



Research paper

Effect of plasma treatment on structure and surface properties of montmorillonite



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ABSTRACT

Plasma treatment of montmorillonite has been investigated as a prerequisite for design of functional nanostructures, based on clay minerals. The effect of short-term (20 s) plasma treatment on structure and bonding of montmorillonite has been analyzed using combination of X-ray powder diffraction and infrared spectroscopy. Results showed that dehydration starts at low discharge power 10 W and at 50 W is completed. The effect of the plasma treatment was compared to the effect of the heat treatment (8 h at 450 °C). Both treatments can be considered as similar when dehydration takes place. However, the dehydroxylation does not seem to be triggered by the plasma treatment. Therefore for dehydration only, the plasma treatment can be used instead of much more energy consuming thermal treatment.

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1. Introduction

Clay minerals, especially montmorillonites (Mt) represent very convenient matrix for design of clay-polymer nanocomposites for a wide range of applications like adsorbents, catalysts, photocatalysts, drug carriers, luminophores, antibacterial nanocomposites etc. (for review see for example Nalwa, 2000; Ray and Okamoto, 2003; Bergaya et al., 2006; Liu and Zhang, 2007; Zhu and Njuguna, 2013). Structural modification of clay minerals by organic and/or inorganic species (neutral polar molecules, cations, complex cations) is based either on the intercalation, or on a surface anchoring of guest species predominantly via thermal and chemical treatment. Only a very few studies are focused on plasma modification of clay minerals (Ming and Spark, 2003; Célini et al., 2007). Ming and Spark (2003) investigated D₂O and Ar plasma modified surface of kaolinite using infrared (IR) spectroscopy. Their results confirmed the scission of Si—O bonds on the surface and subsequent deformation of siloxane basal plane and scission of Al—O bonds in gibbsite basal plane accompanied by creation of plasma-induced hydroxyl groups in the shallow and deep subsurface region of kaolinite. Célini et al. (2007) described the effect of plasma treatment of Na⁺ Mt from Wyoming and synthetic Na⁺ Laponite by cold acetylene plasma in order to change the hydrophilic surface to hydrophobic. The cold acetylene plasma treatment had following effects on clay mineral surface: grafting of CH₂ and CH₃ groups on the external surface of the clay mineral and dehydration and dehydroxylation of clay mineral structure associated with the SiO₄ alteration (scission of Si—O bonds). Dehydration and dehydroxylation observed by cold acetylene plasma

treatment in Célini et al. (2007) led us to the more detailed study focused on the plasma-induced changes of Mt structure.

The thermal treatment can be used as a pretreatment to the various chemical treatments and usually causes dehydration and dehydroxylation of the clay mineral. Dehydroxylation results in creation of active sites in the clay mineral structure, which can improve the catalytic activity (Liu et al., 2011) and in addition can serve as bonding sites for various guest species in design of various functional nanostructures. The mechanism of dehydration and dehydroxylation of Mt obtained by thermal treatment has been studied in details using X-ray diffraction, IR spectroscopy, thermogravimetry, etc. (Horváth and Gálíková, 1979; Guggenheim et al., 1987; Guggenheim, 1990; Emmerich et al., 1999; Wolters and Emmerich, 2007; Che et al., 2011; Holtzer et al., 2011; Derkowski et al., 2012; Muñoz-Santiburcio et al., 2012). Smectites and other dioctahedral 2:1 clay minerals lose water in three temperature ranges during heating: 1) First stage – dehydration at temperatures <220 °C involves the loss of water from the interlayer of expandable space. 2) In the second stage OH groups bound to the surface are released between 220 and 350 °C and 3) dehydroxylation occurs between 350 and 1000 °C (Emmerich et al., 1999). While dehydration results in a decrease of basal spacing, dehydroxylation leads to the breaking of Si—O bonds and subsequent deformation of tetrahedral sheet. Drits et al. (1995) showed that the dehydroxylation behavior of 2:1 clay minerals is influenced by the distribution of the metal ions and vacancies in the octahedral sheet. *cis*-Vacant clay minerals dehydroxylate at about 650–700 °C and *trans*-vacant varieties dehydroxylate at about 500–550 °C. Drits et al. (1995) also described a movement of Al³⁺ from *trans* positions into vacant *cis* positions.

