Research paper

Photoactive hybrid material based on kaolinite intercalated with a reactive fluorescent silane

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ABSTRACT

The main strategies to modify layered silicates with dyes have been based on ion exchange reactions. In this work, the modification was performed via the chemisorption of reactive rhodamine on the surface of kaolinite (Kaol) particles. The reactive dye (RhAptes) was synthesized via the reaction of rhodamine B (RhB) with 3-aminopropyl-triethoxy silane. Efficient modification of the Kaol surface was achieved after the pre-expansion of its structure with dimethyl sulfoxide. RhAptes reacted with the hydroxyl groups of the expanded mineral. The structural characteristics and optical properties of the hybrid material (Kaol-RhAptes) were characterized by X-ray diffraction and spectroscopy in the visible region. Absorption and fluorescence spectra of Kaol-RhAptes were similar to its dye precursors, RhB and RhAptes. Time-resolved fluorescence spectra proved only minor molecular aggregation of bound rhodamine. Partial fluorescence quenching was confirmed by fluorescence quantum yield measurements. We assume that other materials based on Kaol intercalated with various photoactive molecules could be synthesized by the strategy used in this work. Modifications of kaolinite could lead to special materials and might expand their range of applications.

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1. Introduction

Hybrid materials have attracted a lot of attention as alternative substances used in modern industrial applications. One large group of hybrid materials is based on inorganic layered compounds, which play the role of solid state carriers for adsorbed or intercalated organic molecules (Innocenzi and Lebeau, 2005; Shibata et al., 2008; Demel and Lang, 2012). A lot of effort has been focused on the development of hybrid materials based on expandable layered silicates bearing a negative surface charge (Li and Li, 2003; Bujdák and Iyi, 2012). Such hybrids can be easily prepared via an ion exchange reaction using appropriate organic cations (Bergmann and O'Konski, 1963). For solid luminescent and photoactive materials, various cationic dyes have been used. There are many parameters that have to be considered when preparing luminescent hybrid materials based on smectites and cationic dyes. Molecular aggregation is often an undesired process, since it significantly affects the properties of the adsorbed dye molecules and usually reduces their photoactivity (Sasai et al., 2005; Demel

and Lang, 2012). Various strategies have been used to solve this problem: 1. The choice of appropriate dye derivatives, which are not sensitive to the loss of activity in either the adsorbed and/or aggregated state. 2. The modification of smectite (mostly by alkylammonium cations) (Sasai et al., 2004, 2005) or other alternative ways to form hybrid materials (Fujii et al., 2008, 2009). 3. Recently, reactive dyes were used to prepare hybrid materials with high photoactivity. The dye molecules were covalently bound to the edges of smectite particles (Bujdák et al., 2012). Although the fraction of the modified particle edges only represented a minority of the total surface, the prepared materials exhibited significant luminescence. The anchoring of fluorophore groups on the surface sufficiently prevented their mobility and self-aggregation, thus protecting their luminescence properties.

Kaolinites are an important clay mineral used in various industrial fields. Besides their traditional applications for the manufacture of ceramics, they are used in various industries such as additives in the paper industry, coatings and paints, the modification of rubber or other industrial polymers, carriers or additives in medical products, etc. (Annabi-Bergaya, 2008). Chemical modifications of kaolinite could lead to special or multifunctional materials and might expand their range of applications in modern industrial fields (Gardolinski and Lagaly, 2005). For example, luminescent and photosensitive additives and fillers based on kaolinite hybrid materials might be applicable in photoactive or antibacterial paints or light-sensitive paper.

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Kaolinite is a non-expandable clay mineral, and therefore the formation of its intercalation compounds requires special procedures. In contrast to easily swellable smectites, kaolinites do not readily expand under normal conditions (Breiner et al., 2006). Kaolinite layers neither carry a permanent charge nor exhibit osmotic swelling. As a result, kaolinite cannot be intercalated by organic ions promoted by an ion exchange reaction. Kaolinite consists of 1:1 layers joined together via hydrogen bonds between the surfaces of the octahedral $(AlO_2(OH)_4)$ and tetrahedral (SiO_4) sheets. The intercalation of kaolinite must overcome the energetic barrier of the hydrogen bonds. One of several ways to overcome this barrier is based on intercalation with polar organic molecules, which are able to form hydrogen bonds with the hydroxyl groups at the surface of the octahedral sheets (Sun et al., 2011). These include polar aprotic liquids or other compounds such as dimethyl sulfoxide (DMSO), dimethyl formamide, acetate ions, etc. (Kelleher et al., 2002; Tonle et al., 2007; Ding et al., 2011). Intercalation with such organic compounds can be monitored by X-ray diffraction (XRD). Pre-expansion with small organic polar molecules is often necessary before the intercalation of larger or more complex organic molecules (Tonle et al., 2007). Another strategy for the intercalation of kaolinite is based on surface grafting (Bergaya and Lagaly, 2011; He et al., 2013; Detellier and Schoonheydt, 2014). Various organic compounds were used for the grafting of kaolinite surface, such as aliphatic (Matusik and Klapyta, 2013; Matusik et al., 2013; Hou et al., 2014) and aromatic alcohols (Dedzo and Detellier, 2014; Diar-Bakerly et al., 2014), reactive silanes (Zhang et al., 2012; Tan et al., 2014; Tao et al., 2014), organic acids, their salts or derivates (Araujo et al., 2013; de Carvalho et al., 2014). Surface grafting leads to the principal and often irreversible changes of kaolinite surface properties. Kaolinite hybrids prepared via surface grafting have been often used for further modification with larger molecules, such as polymers (Tamasan et al., 2012), catalysts (de Faria et al., 2011) and bioactive substances (Caglar, 2012; Holešová et al., 2014). All types of kaolinite hybrids have potential for industrial applications.

