Title: X-ray photoelectron spectroscopy of chemically modified halloysite

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Background

Halloysite is a clay mineral, chemically similar to kaolin, typically formed by hydrothermal alteration of aluminosilicate minerals [1]. On the microscopic scale halloysite usually occurs as nanotubes with the length in the range of few micrometers [2]. Halloysite nanotubes have high mechanical and chemical strength, high surface area, and unique surface properties and as a result they are very good substitute for other nanotubes, such as carbon nanotubes (CNTs). In our previous works we have studied physicochemical properties of raw HS from strip mine "Dunino" (Poland) and chemically activated samples of the HM using infrared spectroscopy (FT-IR), wavelength dispersive X-ray fluorescence (WDXRF) and X-ray powder diffraction (XRPD) [3,4,5].

Methods

In this work, in order to investigate the sorption properties of the HNT (nonoclay halloysite), the HS (raw) and activated halloysite (HM) were studied with X-ray photoelectron spectroscopy (XPS) technique, which provides an information on the surface structure of the samples. The analysis was carried out at the Institute of Physics of Jan Kochanowski University (Kielce, Poland). The XPS measurements were performed with SPECS XPS system, equipped in XR 50 M x-ray source (Al/Ag anode), FOCUS 500 X-ray monochromator and PHOIBOS 100 electron analyzer equipped with 1D-DLD detector. Additionally, in order to compare the surface sensitive results obtained with XPS system with the elemental composition of the bulk, the studies using the wavelength dispersive X-ray fluorescence (WDXRF) technique were performed. The WDXRF measurements were carried out using Axios spectrometer (PANalytical) equipped with Rh anode X-ray tube with maximum power 2.4 kW.

Results

The surface sensitive results obtained with XPS method show atomic composition changes of the HM halloysite samples activated at different temperatures. At high temperatures Si/Al ratio in the halloysite significantly increase. Additionally, iron content in the bulk of raw halloysite mineral turned to be much higher than at the surface. The results are important for the studies of chemical reactions with the halloysite.

Conclusions

In this work study of the influence of the activation temperature on the structure of halloysite nanotubes were performed. The halloysite samples of the raw (HS), activated with different temperatures (HM) and commercially available halloysite nanoclay (HNT) were studied with XPS method and compared with bulk composition obtained with WDXRF method.

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