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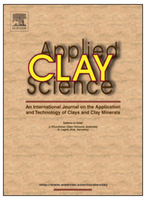

Research paper

Influence of purification method of Na-montmorillonite on textural properties of clay mineral composites with TiO_2 nanoparticles

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A B S T R A C T

Na-montmorillonite purified either by dialysis or by multiple centrifugation was used for the preparation of two types of clay mineral/TiO_2 composites: one obtained by conventional pillaring, the other by mixing of organo-montmorillonite with inverse micelles containing Ti oxo-hydroxy species. The manner of preparation of the parent clay mineral affected strongly the textural properties of pillared montmorillonite materials but had much less effect on the texture of composites prepared with inverse microemulsion. The observed phenomena are discussed in terms of the montmorillonite component structural organization upon formation of composites. Suitability of both purification methods for preparation of Na-montmorillonite designed for synthesis of composite materials is assessed.

1. Introduction

Research on clay mineral composites with metal oxide nanoparticles has been initiated during the oil crisis of 1970s, when the concept of clay pillaring with inorganic polycations has been introduced and developed in response to the need of robust porous catalysts capable of processing heavy fractions of crude oil (Vaughan, 1988). Among various PILC (pillared interlayered clay) materials developed for catalytic applications (Vicente et al., 2013), those based on Ti pillars are of particular interest as potential photocatalysts (Ding et al., 1999; Li et al., 2002; Zhang et al., 2008; Carriazo et al., 2010; Chen et al., 2013). In this field of application the methods of clay mineral/TiO_2 composites preparation extend beyond the concept of conventional pillaring, and include, e.g., a heterocoagulation of positively charged TiO_2 nanocrystallites and negatively charged montmorillonite layers (Mogyorósi et al., 2003; Kun et al., 2006), intercalation of titanium isopropoxide under supercritical CO_2 conditions into Na-montmorillonite or organomontmorillonite (Yoda et al., 2002), interaction of Laponite and a sol of titanium hydrate in the presence of poly(ethylene oxide) surfactants (Zhu et al., 2002), or polycondensation of titanium isopropoxide in the presence of an organoclay (Manova et al., 2010).

Most frequently research on natural clay mineral modification is carried out with the use of a homoionic sodium form of montmorillonite, as it is easily exchangeable and provides uniform properties for intercalation (Romero et al., 2006; Vicente et al., 2013). The material is obtained by means of cation exchange with NaCl solution, and the excess ions (including chlorides) are washed out by dialysis or by the less time-consuming repeated centrifugation (e.g., Kornmann et al., 1998; Michot et al., 2004; Cadene et al., 2005; Fournaris et al., 1999; Janek and Lagaly, 2001; Gates, 2004; Bergaya and Lagaly, 2013).

In the present work we show that the textural properties of clay mineral/TiO_2 composites depend on the manner of purification of the parent montmorillonite. Two types of composites have been investigated: one obtained by means of conventional pillaring, the other by a novel procedure, consisting in mixing of organo-montmorillonite with inverse micelles containing Ti oxo-hydroxy species.

2. Materials and methods

2.1. Materials

The starting material used in the study was the <2 μm particle size fraction extracted by sedimentation from Jelšový Potok bentonite (Slovakia), provided by ZGM Zebiec (Poland). This deposit contains montmorillonite as the only clay mineral phase (Šucha and Kraus, 1999). The sodium-exchanged form was obtained by treatment of the extracted <2 μm fraction with excess of 1 M NaCl solution. After 8 h of stirring the dispersion was left for sedimentation, most of the clear solute removed by decantation, and the exchange with NaCl solution repeated twice. Two types of final products, differing by the method of Cl^- removal, were obtained. One was purified by a multiple centrifugation,

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the other by dialysis, both procedures carried out till the negative result of reaction with $AgNO_3$ solution. Purification by centrifugation was performed with a Thermo Scientific Sorvall Lynx 4000 Centrifuge, using 20 min washing cycles at 5000 rpm, and could be completed within one day, while dialysis treatment, carried out with the use of Spectra/Por tubing, lasted a couple of weeks. Finally, both materials were dried in air at 50 °C. The samples are referred to as Na-Mt(C) and Na-Mt(D) for centrifuged and dialyzed montmorillonite, respectively.

