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Thermal stability investigation of organo-acid-activated clays by TG-MS and *in situ* XRD techniques

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ABSTRACT

Organo-acid-activated clays were prepared with different surfactant contents by reaction of hexadecyltrimethylammonium hydroxide solution and acid-activated clays. The intercalated cations adopted different orientation in the interlayer spacing of the acid-activated clays and their thermal stability depended on the up taken amounts, acidity of the clay sheets and on the heating temperatures. The thermal stability of these materials was investigated using TG-MS, and followed by the *in situ* X-ray diffraction in nitrogen atmosphere. The clay sheets affected the decomposition of the surfactants, and as per consequence the thermal stability of the surfactants. TG-MS revealed that different types of water molecules were detected during the heating process with additional CO_2, alkanes and alkenes species at temperatures above 200 °C. The interlayer spacing collapsed after completed degradation of the intercalated surfactants.

1. Introduction

The modification of the negatively charged surfaces of clay minerals with organic cations, produces an organoclay (OCs) structure. The clay mineral becomes organophilic in character and can be used to remove hydrophobic contaminants from water [1]. Organoclays are often prepared using quaternary ammonium cations of the general form $[(CH_3)_3NR]^+$ or $[(CH_3)_2NRR']^+$ where R and R′ are hydrocarbon groups [2]. The most commonly used quaternary ammonium cation is hexadecyltrimethylammonium ion (with $R = C_{16}H_{33}$, $C16TMA^+$) where the tail group has found to have higher affinity for the exchange sites on clays relative to other surfactants [3–7]. On the other hand, the hydrophilic properties of the natural clays make them difficult to be intercalated with monomers or polymers without being modified by cationic surfactants [8]. The alkyl ammonium cations are also used for this type of modification. The organic ammonium pendent group on these exchanged cations renders the layered silicate hydrophobic, promotes the exfoliation of layered silicates and makes them compatible with the polymer matrix and forms nanocomposite samples [9]. The nanocomposites usually exhibit improved performance properties compared to conventional composites, owing to their unique phase morphology and improved interfacial properties [10,11]. The low stability of ammonium surfactants presents a problem for the melt intercalation and bulk processing of polymer nanocomposites, where high processing temperatures exceeding 200 °C are commonly used. The thermal degradation during processing could initiate/catalyze polymer degradation, in addition to cause a variety of undesirable effects during processing and in final product [12]. Efforts have been made to synthesize thermally stable organoclays based on different cations such as stibonium [13], or imidazolium [14] and phosphonium surfactants [15].

The chemical reactivity of the parent aluminosilicate affected the stability of the organoclays. The degradation of bound surfactants can be facilitated by the proximity to the catalytically active aluminosilicates sites [16]. This reactivity could be modified by acid-activation. The acid treatment led to chemical leaching of some cations from clay sheets accompanied with an increase of surface area and enhances the acidity of the obtained clays [17]. In this regards, we were interested to prepare organoclays from different acid-activated clays to prepare stable porous clay heterostructures with enhanced acidity [18]. The acid-activated clays (OAACs) exhibited different intercalation properties compared to the nonacid-treated raw clay [19]. The thermal stability of the organo-acid-activated clays (OAACs) was related to the amount of up taken surfactants and to acid-activation level. The organoclay prepared from a clay treated at higher acid to clay ratios exhibited higher thermal stability compared to the one prepared from a clay treated at lower acid/clay ratios [20]. The layered structure of OAACs were maintained in the range of 200–400 °C with

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a basal spacing varying from 3 to 4 nm, as indicated by *in situ* XRD taken at reel temperature without cooling the samples [20]. The temperatures at which the *in situ* XRD was performed, were deduced from thermogravimetric analysis (TG) curves. The thermogravimetric analysis alone is so limited, because the chemical identification of the volatile gases is not possible. The use in conjunction with mass spectrometry will enable the identification of the evolved gases and the release temperature of alkyl degradation. The thermogravimetric analysis combined with mass spectrometry (TG-MS) was used to study the thermal degradation of organoclays [21]. To the best of our knowledge, TG-MS studies related to the OAACs were not reported. Here we investigate in detail the evolution of gaseous species from two selected OAACs with different intercalated amount of C16TMA cations, using a. TG-MS technique. The structural changes during the C16TMA decomposition was followed by *in situ* X-ray diffraction. We have tried to correlate the decomposition of the cationic surfactants with the acidity of these acid-activated clays.

2. Experimental

2.1. Materials

The raw clay (Ca-montmorillonite, STx-1) was purchased from the Source Clays repository, Purdue University (USA) and used as received. The acid-activation was performed with sulphuric acid (98%) at a fixed acid/clay ratio of 0.3 (in weight) at room temperature (Amt-RT) or at 90 °C (Amt-90), as described in our previous work [22]. The organo-acid-activated clays (OAACs) were prepared by an exchange reaction using C16TMAOH solution. Briefly 1 g of each acid-activated clay was added to 3 g of C16TMAOH solution and 22 ml of deionized water, corresponding to a concentration of 2.47 mmol. This concentration value was selected according to our previous studies. After overnight, the samples were collected by filtration and washed with deionized water. The samples will be assigned as follows: C16TMA-Amt-RT and C16TMA-Amt-90. The sample C16TMA-mt is identified as the organoclay prepared from the starting clay without a prior acid treatment.

