Vibrational spectroscopy of acid treated vermiculites

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ABSTRACT

The natural vermiculites from different localities (Bulgaria, Brazil, and South Africa) after acid treatment were used for this study. Differently acidified vermiculite samples were prepared from the natural vermiculite sample using different concentrations of hydrochloric acid (0.5 M and 1 M) and different reaction time (2 h and 4 h) at 80 °C. Natural vermiculites and acid treated vermiculites were analyzed by elemental analysis, X-ray diffraction (XRD) analysis and studied using Fourier transform infrared (FTIR) spectroscopy and dispersive Raman spectroscopy. According to the XRD analysis vermiculites are interstratified structures created in the different two-one-zero sheet hydrated phases. Ratio of intensities of spectrally deconvoluted bands at 1075 cm^{-1} and 1000 cm^{-1} (stretching vibration of Si—O bonds of vermiculites and stretching vibration of Si—O bonds of amorphous silica, respectively) was used to determine the content of amorphous silica in acid treated vermiculite samples. Study of the infrared and Raman spectra of the acidified vermiculites enable a comparison of these two spectroscopic data that have not yet been performed.

1. Introduction

Vermiculites are secondary 2:1 clay minerals (phyllosilicates) formed primarily by alteration of mica and less commonly by alteration of amphibole, chlorite, olivine, pyroxene or other clay minerals. The 2:1 layer is composed of one octahedral sheet between two tetrahedral sheets. The positive charge deficiency is compensated by the hydrated exchangeable cations Mg^{2+}, Ca^{2+}, Na^{2+} and K^+ located in the interlayer space between the parallel 2:1 layers. Macroscopic vermiculite occurs in four types of host rocks: (1) ultramafic and mafic; (2) gneiss and schist; (3) carbonate rocks; and (4) granitic rocks, and each of these has characteristic features. The major commercial deposits belong to the first category. Structural analysis revealed predominantly mixed-layer vermiculite-biotite or vermiculite-phlogopite composition [1].

Vermiculites show the diversity of properties related to the structural characteristics, such as layer charge associated with the numerous isomorphic substitutions, mixed layered structure and to dehydration-rehydration ability. The existence of a number of definite states of hydration and the regular interstratification of layers with a basal spacing of 2.060 nm were determined as consistence of approximately regular alternations of 1.150 nm and 0.902 nm layered domains [2]. The variation of basal reflections corresponding

to the interstratified one-zero sheet hydrate (d-values of 1.04 nm) with probably a random interstratified phase of two- and one-sheet hydrates (d-values of 1.28 nm) in vermiculite from Llano (Texas, USA) were studied using powder neutron diffraction [3]. Reflection with d-value 1.002 nm was detected in a phlogopitic vermiculite from Madagascar [4]. Those authors highlighted the existence of two superstructures formed by a regular 1:1 interstratification with $d(0\,0\,1) = 2.541$ nm (the result of alternation of layers with basal spacings of 1.376 nm and 1.165 nm) and with $d(0\,0\,1) = 2.153$ nm (the result of alternation of layers with basal spacings of 1.151 nm and 1.002 nm).

Acid activated clay minerals find wide industrial applications as catalysts or catalyst supports [5–7]. Several workers studied structure of smectites after treatment with the hydrochloric acid [7–11] and sulphuric acid [6,12,13]. A comparable study of the swellable clay minerals was conducted after leaching by H_2SO_4 and HCl of different concentrations [14]. Authors have found that acidified smectites had higher specific surface area than the original materials and displayed still the ability to exchange cations.

Selective acid leaching is an important method for preparing porous materials. The leached vermiculite shows a microporous structure with good thermal and hydrothermal stability and acidic properties. The residual porous silica has a higher specific surface area in comparison with original vermiculite. The effect of grinding was studied on the formation of porous materials by acid-leached vermiculite [15]. Authors observed the most significant difference in the values of specific surface area between ungrounded

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$(504\,m^2\,g^{-1})$ and grounded $(720\,m^2\,g^{-1})$ vermiculite leached with 1 M HCl. The catalytic properties of leached vermiculite were characterized as pre-cracking matrices of heavy oil fractions [16]. Many authors have primary used FTIR spectroscopy to follow the changes of the acid treated smectites and vermiculites. In comparison with IR spectroscopy, one of the advantages of Raman spectroscopy lies in the fact that Raman spectra do not contain overtone and combination band [17]. Additionally, Raman spectroscopy allows simple arrangement of solids samples without the preparation of pellet. The most handicap of Raman spectroscopy is occurrence of fluorescence. Since the Raman effect is very weak even relatively small fluorescence can overlap Raman bands. The probability of exciting fluorescence falls off substantially at long wavelength of laser [18].

So far, in the literature there are not many studies on the IR and Raman spectroscopy of the vermiculites and acidified vermiculites and their comparison are lacking. The aim of this study was to assess changes in the IR and Raman spectra of three natural vermiculites from different localities after their treatment with the 0.5 M and 1 M hydrochloric acid for 2 h and 4 h.