Both Na-Mt(C) and Na-Mt(D) were used as components in the preparation of montmorillonite/titanium oxo-hydroxy species composites by two methods. One involved synthesis of conventional Ti-pillared samples, prepared according to the previously described procedure with the use of Ti-pillaring solution obtained by controlled hydrolysis of $TiCl_4$ (Sterte, 1986; Bahranowski et al., 2000). In a typical experiment, 6.5 cm^3 of 6 M HCl was added to 9 cm^3 of $TiCl_4$ (0.082 M). This mixture was further diluted to 100 cm^3 by addition of distilled water under constant stirring. The resulting solution was aged for 3 h prior to use. It was added dropwise to the aqueous dispersion of Na-Mt(C) or Na-Mt(D) in the amount corresponding to 10 mmol Ti per gram of montmorillonite. After 3 h ageing at room temperature the product, centrifuged until free of Cl^-, was air dried at 50 °C and calcined for 3 h at 450 °C. The resulting materials are referred to as Ti-PILC(C) and Ti-PILC(D). The other method employed a novel procedure, consisting in mixing of organo-montmorillonite with inverse micelles containing Ti oxo-hydroxy species. For this purpose, the Na-Mt(C) and Na-Mt(D) component was transformed into an organoclay by a routine cation exchange procedure with the cetyltrimethylammonium bromide (CTABr) solution and centrifuged free of Br^- with distilled water. The product, CTA-Mt, from which the excess water was removed by successive washings with isopropanol and 1-hexanol, was subjected to an exfoliation treatment (Venugopal et al., 2006) by dispersing in 1-hexanol (ca. 0.1 g per 100 ml) and 5 h ultrasonication. Inverse Ti oxo-hydroxy microemulsion was prepared following the approach proposed by Tai et al. (2004). The Ti-pillaring solution, constituting the aqueous phase, was added to CTABr and 1-hexanol in weight proportions 16:30:54. The system was stirred till the mixture turned into a stable transparent liquid, indicating formation of inverse microemulsion. The Ti-containing microemulsion was added to CTA-Mt dispersion in 1-hexanol, at 60 °C, in the amount providing Ti loading similar as in the case of Ti-PILC samples. Subsequently, the pH was raised to 7 by drop-wise addition of 1 M NaOH solution and the dispersion stirred for 18 h. The precipitate, centrifuged until free of bromide ions, was dried in air at 50 °C and calcined at 600 °C for 6 h. The choice of the calcination temperature was dictated by the necessity to remove all carbonaceous remnants of the organic compounds present in the precursors. The obtained inverse microemulsion/clay mineral (IMEC) composites are referred to as Ti-IMEC(C) and Ti-IMEC(D).

