Surface and interface physicochemical aspects of intercalated organo-bentonite

Ceyda Bilgiç [a], Demet Topaloğlu Yazıcı [a,*], Naile Karakehya [a], Hayrullah Çetinkaya [a], Ajay Singh [b], Mohamed M. Chehimi [c]

[a] Department of Chemical Engineering, Faculty of Engineering and Architecture, Eskişehir Osmangazi University, 26480 Eskişehir, Turkey
[b] Technical Physics Division, Bhabha Atomic Research Centre (BARC), Mumbai 400085, India
[c] Univ Paris Diderot, Sorbonne Paris Cité, ITODYS, UMR CNRS 7086, 15 rue J-A de Baïf, 75013 Paris, France

ARTICLE INFO

ABSTRACT

The detailed understanding of the surface and interface physicochemical aspects of intercalated organo-bentonite is of importance in the design of organoclay based materials and in their industrial applications. In this study X-ray photoelectron spectroscopy (XPS), diffuse reflectance infrared Fourier transform spectra (DRIFT), X-ray diffraction (XRD) have been used to provide new insights into the surface composition, surface functional groups, interlayer structure and morphology of hexadecyl trimethyl ammonium bromide (HDTMAB)/bentonite organoclays (oMMT). Inverse gas chromatography (IGC) is used for understanding the effect of the HDTMAB on the dispersive component of the surface energy (γ_S^d) which is closely related with the adhesion and wettability properties of materials. The increasing amount of HDTMAB in organoclays was found to significantly reduce the γ_S^d values up to 1.5 oMMT. 1.5 oMMT and 2 oMMT values were found so closer to each other. More importantly, the γ_S^d values were correlated with the XPS-determined surface N/Al atomic ratio, taken as a chemical descriptor for the modification of the clay.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Clay minerals have been used for years in many applications such as nanocomposites [1], catalysts [2], adsorbents for removal of hazardous compounds [3], supports for highly fluorescent probes [4] to name but a few. The demand for clays in diverse scientific and technological areas lies in their low cost and natural abundance, high adsorption and absorption capacities, fire retardancy among other properties. However, in most cases clays cannot be employed as received and performances of clay-based materials rests on appropriate chemical modification by a range of molecular and macromolecular compounds.

The most common smectite clay mineral is montmorillonite (MMT). MMT is evolved from volcanic ashes by weathering or hydrothermal effects like other aluminum-rich minerals and composed the highest part of the volcanic ash clay called as bentonite. The terminology of the word of bentonite can be summarized like that: The rock term bentonite which is commonly used for smectite group minerals (sodium montmorillonite, calcium montmorillonite, saponite (Mg), nontronite (Fe), and

hectorite (Li)) as a clay material altered from a glassy igneous material, usually volcanic ash. In the latest papers, the term bentonite was used for any clay which was dominantly comprised of a smectitemineral without regard to its origin. Those bentonites that are used industrially are predominantly comprised of either sodium montmorillonite, calcium montmorillonite, or, to a much lesser extent, hectorite [5].

Each 2:1 layer of smectites has two silica tetrahedral (T) sheets bonded to a central alumina octahedral (O) sheet. (yener.pdf) montmorillonite is a 2:1-type aluminosilicate. The net negative electric charge of the 2:1 layers arising from the isomorphous substitution of Al^{3+} with Fe^{2+} and Mg^{2+} in the octahedral sites and Si^{4+} with Al^{3+} in the tetrahedral sites, is balanced by hydrated exchangeable cations in the interlayers (mostly Ca^{2+} and Na^+) [6,7].

The surface of clay mineral is hydrophilic; this property limits some applications of clays such as making them weak adsorbents for organic compounds and reducing the dispersion of clay in polymer matrices. One way to change the clay from hydrophilic to hydrophobic can be achieved by exchanging the inorganic cations found naturally in clays with organic cations.

The organic cations most commonly used for clay mineral modification are non-functionalized quaternary ammonium ions of the general formula $[(CH_3)_3NR]^+$ or $[(CH_3)_2NR_2]^+$, where R is an

* Corresponding author. Tel.: +90 222 2392840; fax: +90 222 2393613.
E-mail address: demett@ogu.edu.tr (D. Topaloğlu Yazıcı).

aromatic or aliphatic hydrocarbon [8,9]. When R is a relatively small group (e.g. R=–CH3, –C6H5) the organic cations in the interlamellar region of the clays are isolated from each other. Such organoclays have relatively high surface areas and display characteristics of surface adsorbents. Alternatively, when R is a large alkyl group [e.g. hexadecyltrimethylammonium (HDTMAB), R= –C16H33], the resultant organoclays have low surface areas and act as partitioning media in the sorption [10]. The ammonium salt used for the most organoclay preparations has been hexadecyl trimethylammonium from its bromide or chloride forms [11]. HDTMAB modified clays have been widely studied in previous literatures [12]. Hexadecyl trimethyl ammonium bromide is a common surfactant that is widely used in the daily life [13]. Smectite surfaces have a high selectivity for organic cations such as hexadecyl trimethyl ammonium cations. In addition, the concentration of organic cations employed to modify the clay can be as high as the cation exchange capacity of clays. Typical cation exchange capacities for montmorillonite clays are 70-110 mmol/ 100 g [8]. The cation exchanged, hydrophobic clay is termed organoclay. This modification expands the applications of clays such as purification and remediation of water by adsorption of organics [14,15] and evaluation of organoclays in advanced composites [16,17]. The performance of the organoclays in these applications closely related to the structure of organic materials without any doubt. Also the effects of the amount of organics have been researched by using XRD, IR spectroscopy, TGA and swelling volume measurements [18], transmission electron microscopy (TEM), scanning electron microscopy (SEM) and X-ray diffraction (XRD) have been used to provide new insights into the interlayer structure and morphology of HDTMAB/montmorillonite organoclays [19], thermal stability and water vapor transmission properties of organoclay polymer composites were compared [20]. IGC was used to examine the effects of treating MMT clay with different amounts of octadecyl trimethyl ammonium bromide by determining the dispersive component of the surface free energies (γ_s^d) [21]. The isotherms of some organic compounds on modified bentonites with different amount of CEC were obtained by IGC [22].