Structural changes induced by plasma treatment have not been studied in detail. The aim of this work is to investigate the effect of

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plasma treatment on Mt structure as the necessary prerequisite for the design of clay based functional nanostructures prepared in plasma reactor.

2. Materials and methods

Natural Na⁺ Mt (supplier Alfa Aesar declares the powder was sieved through 200 μm mesh) with the basal spacing $d = 12.35 \text{ \AA}$ and crystallochemical formula: $\text{Na}_{0.25} \text{K}_{0.07} \text{Ca}_{0.10} (\text{Si}_{4.0}) (\text{Al}_{1.45} \text{Fe}^{3+}_{0.21} \text{Mg}_{0.24} \text{Ti}_{0.01}) \text{O}_{10} (\text{OH})_2$ has been used for the present experiments. The basal spacing was measured by X-ray diffraction (XRD) and the formula was determined using X-ray fluorescence. The Mt powder was plasma treated in fluidized bed reactor (Fig. 1). The reactor is made of glass tube 80 cm long and 2 cm in diameter. The working gas (Ar) flowed to the reactor in its bottom part and the powder was fluidized. Two outer ring electrodes, attached to the lower part of the reactor 1 cm apart from each other, were used to ignite RF plasma discharge. The electrodes were attached through the matching network to RF generator Dressler Cesar 133. Argon flow rate 150 sccm (standard cubic centimeters per minute) was used and the pressure was 560 Pa. Various discharge powers were used, namely 10 W, 20 W, 50 W, 100 W and 150 W. All samples have been exposed to plasma treatment for 20 s. Heating control experiment was also performed to compare the effect of thermal treatment with the plasma treatment. The Mt powder was placed to a furnace and the temperature was kept at 450 °C for 8 h.

Structure and bonding of plasma treated Mt powder has been analyzed using IR spectroscopy and XRD. FTIR study was carried out using Nicolet 6700 having mid-IR DTGS detector. FTIR spectra were recorded in the range 700–4000 cm^{-1} at a resolution of 4 cm^{-1} with ATR technique. The spectrum of each sample was recorded by accumulating 64 scans, at room temperature in air. Baseline correction was performed by using the Omnic software. XRD analysis has been carried out using Philips X-pert powder diffractometer in Bragg-Brentano arrangement with radiation $\text{CuK}\alpha$. X-ray photoelectron spectra (XPS) were recorded using hemispherical analyzer Phoibos 100 (from Specs) operated in FAT mode. The spectral line $\text{AlK}\alpha$ with energy 1486.6 eV was used and the spectra were referenced to the aliphatic carbon bonds at 285 eV. High resolution spectra for pass energy 10 eV were used for the quantification and software CasaXPS was used for the calculations (including RSF factors). The cation exchange capacity (CEC) was measured using

Cd(II) ions, $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ solution respectively. The CEC procedure is described in detail e.g. in Weiss et al., 1998.

3. Results and discussion

In X-ray diffraction patterns (Fig. 2) for plasma treated and pristine Mt powder, the shift of basal reflection (001) towards the higher angles indicates the gradual decrease of basal spacing due to the plasma treatment. The positions of hk-bands remained unaffected by plasma treatment. Reflection profiles show significant shift of the reflection maxima to lower basal spacing and profile broadening indicating a disorder in interlayer structure especially for low discharge power 10 and 20 W (see Table 1). The basal spacing is even smaller in case of the heat treatment and the FWHM is also lowest in this case. This is discussed later.

Basal spacing has changed significantly by exposure of Mt to plasma treatment (Table 1, Fig. 2), however the discharge power itself has less striking effect. The discharge power results in stronger decrease of the basal spacing in the range 10–50 W, slight decline above 50 W and almost constant basal spacing (within the limits of experimental error) for the range 100–150 W. The profiles were also characterized by the full width at half of the maximum (FWHM), the FWHM values decreased from $\text{FWHM} = 1.5^\circ$ at 10 W to $\text{FWHM} = 1.1^\circ$ at 150 W.