2. Samples and methods

2.1. Samples

Three natural vermiculites of different mineralogical origin, supplied by Grena, Co., Czech Republic, were chosen as the natural material for the present study. Vermiculite from northwestern region of Bulgaria (designated as V1) is found in calc-alkaline rocks, biotite-hornblende granodiorites and tonalities [19] that apparently resulted from the action of rain water on the biotite (phlogopite). Vermiculite from the Santa Luzia mine in the Paraiba region of Brazil (designated as V2) resulted from the change of phlogopite and biotite and occurs mainly within zones of complex mafic, ultramafic and carbonatite. Vermiculite from Palabora mine in the Limpopo province of South Africa (designated as V3) is product of hydration of phlogopite/biotite occurring in the phlogopite and apatite rich pyroxenites. The vermiculite from Palabora was described as mixed-layer vermiculite-phlogopite with the content less than 50% vermiculite [20].

2.2. Acid treatment

All samples were milled in a vibratory mill for 3 min. The particle size fractions less than 0.004 mm were obtained by sieving and then were used for acid treatments. An amount of 5 g of powdered native vermiculite samples were placed in the reagent flasks and treated with 200 ml of acid solutions. Two different concentrations of $0.5\,mol/dm^{-3}$ (0.5 M) and $1\,mol/dm^{-3}$ (1 M) aqueous solution of hydrochloric acid were used. Designation of acid treated samples is in the Table 1.

The acid leaching was performed in glass vessel at temperature 80 °C for 2 and/or 4 h. The obtained suspensions were washed several times with demineralized water to remove chlorides (it was checked by silver nitrate test). Then samples were centrifuged (frequency of rotation was 4000 rpm; centrifugation time was 7 min) and dried at 80 °C overnight.

2.3. Infrared spectroscopy

IR spectra of vermiculite samples were measured by potassium bromide pellets technique. Exactly 2.0 mg of sample was ground with 200 mg dried potassium bromide. This mixture was used to prepare the potassium bromide pellets. The pellets were pressed by 8 tons for 30 s under vacuum. The IR spectra were collected

Table 1
List of analyzed vermiculite samples.

Sample	Description of samples
V1	Raw vermiculite from Bulgaria
V1A	Sample V1 treated with 0.5 M HCl for 4 h
V1B	Sample V1 treated with 1 M HCl for 2 h
V1C	Sample V1 treated with 1 M HCl for 4 h
V2	Raw vermiculite from Brazil
V2A	Sample V2 treated with 0.5 M HCl for 4 h
V2B	Sample V2 treated with 1 M HCl for 2 h
V2C	Sample V2 treated with 1 M HCl for 4 h
V3	Raw vermiculite from South Africa
V3A	Sample V3 treated with 0.5 M HCl for 4 h
V3B	Sample V3 treated with 1 M HCl for 2 h
V3C	sample V3 treated with 1 M HCl for 4 h

using FT-IR spectrometer Nexus 470 (ThermoScientific, USA) with DTGS detector. The measurement parameters were the following: spectral region 4000–400 cm^{-1}, spectral resolution 4 cm^{-1}; 64 scans; Happ-Genzel apodization. Treatment of spectra: polynomial (second order) baseline, subtraction spectrum of pure potassium bromide. IR spectra of all samples of vermiculite (natural and after exposure to acid) were measured under above mentioned conditions.

2.4. Raman spectroscopy

A 180 degree sampling was used as measurement technique. Only vermiculite samples (without additional substances) were used for measurement of Raman spectra at dispersive Raman spectrometer DXR SmartRaman (ThermoScientific, USA) with CCD detector. The measurement parameters were as follows: excitation laser 780 nm, grating 400 lines/mm, aperture 50 μm, exposure time 1 s, number of exposures 500, spectral region 2500–50 cm^{-1}. An empty sample compartment was used for background measurement. Treatment of spectra: fluorescence correction (6th order).

2.5. Elemental analysis

The elemental analysis of Si, Al, Ca and Ti was performed using the energy dispersive X-ray fluorescence spectrometer Spectro Xepos (Spectro Analytical Instruments, Germany). Sample were mixed with the wax and pressed into the pellets.

The elemental analysis of Na, K, Mg, and Fe was determined also using an atomic emission spectrometer with inductively coupled plasma Spectro Vision (Spectro Analytical Instruments, Germany) after total sample decomposition in hydrochloric and hydrofluoric acids and acid mixture $(H_3PO_4 + H_2SO_4 + H_3BO_3)$ [21]. The content of Fe^{2+} was determined using titration with 0.1 M solution of $K_2Cr_2O_7$ after the previous decomposition of each sample in hydrochloric and hydrofluoric acids in a carbon dioxide atmosphere, according to Czech norm CSN 722041 Part 11.

2.6. X-ray powder diffraction analysis

The X-ray powder diffraction (XRD) patterns were measured on the X-ray diffractometer Ultima IV RIGAKU (reflection mode, Brag-Brentano arrangement, CuKα$_1$ radiation) in ambient atmosphere under constant conditions (40 kV, 40 mA). The CuKα$_2$ was removed by the Rachinger method which is based on separation of overlapping α1 and α2 components in PDXL: Integrated X-ray powder diffraction software.