Research paper

Structural and energetical characterization of exfoliated kaolinite surfaces

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ABSTRACT

Understanding the surface and structural properties of kaolinite/halloysite nanostructures is of utmost importance from the points of view of nanohybrid preparation. The formation of nano-sized particles depends on the quality and quantity of bonding sites as well as on the required degree of dispersity. The basic goal of this work is the study of the effect of the morphology (as secondary structure) on the surface properties as well as the demonstration of the applicability of inverse gas chromatography (IGC) to characterize exfoliated surfaces. The surface properties of nanostructures made of kaolinites of varying structural order were investigated with N_2 adsorption and inverse gas chromatography (IGC). The spectral changes of the OH groups sensitive to the changes in the outer chemical environment were followed by FTIR spectroscopy. The nanostructures made of a highly ordered kaolinite (HI = 1.4) were investigated as a function of the way of energy-input, as well. Exfoliation resulted in a mixture of nanoparticles with pseudo-hexagonal and tubular morphology. The pseudo-hexagonal morphology favored the formation of pores with cylindrical symmetry. Structural order can primarily influence the pore size distribution, the dispersion component of surface energy and the acidity parameter. The deformation band of the inner OH groups can be considered as an indicator of the changes in the secondary structure. The relative band intensity of the inner OH groups increased with the increase of the structural order.

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1. Introduction

The industrial utilization of kaolinite is closely related to its reactivity and surface properties. The physical and chemical nature of the active clay surface strongly depends on the parameters of surface modification by several methods including mechanochemical activation, cascade intercalation, thermal treatment or combination thereof. (Frost et al., 2003; Gardolinski and Lagaly, 2005a, 2005b; Horváth et al., 2005).

The mechanochemical activation as a surface modification tool of kaolinite has been studied for a considerable length of time (Dragsdorf et al., 1951; Gregg et al., 1954a, 1954b; Holt et al., 1964; Juhász and Opoczky, 1990; Laws and Page, 1946; Takahashi, 1959). The mechanochemical activation changes significantly the morphology (specific surface area, pore volume) (Juhász and Opoczky, 1990), the thermal behavior (dehydroxylation temperature) (Horváth et al., 2003), and the molecular structure of the surface (active sites of the tetrahedral and octahedral sheets) (Horváth et al., 2005) of the clay. The surface

can be modified by one- or multi-step intercalation, grafting and exfoliation processes, as well. However, intercalation processes not only modify the kaolinite surface through complexation via hydrogen bonding, but also result in a nanostructured mineral (Ledoux and White, 1966; Wada, 1961).

The characterization of clay mineral surfaces is generally made by N_2 adsorption, often complemented with Scanning Electron Microscopic/ Transmission Electron Microscopic (SEM/TEM) studies. Specific surface area and pore size distribution (BET/BJH method) measurements can be used to follow the surface changes caused by grinding, intercalation or thermal deintercalation (Aylmore et al., 1970; Brunauer et al., 1938; Yukselen-Aksoy and Kaya, 2010). Identification of acid–base properties can be made by surface titration with test materials like CO_2, CO and NH_3. Adsorption of CO_2 and CO can represent the population of basic sites, while that of NH_3 is characteristic of the acidic sites. The type and strength of adsorption of different reagents can be followed in vacuum as a function of the temperature under in situ conditions with Fourier-Transform Infrared (FTIR) spectroscopy with a heatable reflection adapter (Eischens and Pliskin, 1958; Knötzinger and Ratnasamy, 1978; Lercher et al., 1996; Little, 1966; Morterra et al., 1992; Morterra and Magnacca, 1996). The donor-acceptor properties of the inner/ outer surfaces of thermally deintercalated organoclay complexes can

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also be studied by thermogravimetry combined with mass spectroscopy (TG-MS), if during deintercalation decomposition products of acidic/basic character (e.g. CO, CO_2, NH_3) are formed (Vágvölgyi et al., 2008).

In addition to the SEM/TEM technique, the atomic force microscopy (AFM) method is also suitable for the atomic-scale topographic characterization of nano-clay composites and their thin layers (Aparicio et al., 2009; Gupta et al., 2010; Sayed Hassan et al., 2006; Szabó et al., 2003;). The determination of the zeta-potential can also be useful for surface characterization, on condition that a layer charge exists or ions are adsorbed to the (nano)particles (Yi et al., 2016).

One of the most informative surface analytical methods is the inverse gas–solid chromatography (IGC), which is a good source of physicochemical data and has been widely used to study surface energies (Mohammadi-Jam and Waters, 2014; Voelkel et al., 2009; Voelkel et al., 2014) and other surface characteristics (Kunaver et al., 2005) of adsorbents and catalysts. The enthalpy and entropy of adsorption, specific surface area, the dispersive and specific components of the surface energy, solubility parameters, surface heterogeneity, energy profile and distribution, glass transition temperature can be calculated using the IGC technique. Therefore IGC is the mostly applied method for determination of surface properties of various solid materials such as polymers (Santos and Guthrie, 2005), cellulose (Jacob and Berg, 1994), wood (Kamdem et al., 1993; Liu and Rials, 1998), cotton fiber (Benczédi and Cantergiani, 2002), carbon fibers (Lavielle and Schultz, 1991) and carbon nanotubes (Menzel et al., 2009). Futhermore, the usefulness of IGC for investigating the surface energies of various natural and modified mineral solids have been demonstrated by several authors: cationic (montmorillonite) and anionic (hydrotalcite) clays (Bandosz et al., 1993), various zeolites (Díaz et al., 2004), molecular sieves (Bilgiç and Tümsek, 2007), untreated and chemically treated kaolinites (Kubilay et al., 2006), attapulgite clay after acid and thermal treatments (Boudriche et al., 2011, 2012), montmorillonite/polypyrrole nanocomposites after organic modification (Mravčáková et al., 2006), intercalated organo-bentonite (Bilgiç et al., 2014), sodium montmorillonite and six organophilic montmorillonites coated with different surfactants (Kádár et al., 2006), sepiolite (Aşkın and Topaloğlu Yazıcı, 2005), intercalated montmorillonites (Picard et al., 2007), bentonites (Cordeiro et al., 2010), thermally and chemically treated natural smectite clays (Tamayo et al., 2012).

