SORPTION OF WATER AND AROMATIC COMPOUNDS ON Li-, HDTMA-, TMA-MONTMORILLONITES WITH REDUCED LAYER CHARGE

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To determine the influence of the layer charge on sorption properties of Li-, HDTMA- and TMA-montmorillonites, the series with reduced-charge were prepared from Li-exchanged fine fractions of Cheto (SAz–1, USA) and Cressfield (Cress, Australia) bentonites by heating at 100 to 300°C for 24 hours. The exchangeable Li^+ cations in reduced-charge series were replaced with hexadecyltrimethylammonium (HDTMA) or tetramethylammonium (TMA) cations. The adsorptions of two non-polar aromatic compounds biphenyl and naphthalene were studied.

Heat-treatment caused migration of interlayer cations into the previously vacant octahedra and/or ditrigonal cavities of the tetrahedral sheets. The appearance of new bands near 3670 cm^{-1} and 7170 cm^{-1} in the IR spectra of heated Li-SAz–1 and Li-Cress proved the presence of Li(I) in previously vacant octahedra. The d(001) value of cca. 9.7 Å for samples heated at 300°C indicated the collapse of smectitic, i.e. swelling interlayers and the creation of pyrophyllite-like layers.

As revealed XRD patterns, the configuration of $HDTMA^+$ depended on the layer charge of smectites. For unheated HDTMA-SAz–1 and HDTMA-Cress samples the arrangement from pseudotrimolecular to bilayers transition (20.6 or 18.3 Å) was observed. Samples heated above 150°C contained monolayer configuration of $HDTMA^+$ with d-spacing cca. 13.9 Å. The configuration of TMA^+ was different as that of $HDTMA^+$. Small TMA^+ cations form "pillars" which held two adjacent layers apart in constant distance (13.9 Å). Thermogravimetric measurements showed decreasing amount of $HDTMA^+$ and TMA^+ with increasing temperature utilised for the reduced-charge samples preparation. For HDTMA-SAz–1 series the amount of organic cations decreased from 1.05 mmol/g for unheated sample to 0.29 mmol/g for sample heated at 300°C. The IR spectra of HDTMA- and TMA-montmorillonites revealed the correlation of the area of the CH_3 and CH_2 deformation bands with the amount of alkylammonium cations.

Water sorption experiments showed decreasing hydration of Li-SAz–1 and Li-Cress with the layer charge reduction. The water uptake at 100% RH dropped to 15wt% for samples heated at 300°C (Li-Cress, Li-SAz–1). The presence of alkylammonium cations in the interlayers supplied more hydrophobic character to the smectite surface and a sorption of water decreased in order Li > TMA > HDTMA saturated montmorillonites.

The ability of Li-, HDTMA- and TMA-montmorillonites to adsorb biphenyl and naphthalene was studied. The nature of the interlayer cations played an important role in the adsorptive sufficiency of the samples. Only negligible amount of biphenyl and naphthalene were adsorbed onto unheated Li- and TMA-samples. On the other hand, the sorption efficiency of unheated HDTMA-exchanged samples was high, e.g. HDTMA-SAz–1 adsorbed 43 mg/g of biphenyl from water solution in comparison to TMA-SAz–1 or Li-SAz–1 where only 5 mg/g or 6 mg/g, respectively, of biphenyl were adsorbed.

Heat treatment slightly improved the adsorption of aromatic compounds on Li-samples. On the contrary, decrease of adsorption was observed for HDTMA-SAz–1 heated at 300°C (27 mg/g) in comparison with unheated sample. Thus reduction of layer charge and decreasing amount of $HDTMA^+$ caused the lower adsorption of aromatic compounds.

With increasing amount of TMA^+ cations present in interlayers and decreasing layer charge, the sorption ability of TMA-exchanged montmorillonites markedly increased. The highest adsorption of biphenyl and naphthalene was observed for sample TMA-Cress heated at 180°C (49 mg/g).

These results showed that layer charge significantly influences the adsorption of organic compounds on montmorillonites. Considering all studied samples the most effective adsorbents for naphthalene and biphenyl were HDTMA-SAz–1, TMA-Cress heated at 180°C and TMA-Cress heated at 300°C. These samples adsorbed about 80% of organic compounds present in water solutions of biphenyl and naphthalene.