2.2. Methods

X-ray diffraction patterns were recorded with a Philips APD PW 3020 X'Pert diffractometer with CuKα radiation and graphite monochromator. The samples, prepared as randomly oriented specimens, were analyzed in the range of $2\Theta = 2–72°$ with a constant step of 0.05°. In addition, for Ti-PILC samples the oriented thin films were prepared by drying a dilute dispersion of clay mineral on a glass slide, followed by calcination. Crystal sizes of montmorillonite particles (the sizes of coherently scattering domains) in the direction perpendicular and parallel to the basal plane were evaluated by analyzing the (001) and (060) reflections, respectively, using the Scherrer formula and taking into account the instrumental broadening. A similar analysis of the anatase (101) reflection yielded estimated size of titania nanocrystals. Raman spectra were collected with a DXR Raman microscope (Thermo Scientific) using 532 nm excitation laser wavelength, power level 6 mW, and spectral resolution 2 cm^{-1}. Transmission electron microscopic (TEM) studies were performed with FEI Tecnai G2 transmission electron microscope at 200 kV. 20 images were recorded for each analyzed sample. Textural parameters were derived from N_2 adsorption/desorption measurements performed at −196 °C with the use of Quantachrome AUTOSORB 1 instrument. Prior to the measurement the samples were outgassed at 200 °C for 3 h. Specific surface areas (S_{BET}) were calculated according to the Brunauer–Emmett–Teller (BET) method in the relative pressure range 0.02–0.04. The micropore surface area (S_{micro}) and micropore volume (V_{micro}) were calculated by t-plot analysis. The total pore volume (V_{tot}) was calculated from the amount of adsorbed N_2 at a relative vapor pressure $p/p_0 = 0.996$. The mean diameters of all pores (D^{av}) was evaluated using the Gurvitch formula $D^{av} = 4V_{tot} / S_{BET}$. In a similar manner, in microporous samples, the average micropore dimension (D^{av}_{micro}) was estimated from the $D^{av}_{micro} = 4V_{micro} / S_{micro}$ equation. Particle size distribution in water dispersion of the analyzed powders was determined using the laser light scattering (LLS) analyzer LS 13 320 Beckman Coulter Inc. The content of TiO_2 was determined with a WD-XRF ZSX Primus II Rigaku spectrometer a Rh anode as X-ray source.

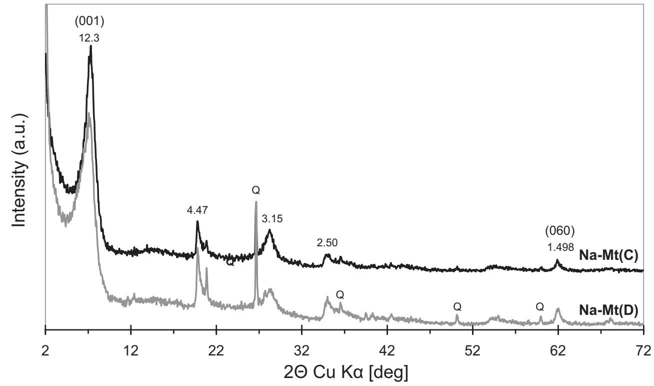

Fig. 1. Powder XRD patterns of randomly oriented Na-Mt(C) and Na-Mt(D) samples. The (001) and (060) reflections used in crystal size determination are indicated.

3. Results and discussion

3.1. Structure and texture of the starting montmorillonites

Fig. 1 shows the PXRD patterns of Na-Mt(C) and Na-Mt(D) samples prepared as randomly oriented specimens. Both the basal reflections and reflections from planes perpendicular to the *c* axis are clearly seen. The diagrams are similar and typical of a montmorillonite material containing some quartz impurities.

N_2 adsorption/desorption isotherms obtained for Na-Mt(C) and Na-Mt(D) samples are presented in Fig. 2. It is apparent that

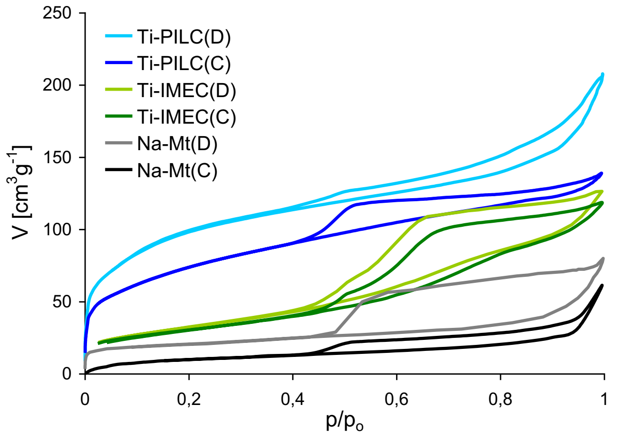

Fig. 2. N_2 adsorption/desorption isotherms of Na-Mt(C), Na-Mt(D), Ti-PILC(C), Ti-PILC(D), Ti-IMEC(C) and Ti-IMEC(D) samples.