature. The sample will be assigned as C16TMA-XAMt (where X is equal to acid to montmorillonite ratios (w/w) 0.0, 0.1, 0.2, 0.3, 0.4 and 0.5). In some cases, C16TMA-AMt was prepared at different quantity of the organic cation. The resulting organoclay was identified by the amount in mmol per g of organic cations adsorbed.

2.3. Characterization

The powder X-ray diffraction (PXRD) patterns were recorded on a Bruker Advance 8 diffractometer (Ni-filtered Cu-Kα radiation). *In-situ* high temperature PXRD patterns between room temperature and 425 °C, were recorded using an Anton Parr heating stage KT450, under nitrogen atmosphere. The cation exchange capacity (CECs) of montmorillonite and AMt were measured by the micro-Kjedahl method (Mackenzie, 1951). The contents of carbon, nitrogen, and hydrogen in the organoclays were determined by EURO EA elemental analyzer. These data were used to estimate the intercalated amounts of C16TMA$^+$. Thermogravimetric analysis (TGA) was performed on the TA instrument calorimeter, SDT2960, in air flow 100 ml min^{-1} heated from 25 to 900 °C, at a heating rate of 5 °C min^{-1}. Solid-state nuclear magnetic resonance (NMR) experiments were performed on a Bruker 400 spectrometer operating at ^{29}Si NMR frequency 78 MHz. A 4-mm magic-angle spinning (MAS) probehead was used with sample-rotation rates of 4.0 kHz for ^{29}Si NMR experiments. 80–100 scans were accumulated with the recycle delay of 200 s. The ^{29}Si chemical shift is reported with tetramethylsilane (TMS) taken as reference. ^{1}H–^{13}C cross-polarisation solid-state NMR (^{1}H–^{13}C CP/MAS) were acquired with a Bruker Advance DSX400 spectrometer operating at 400.16 MHz for ^{1}H and 100.56 MHz for ^{13}C with a MAS triple resonance probehead using zirconia rotors 4 mm in diameter. The spinning rate was 4.0 kHz, ^{1}H π/2 pulse length was 4.40 μs and the pulse delay 10.0 s. ^{13}C chemical shifts were quoted in ppm with respect to TMS. The specific surface area and pore volume of the acid activated clays and organoclays were measured by nitrogen sorption using a quantachrome Autosorb 6 instrument. Prior to analysis, the samples were degassed under vacuum at 120 °C, overnight. The BET equation was used to calculate the surface areas, while the total pore volume have been calculated from the adsorbed amount at relative pressure $p/p_o = 0.95$.

3. Results and discussion

3.1. C, H, N contents

Gradual increase of adsorbed C16TMA$^+$ cations was observed as the initial loading concentrations arise, then the amount of organic cations adsorbed reached a plateau. The value of this plateau depends on the extent of acid activation extent (Fig. 1). The parent Mt contains the largest amount of intercalated C16TMA cations. With increasing extent of acid-activation, the surfactant value decreases (Table 1). Similar results were obtained for the alumina and zirconia pillared acid-activated saponites (Kooli and Jones, 1998). The surfactant amount decreases with increasing the acidic treatment, and could be related to the decrease in CEC during acid activation, as already shown by Bovey and Jones (1995). Previously, different results were obtained by using C16TMAOH solution. The content of C16TMA$^+$ increased with the increase of the extent of acid-activation process (Kooli et al., 2005). The amount of adsorbed surfactant was distinctly higher than that predicted by the CEC of the starting montmorillonite, and could be attributed to a partial adsorption of C16TMA$^+$ cations on amorphous silica formed during the acid-activation (Pradubmook et al., 2003). However in this study, the surfactant content decreases as the silica phase increases with acid\montmorillonite ratio. The adsorption of long chain quaternary ammonium ions on clay minerals involves at least three reactions i) cation exchange, ii) adsorption of ion-pairs and iii) chain–chain interactions (Zhang et al., 2003). The arrangement and the orientation of the intercalated surfactant

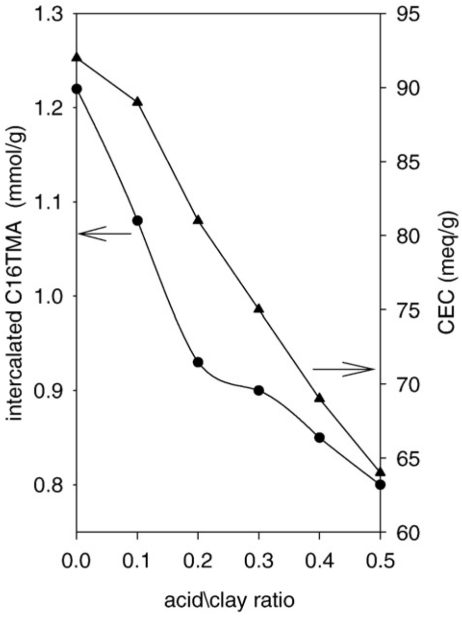

Fig. 1. Cation exchange capacity (CEC, ▲) and amount of C16TMA intercalated (●) by acid activated montmorillonites.