



Infrared and Raman spectroscopy of three commercial vermiculites doped with cerium dioxide nanoparticles

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ARTICLE INFO

Article history:

Received 2 March 2018

Received in revised form 10 April 2018

Accepted 26 April 2018

Available online 28 April 2018

Keywords:

Vermiculite mixed layer structure

Vermiculite/CeO₂ nanoparticles

IR spectroscopy

Raman spectroscopy

X-ray diffraction

ABSTRACT

Three commercial vermiculites and these vermiculites doped with cerium dioxide nanoparticles were investigated by infrared and Raman spectroscopy. Infrared spectroscopy in middle infrared region (4000–400 cm^{−1}) was supplemented by separation of overlapped spectral bands in the region of stretching vibration of hydroxyl groups. Detailed structural properties of vermiculites were completed based on the Raman spectroscopy in the spectral region between 800 and 100 cm^{−1} and X-ray diffraction analysis. Raman spectroscopy provided evidence of trioctahedral-dioctahedral vermiculite-mica in original vermiculite and trioctahedral phyllosilicate structures in vermiculites after precipitation procedure of cerium dioxide nanoparticles. The wavenumber shifts of the Raman bands at about 670 cm^{−1} and 190 cm^{−1} in spectra of vermiculites showed strong trend with increasing Fe³⁺ and Al substitution in tetrahedra and octahedra, respectively.

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1. Introduction

Vermiculites are phyllosilicates occurring at all the major commercial deposits as the secondary macroscopic mixed-layer vermiculite-biotites or vermiculite-phlogopites. Most macroscopic vermiculites have been formed by the degradation of pre-existing layer silicates (biotite and phlogopite) and much of their properties are determined by that of original mineral. Vermiculite unit layer is a 2:1 layer with variable total amount of layer charge arising from octahedral and tetrahedral charges. The transformation in the series of phlogopite-vermiculite-montmorillonite can be assumed according to a variation in a negative layer charge within the individual layers [1]. The structural formulas calculated for macroscopic vermiculites brought evidence that these vermiculites have octahedral composition similar to phlogopites, Mg-biotite, Mg-chlorite, but due to the oxidation of much of the iron, tend to have a higher proportion of trivalent octahedral cations [2,3].

Vermiculites selected from commercial mined deposits were studied as layered silicate matrix for precipitation and anchoring of cerium dioxide (CeO₂) nanoparticles [3]. Cerium dioxide nanoparticles on the matrix of vermiculite named Ver-S from the Paraíba region (Brazil) were evaluated as catalyst for photocatalytic decomposition of N₂O [4]. Similarly, Ver-S/CeO₂ nanoparticles in ceramic mixtures were used

as precursor of photocatalytic active CeO₂ nanoparticles in cordierite/CeO₂ nanoparticles ceramics [5].

Infrared (IR) and Raman spectroscopy is a successful spectral method for study of clay minerals and composites prepared from them. In the last three decades, the Raman spectroscopic studies (e.g. [6–10]) as well as IR spectroscopy studies (e.g. [11–15]) have been performed especially on smectites and minerals of kaolin-serpentine group and not so often on vermiculites [16]. Although IR spectral bands of vermiculites are relatively detailed assigned (e.g. [17–19]), Raman spectral bands are often presented without more detailed descriptions (e.g. [20–23]) and moreover, the two articles focusing on the detailed study of vermiculites using Raman spectroscopy provide a different assignment of Raman bands [24,25].

Since all the previous works [3–5,26] deal with the structural and photocatalytic properties of vermiculite/CeO₂ nanoparticles, characterization of vermiculites in comparison with vermiculites carrying anchored ceria nanoparticles using vibrational spectroscopy have not yet been performed. This work presents assignment of bands in IR and Raman spectra of vermiculites with regard to their structural and chemical properties.

2. Experimental

2.1. Samples

The study using vibrational spectroscopy is performed on the following samples of vermiculites and vermiculites/CeO₂ nanoparticles

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prepared and characterized in the previous work [3]: sample **Ver-B** from the Village Belitsa, northwestern region of Bulgaria, sample **Ver-S** from the Paraíba region of Brazil and sample **Ver-C** from the Qieganbulak apatite-vermiculite deposit in Xinjiang, China and their derived samples **Ver-B/CeO₂**, **Ver-S/CeO₂**, and **Ver-C/CeO₂**. The cerium precursor was a solution of 80 mL aqueous cerium nitrate Ce(NO₃)₃·6H₂O (0.4 mol·L⁻¹) and 13 mL of ammonia hydrate NH₄OH (1.4 mol·L⁻¹) (pH = 11). The precipitation of cerium dioxide nanoparticles on the negative vermiculite layers has occurred in alkali pH 10.4 ± 0.2 at water dispersion. The authors observed that NH₄⁺ ions partly replaced the cations present in the interlayer space of vermiculite and firmly anchored CeO₂ nanoparticles, their amount of about 30 mass %, contained agglomerates of CeO₂ nanocrystals with the sizes between 5 and 10 nm.

The purity of vermiculites was checked by X-ray diffraction analysis. The trace amounts of accompanying minerals tremolite and rutile in vermiculite samples Ver-B and Ver-S and calcite in Ver-C were identified on their X-ray diffraction patterns [26].

2.2. X-ray Fluorescence Analysis

The elemental composition was performed using the elemental analyzer the SPECTRO XEPOS energy dispersive X-ray fluorescence (ED-XRF) spectrometer (Spectro Analytical Instruments, Germany). Each sample (4 g) in duplicate was mixed with the wax (0.9 g) and prepared in pellets using manual hydraulic pressing at 10 tons. The results from the XRF analysis were calculated to the stoichiometric metal oxides concentrations. The total concentration of Fe was related to Fe₂O₃. The content of Fe²⁺ was subtracted from the total Fe, when it was determined using titration with 0.1 M solution of K₂Cr₂O₇ in sample decomposed in HCl and HF in a CO₂ atmosphere [3].

