

Preparation and characterization of azobenzene-smectite photoactive mineral nanomaterials

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Smectites are 2:1 layered minerals built of one octahedral sheet located between two tetrahedral sheets. The layer charge derived from the isomorphic substitutions in the mineral structure is compensated by the interlayer cations. The capability to exchange the interlayer cations is an important property of smectites as it enables to design and produce new nanomaterials through their modification with organic compounds. Such hybrid materials are highly desirable in industry and environmental protection due to their specific properties that may be designed in nanoscale. Preparation of photoactive materials using intercalation of layered minerals, mainly synthetic micas, with azobenzene and other azo-compounds was proposed previously (Fujita et al. 2003, Ogawa et al. 2003, Heinz et al. 2008). Azobenzene molecules show a change in their shape and dimensions upon the UV irradiation, what may affect the structure of host mineral. The photoactive materials may find application in nanotechnology as molecular nanoswitches and nanosensors controlled by UV radiation (Klajn 2010). The objective of this study was to prepare azobenzene-smectite intercalation compounds. The results of structural and chemical characterization of obtained materials are crucial for further improvement of their photoresponsive properties.

The Na-montmorillonite (SWy), Ca-montmorillonite (STx), beidellite (BId) and synthetic laponite

(SynL) were used in the experiments. The modification procedure involved (1) the intercalation of smectites with hexadecyltrimethylammonium bromide (C16), and (2) insertion of azobenzene into the interlayer space. The reaction with C16, in amount equal to 1.0 CEC (cation exchange capacity) of the smectite, was performed in an aqueous suspension (20 g/L) for 2 h in 60°C. The obtained organo-smectites were prepared as thin films on the glass plates and reacted with azobenzene in a teflon vessel at ~100°C for 24 h. In such conditions the azobenzene vaporizes and penetrates the interlayer space of the organo-mineral. The azobenzene/smectite weight ratio was equal to 0.2. The chemical and structural analyses of all obtained samples were carried out using X-ray diffraction (XRD), infrared spectroscopy (FTIR), and CHN (carbon-hydrogen-nitrogen) elemental analysis.

The increased amount of nitrogen and carbon in modified samples confirmed the occurrence of intercalation process of both the ammonium salt and the azobenzene. Moreover, new bands appeared in the infrared spectra of the C16-smectites at ~2924 cm⁻¹ and ~2851 cm⁻¹ due to the C-H stretching vibrations in the C16 molecules. The spectra of azobenzene intercalation compounds showed additionally a series of bands corresponding to the vibrations characteristic for the azobenzene

molecule at $\sim 3061\text{ cm}^{-1}$, $\sim 1581\text{ cm}^{-1}$, $\sim 1455\text{ cm}^{-1}$, and $\sim 1302\text{ cm}^{-1}$. The basal spacing of tested minerals increased after the C16 intercalation, as confirmed by XRD analysis. The increase was equal to 6.1 Å, 3.3 Å, 4.1 Å and 3.5 Å for SWy, STx, BId and SynL samples, respectively. This suggests nearly horizontal arrangement of the C16 molecules and formation of a monolayer in the smectite's interlayer space. Introduction of azobenzene lead to a further increase of d_{001} . The increase was visibly different for all the samples and it was equal to 7.0 Å, 15.0 Å, 21.7 Å and 23.5 Å for SWy, STx, Bid, and SynL samples, respectively. The arrangement of organic molecules in the interlayer space is influenced by a number of factors including (1) type of the mineral, (2) layer charge and its location in the layer, and (3) the amount and arrangement of the cationic surfactant (Klapyta et al. 2001, Lagaly et al. 1976). A correlation between azobenzene location in the interlayer space and the photoresponse behaviour of tested materials will be the subject of further studies.

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