Despite the achievements in the study of the chemical modification of clays in relation to clarifying the structure and the morphology, the surface and interface physicochemical aspects of intercalated organo-bentonites and the evaluation of the extent of their modification is sparse and usually concerned synthetic clays. This study bridges the gap by focusing on the purification of local raw bentonite clay first and then synthesizing and characterization of these organo bentonites. For this reason, different amounts of hexadecyl trimethyl ammonium bromide (HDTMAB)/bentonite organoclays were prepared. IGC has been used to determine the dispersive component of surface energy of organo-bentonites. From the retention volumes at infinite dilution over a range of temperatures, the dispersive component of the surface energies were calculated. The surface compositions of organo-bentonites were determined by X-ray photoelectron spectroscopy (XPS). XRD permitted to investigate the structural and morphological properties of organo-bentonites. The surface functional groups and the changes after modification (information on organo-clay intercalations) were determined by diffuse reflectance infrared Fourier transform spectra (DRIFT).

2. Material and methods

2.1. Preparation of organoclays

Bentonite used in this investigation was supplied from SAMAŞ AŞ/Turkey. Sedimentation was used to purify the clay sludge to increase the amount of MMT. Light yellow clay was obtained after this precipitation operation, dried in the oven and then grinded.

A 1 L of 2 mol/L NaCl solution is added to the 20 g of purified clay and was mixed at 500 rpm with magnetic stirrer for 24 h at room temperature (or 23 °C). The relative humidity of laboratory was 35%. Then, the mixture was filtered and washed with distilled water several times. Na saturated bentonite was dried at 110 °C in the oven. The cation exchange capacity (CEC) of the clay was determined by methylene blue adsorption technique as 110 mmol/ 100 g clay.

A 10 g Na-bentonite aqueous suspension and the specific amounts of (0.5, 1, 1.5 and 2 times the value of CEC) HDTMAB [CH_3 $(CH_2)_{15}N$ $(CH_3)_3Br$] were mixed for 24 h by adding distilled water heated at 60 °C. Then the mixture was washed with distilled water four times and then dried at 60 °C. The abbreviations of 0.5 oMMT, 1 oMMT, 1.5 oMMT and 2 oMMT will be used for the amounts of times the value of CEC in preparation of organo montmorillonites.

2.2. Characterization of organoclays

2.2.1. X-ray diffraction (XRD)

XRD patterns were recorded on a X'pert Pro diffractometer (Panalytical Company) operating at 40 kV and 40 mA, with an anode using Co $K\alpha$ as radiation source (λ=1.7902 Å).

2.2.2. X-ray photoelectron spectroscopy (XPS)

The specimens were pressed against insulating double-sided adhesive tapes on sample holders and pumped overnight in the fast entry lock at ~5×10^{-8} mbar. XPS spectra were recorded with a Thermo VG Scientific ESCALAB 250 spectrometer (East Grinstead, UK) equipped with a monochromatic Al $K\alpha$ X-ray source (1486.6 eV and 650 µm spot size). The pressure in the analysis chamber was ca. 2×10^{-8} mbar. The pass energy was set at 150 and 40 eV for the survey and the narrow scans, respectively. Ultimate spectral resolution was achieved for the C1s region by setting the pass energy at 15 eV. The step size was 1.0 eV for the survey spectra and 0.1 for the narrow regions, respectively. Charge compensation was achieved with an electron flood gun operated in the presence of argon at a partial pressure of 2×10^{-8} mbar in the analysis chamber. In these conditions, the surface charge was negative but perfectly uniform that is without any peak distortion. XPS data were acquired and processed using the Avantage software, version 4.67. The internal standard method was chosen for spectral calibration and the C–C/C–H C1s component was set at 285 eV.

The surface composition was determined using the manufacturer's sensitivity factors. The fractional concentration of a particular element A (%A) was computed using:

$$\%A = \frac{(I_A/S_A)}{\Sigma(I_n/S_n)} \times 100 \tag{1}$$

where I_n and S_n are the integrated peak areas and the Scofield sensitivity factors corrected for the transmission function of the analyzer, respectively.

2.2.3. DRIFT spectra

The spectra of pure bentonite, HDTMAB and organo montmorillonites were recorded on a Perkin Elmer 100 FTIR spectrometer in the 4000 to 400 cm^{-1} wave number range using DRIFT (Diffuse Reflectance Infrared Fourier Transform) technique. The spectrums of the samples were obtained using KBr dilution and finely powdered KBr as reference. Each sample spectrum was obtained by collecting 64 scans at a 4 cm^{-1} spectral resolution.