2.3. X-ray Diffraction Analysis

The X-ray powder diffraction (XRD) analyses of the vermiculites and the Ver/CeO₂ nanoparticles were performed with CuKα radiation (λ = 0.15418 nm) on the X-ray diffractometer Ultima IV (Rigaku, Japan). The XRD patterns of the samples pressed on the glass sample holder were recorded in the symmetrical Bragg-Brentano diffraction geometry in the 2θ range between 2° and 60° with a scanning rate of 2°/min at 40 kV and 40 mA using a scintillation counter as detector. The divergence of the primary X-ray beam was limited by a 2/3° × 10 mm slit. In the diffracted beam, a 2/3° scattering slit and a 0.45 mm receiving slit were inserted.

2.4. Vibrational Spectroscopy

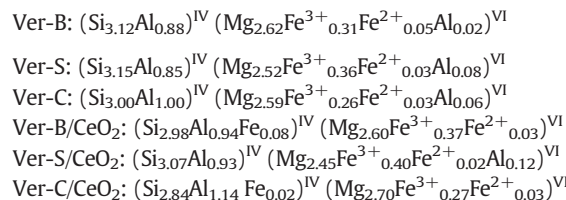
The infrared spectra of all samples were measured by potassium bromide pellets technique. Exactly 1.0 mg of sample was ground with 200 mg dried potassium bromide. This mixture was used to prepare the potassium bromide pellets. The pellets were pressed by 8 tons for 30 s under vacuum. The infrared spectra were collected using FT-IR spectrometer Nexus 470 (ThermoScientific, USA) with DTGS detector. Following parameters were used for measurement: 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.

Raman spectra of all samples were measured using a 180° degree measurement technique without any sample preparation. Raman spectra were measured 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 3000, and the spectral region 1800–50 cm⁻¹. An empty sample compartment was used for background measurement. Treatment of spectra: fluorescence correction (6th order).

3. Results and Discussion

3.1. Chemistry and Structure of Vermiculites

The elemental composition of the vermiculite samples Ver-B, Ver-S, and Ver-C prepared in the particle size fraction < 0.04 mm was used to calculate the mean cation occupations in the tetrahedral (IV) and octahedral (VI) positions by assuming that the trioctahedral structure of the vermiculites is based on 22 negative charges resulting from O₁₀(OH)₂, on cations per formula units (p. f. u.), as follows [3]:



The XRD patterns of vermiculite samples Ver-B and Ver-S show an intensive basal 002 reflection at the interlayer space *d*-value of 1.43 nm and a less intensive reflection at 1.24 nm (Fig. 1a). The value of 1.43 nm is consistent with a vermiculite layer domain with two slightly incomplete water bilayers around interlayer cations and the

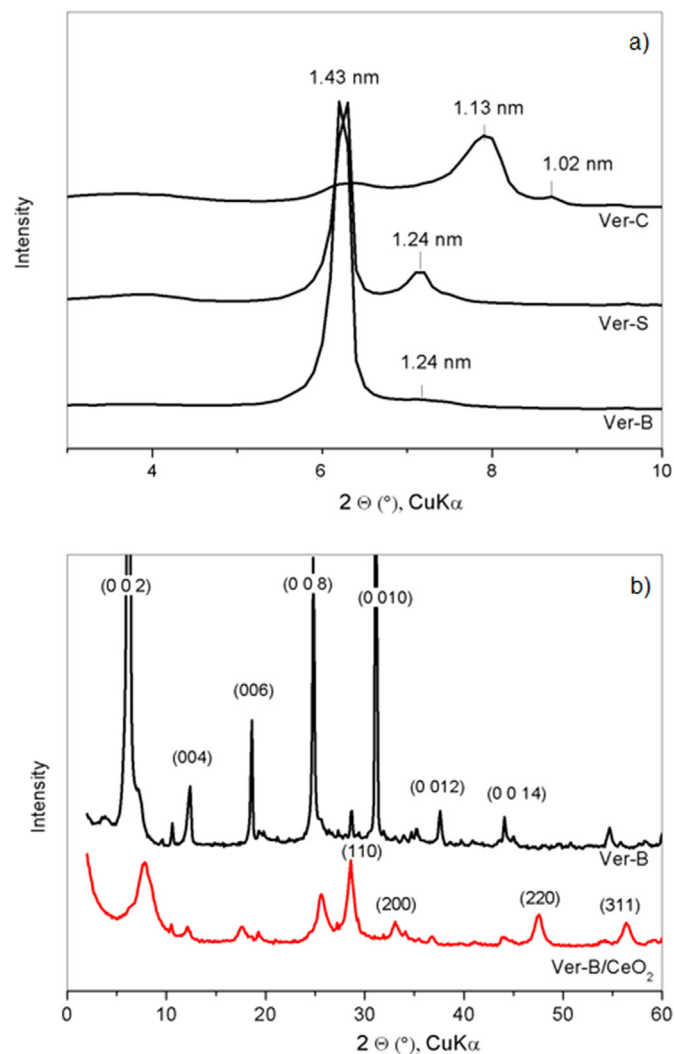


Fig. 1. X-ray diffraction patterns of: a) the 2θ section with the basal reflection 002 of vermiculite samples and b) vermiculite Ver-B and Ver-B/CeO₂. The indices (hkl) are given for basal reflections of Ver-B and for CeO₂ at Ver-B/CeO₂.

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