The intercalation of fluorescent rhodamine dye into kaolinite pre-expanded with DMSO was studied in this work. The key step in the synthesis was the replacement of a fraction of the intercalated DMSO molecules with larger fluorophore molecules. In order to achieve strong bonding and a fast reaction, reactive fluorophore molecules were used. The intercalation is unfavorable from the entropy point of view. In order to achieve efficient and irreversible adsorption and intercalation, strong bonding between the adsorbent and adsorbate must be achieved, to increase the contribution of the enthalpy of the reaction. For an irreversible adsorption, chemisorption i.e. surface grafting represents an optimal method (de Faria et al., 2010; Yang et al., 2012). In our study, we chose the adsorption of a fluorescent rhodamine dye bearing reactive silane alkoxy-groups (Bujdák et al., 2012; Danko et al., 2013). The exothermic reaction of the reactive silane with the kaolinite surface led to the efficient formation of strong Si–O–Al bonds. DMSO was used to pre-expand the mineral. The release of ethanol as a side-product supported a shift in the equilibrium towards the formation of linkages between the dye moieties and kaolinite surface. This is the first report of a luminescent hybrid material of this kind. We predict that the synthetic procedure can be used for the preparation of various photoactive materials by selecting an appropriate reactive dye component.

2. Materials and methods

2.1. Materials

Kaolinite (Kaol) from Gold Field (Pugu Hills, Tanzania) was from the depository of the Department of Hydrosilicates at the Institute of Inorganic Chemistry, Slovak Academy of Sciences. The properties of this mineral were described in an earlier paper (Pentrák et al., 2009). Rhodamine B (RhB), DMSO, and 3-aminopropyltriethoxysilane (Aptes, 97%)

were obtained from Sigma Aldrich (Germany). Chloroform (p.a.) was purchased from AFT (Bratislava, Slovakia).

2.2. Synthesis of reactive dye precursor

The reactive precursor, 2-(3-(diethylamino)-6-(diethylimino)-6H-xanthen-9-yl)-N-(3-(triethoxysilyl) propyl benzamide (RhAptes), was prepared by the reaction of RhB with Aptes (see reaction scheme SD1 in the Supplementary data (SD)) according to the procedure described earlier (Nedelčev et al., 2008). Briefly, RhB solution in dried chloroform was heated to its boiling point under an argon atmosphere. Aptes with 1.2:1 molar ratio to the RhB was added to the hot solution in order to avoid the presence of free RhB dye in reaction mixture. Water formed during the condensation reaction between the reactants was slowly distilled out together with a small portion of chloroform using an azeotropic adapter. After 3 h, the chloroform was distilled from the reaction mixture. The formation of the final product was verified by Fourier transform infrared spectroscopy (FTIR). The carbonyl absorption band at 1710 cm^{-1} was shifted to 1755 cm^{-1}, which was assigned to the formation of the amide bond (SD2). The structure of the product was also confirmed by nuclear magnetic resonance (^{1}H NMR) spectra (SD1). For the modification of Kaol, fresh RhAptes was used as synthesized without further purification.

2.3. Intercalation of reactive dye precursor

Before the intercalation, Kaol was dried at 80 °C for 24 h to remove adsorbed water. Pre-expansion of the mineral was achieved in DMSO at 60 °C for 24 h. The interlayer expansion was verified by XRD. The molar ratio 2:1 of Aptes and RhAptes was prepared in dry ethanol. The mixture was added to a Kaol colloid in DMSO to obtain an organic silane/kaolinite ratio of 10^{-5} mol g^{-1}. The presence of Aptes and a low RhAptes loading prevented the formation of molecular aggregates of the fluorophore after chemisorption. A partial and reversible bleaching of the chromophore occurred (see below). The end of the reaction was identified by the separation of a pink colloidal dispersion of modified kaolinite (Kaol-RhAptes) from the colorless supernatant. A similar material with Aptes alone was also prepared for comparison (Kaol-Aptes). The amounts of the silanes were the same in both materials. The thermal stability of the prepared materials was tested using heating at 80 °C for 10 h. The heated products were reexpanded in liquid DMSO at 60 °C for 24 h. The changes were monitored using XRD.

2.4. Methods

The XRD was analyzed using a PANalytical Empyrean in a 2Θ range from 2 to 15°, using a step of 0.02° 2Θ, counting rate 2 s/step, and operating at 40 kV and 40 mA with CuK$_\alpha$ radiation. Measurements were carried out in step-scanning mode. The d_{001} values were obtained using the first rational orders corresponding to the 001 reflection. Specimens for XRD were prepared from the colloid dropped onto a glass slide. Infrared spectra were recorded in the middle region IR (MIR) (400–4000 cm^{-1}) with a FTIR Nicolet 6700 spectrometer. For each sample, 64 scans were recorded. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and the pressed KBr disk technique were used (0.4 mg of sample and 200 mg of KBr). UV–VIS absorption spectra were measured in ethanol and DMSO with a double-beam UV–Vis spectrophotometer Cary 100 (Varian Inc.). Diffuse reflectance in the visible region was used to characterize the Kaol-RhAptes powder. It was measured with a Cary 5000 spectrometer (Varian Inc.) equipped with an external diffusion accessory (DRA), using a Labsphere spectralon reflectance standard. The absorption spectrum was calculated using the Kubelka–Munk algorithm (Varian Cary WinUV software package). A blank spectrum obtained for pure Kaol powder was subtracted from that of Kaol-RhAptes. Fluorescence emission and excitation spectra were measured with a Fluorolog 3 (Horiba Jobin Yvon). The solid powder sample was