2.2. Characterization of organo-acid-activated clays

The elemental analysis of C, N, and H was performed using EURO EA elemental analyzer. The powder X-ray diffraction (XRD) patterns were collected on a Bruker Advance 8 diffractometer (Ni-filtered Cu Kα radiation). The *in situ* powder XRD patterns between RT and 425 °C were taken using an Anton Parr heating stage KT450, under nitrogen atmosphere at real temperature values, without cooling the samples. Thermogravimetric coupled with mass spectrometry (TG-MS) experiments were carried out using SETSYS$_{\text{évo}}$ thermoanalyzer (SETARAM instrumentation) coupled to mass spectrometer (omnistar) from pfeiffer by stainless capillary at temperature of 300 °C. The measurements were carried out in flow of dry nitrogen heated from room temperature to 900 °C, at a heating rate of 5 °C min^{-1}. Only selected gases were analyzed. The acidity of acid-activated clays was measured by using the cyclohexylamine as a probe molecule [23].

3. Results and discussion

3.1. Powder X-ray diffraction

Fig. 1 depicts the powder XRD of the two acid-activated clays and their organo-acid-activated counterparts. The Amt-90 exhibited a higher partial destruction compared to Amt-RT, with a decrease in intensity of 0 0 1 reflection and a relative increase of the amorphous silica phase in the range between 25° and 30°. The intercalation of C16TMA cations was successfully achieved with an increase of the basal spacing of Amt-RT and Amt-90 clays from 1.54 to 2.20 and 3.83 nm, respectively. The significant expansion of the basal spacing from 2.20 to 3.83 nm indicates a possible transition of alkyl chain configuration from the monolayer paraffin structure (2.20 nm) to a bilayer paraffin complex (3.83 nm) [2,22]. The montmorillonite sheet thickness is 0.96 nm, and the length of the fully extended of C16TMA cations was estimated about 2.53 nm [24]. The interlayer gallery is about of 1.22 nm (deduced from the subtraction of the basal spacing of OAACs from 0.96 nm), where the intercalated molecules adopted a monolayer paraffin type arrangement where C16TMA cations were titled of 29° (degree). This value was close to that reported for a monolayer paraffin structure in the case of nonacid-activated montmorillonite [2]. While, C16TMA-Amt-90 material exhibited an interlayer gallery of 2.84 nm which exceeded the length of C16TMA cations. In this case, the cations adopted a tilted bilayer paraffin arrangement. For a simple case of a bilayer structure where methylene chains are exclusively all-*trans*, the tilt angle is about 35° with respect to the layers [22].

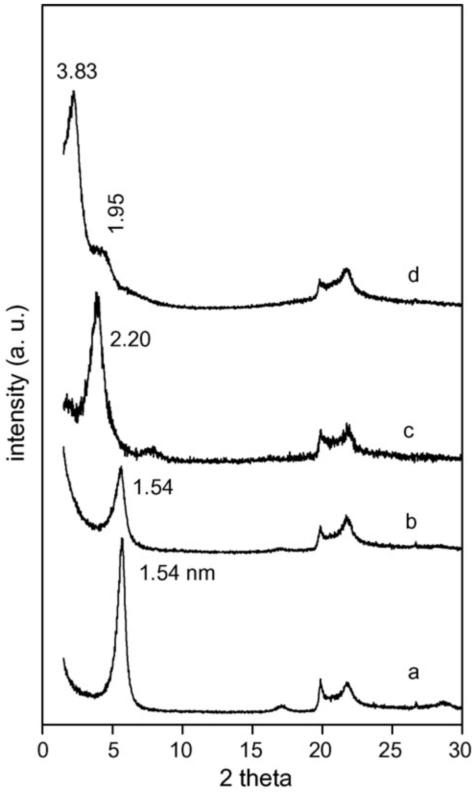

Fig. 1. Powder XRD of clay acid-activated at (a) RT and (b) 90 °C, and their organo-derivatives (c) C16TMA-Amt-RT and (d) C16TMA-Amt-90, respectively.

3.2. Elemental analysis

The validity of C, N and H elemental analysis was compared to the pure C16TMABr salt. The data indicated that Amt-90 intercalated more surfactants (1.24 mmol g^{-1}) than Amt-RT (0.84 mmol g^{-1}). These data were surprising, because the Amt-RT exhibited higher cation exchange capacity (CEC of 0.82 meq g^{-1}) compared to Amt-90 (0.74 meq g^{-1}). The up taken amount was higher than the CEC value for Amt-90. This fact indicated that the intercalation in the latter did not occur via cation exchange reaction [25], and other process could occur [20]. The pH values of the C16TMA-clay suspensions was above 10, the surface of Amt-90 clay became more negatively charged, and thus favored the adsorption of C16TMA