The surface studies of nanostructures with varying morphology require the joint use of several methods to increase the scope of properties to be determined and to validate the results obtained by the different methods.

The main goal of the present study is the investigation of the applicability of IGC for analysis of kaolinite nanostructures of varying surface morphology. An attempt is made to find correlations among the results of N_2 adsorption and FT-IR spectroscopic studies, the amount of surface energy and the parameters of acid–base properties, as well.

2. Experimental methods

2.1. Sample preparation and reagents

Starting from kaolinites of varying structural order (with Hinckley-indices of 0.3, 0.8 and 1.4) pseudo-hexagonal and tubular type nanostructures were prepared with a 3-step intercalation process. The chemical compositions of the raw kaolins used are given in Table 1, while the steps of the intercalation process are summarized in Table 2, according to Makó et al. (2014) and Zsirka et al. (2015).

The raw kaolins used for precursor preparation were ground in an agate mortar and passed through a 125 μm sieve. For the synthesis of the intercalation complexes the following analytical grade reagents were used: potassium-acetate (KAc, Reanal), ethylene glycol (EG, Sigma-Aldrich, anhydrous 99.8%), hexylamine (HA, Sigma-Aldrich), toluene (T, Reanal), 1-propanol (IPA, Fluka) and acetone (Ac, Reanal).

Table 1
The chemical composition of the kaolins used.

Location	Surmin, Poland	Zettlitz, Czech	Szegilong, Hungary
Hinckley index (HI)	1.4	0.8	0.3
Chemical composition (% w/w)			
SiO_2:	52.10	46.23	46.73
Al_2O_3:	34.10	36.74	33.94
Fe_2O_3:	0.60	0.88	3.21
K_2O:	0.60	0.66	0.22
Na_2O:	0.10	–	0.1
MgO:	0.10	0.28	0.15
CaO:	0.10	0.80	0.55
TiO_2:	0.60	0.05	0.06
Kaolinite/**h**alloysite content	82	91	46 **k**/49 **h**
Quartz	12	2	3
Other minerals	5	7	2
Loss on ignition	11.8	13.36	14.12

2.2. Structure elucidation methods used

X-ray powder diffraction (XRD) analyses were carried out by means of a Philips PW 3710 type instrument (CuKα radiation, λ = 1,54,056, 50 kV, 40 mA). XRD pattern was measured from random powder samples in the 4° to 40° 2θ range with 0.02° 2θ step size and 1 s time per step to follow the efficiency of the synthesis steps. The diffractometer was equipped with 1° divergence, two Soller, 0.2 mm receiving and 1° anti-scatter slits. After the intercalation of HA, the 1.5° to 40° 2θ range and the 1/6° divergence slit was applied.

The specific surface area and pore size distribution in the micropore (0–2 nm), mesopore (2–50 nm), and the macropore (50–300 nm) diameter ranges were determined by nitrogen adsorption/desorption isotherms measured with a Micromeritics ASAP 2000-type instrument on samples previously outgassed overnight in vacuum at 60 °C. The surface areas of the samples were determined by the BET (Brunauer–Emmett–Teller) method from the corresponding nitrogen adsorption isotherm. The meso- and macropore volume values were calculated from the nitrogen desorption isotherms using the BJH (Barret–Joyner–Halenda) theory.

Table 2
The procedure of nanostructure preparation and sample identification.

	Reagent	Reaction conditions and processes
1	KAc	Precursor
		2.1.A (P1) homogenization with KAc powder
		washing, drying at 110 °C for 12 h
		2.1.B (P2) treating with 8 M KAc solution
		washing, drying at 110 °C for 12 h
2	EG	2.2.A Exchange intercalation
		1 g precursor + 7 mL EG at 150 °C, 2 h in Ar atmosphere, separation, washing with Ac, drying at 70 °C for 12 h
		2.2.B Exchange intercalation
		Heating with microwaves (MW) at 150 °C for 30 min
3	HA	Exchange intercalation
		1 g complex 2 + 5 mL HA at 25 °C for 48 h,
		separation, washing with Ac, drying at room temperature
		for 12 h; drying at 50 °C for 2 h.
4	T	Exfoliation
		1 g complex 3 + 5 mL T at 25 °C for 2 h
		separation, washing with Ac and IPA, drying at 25 °C for 12 h

Sample identification of exfoliated samples

Sample	HI	KAc precursor	Exchange intercalation with EG
(1)	0.3	P1	heat + stirring
(2)	0.8	P1	heat + stirring
(3A)	1.4	P1	heat + stirring
(3B)	1.4	P2	heat + stirring
(3C)	1.4	P1	MW