X-ray diffraction profiles in the Fig. 2 exhibit large broadening for samples exposed to low discharge power 10 and 20 W. This is due to the massive dehydration, when water molecules moves out of the interlayer space causing disorder in the interlayer structure and composition resulting in the inhomogeneity of basal spacing. This process of dehydration is completed at about 50 W, when water is out of the interlayer space, which becomes more homogeneous. This is reflected in the sharpening of the X-ray diffraction profiles for discharge power higher than 50 W.

Heating of the Mt powder at 450 °C for 8 h led to decrease of the basal spacing to 9.65 Å, which is value even lower than basal spacing obtained for the highest discharge power. This indicates that there still could be some water in the powder that was not removed by the plasma treatment. For this heating temperature also dehydroxylation was reported, which could result in lowering the basal spacing too.

3.1. Stability of the plasma treatment

As the Mt is sensitive to water content, the changes of the effect caused by the plasma has to be checked. This was done for 150 W

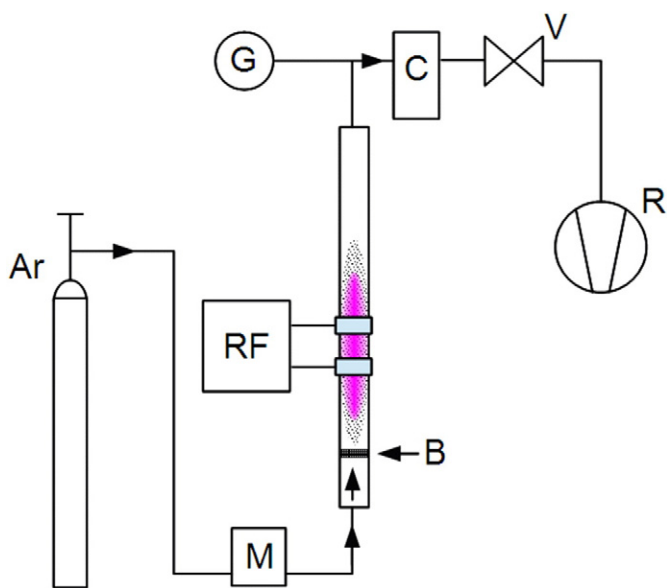


Fig. 1. Schematic drawing of the FBR. Ar – argon bottle, M – mass flow controller, B – porous membrane, RF – generator with matching unit and electrodes, G – pressure gauge, C – cyclone, V – valve, R – rotary vane pump.

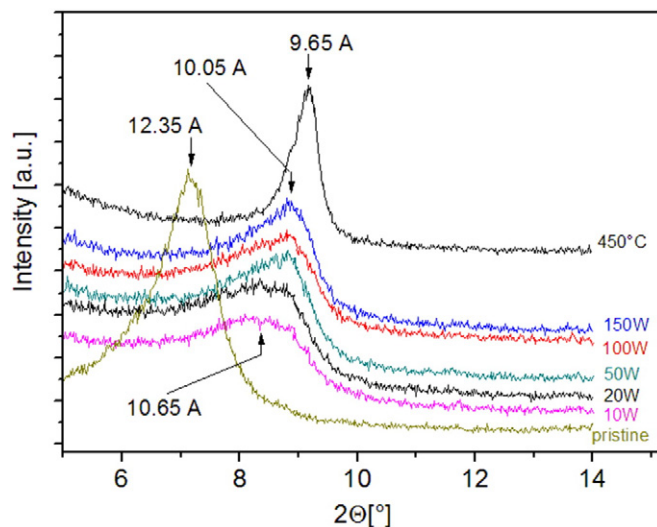


Fig. 2. X-ray profiles of basal reflection 001, from bottom: for pristine Mt and for discharge powers (from bottom to top) from 10 W to 150 W. The top spectrum is for sample heated to 450 °C.

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