



Contents lists available at ScienceDirect

Applied Clay Science

journal homepage: www.elsevier.com/locate/clay

Research paper

Comparable study of vermiculites from four commercial deposits prepared with fixed ceria nanoparticles

Marta Valášková^{a,*}, Jana Kupková^a, Gražyna Simha Martynková^a, Jana Seidlerová^a, Vladimír Tomášek^a, Michal Ritz^b, Kamila Kočí^c, Volker Klemm^d, David Rafaja^d

^a Nanotechnology Centre, VŠB-Technical University of Ostrava, 17. listopadu 15/2172, Ostrava, Poruba 708 33, Czech Republic

^b Department of Chemistry, VŠB-Technical University of Ostrava, 17. listopadu 15/2172, Ostrava, Poruba 708 33, Czech Republic

^c Institute of Environmental Technologies, VŠB-Technical University of Ostrava, 17. listopadu 15/2172, Ostrava, Poruba 708 00, Czech Republic

^d Technical University Bergakademie Freiberg, Institute of Materials Science, Gustav Zeuner Str. 5, Freiberg 09599, Germany

ARTICLE INFO

Keywords:

Raw vermiculites
Structural alteration
Vermiculite/CeO₂ nanoparticles composites
X-ray diffraction
(FR-IR) and Raman spectroscopy
HRTEM

ABSTRACT

Four commercial macroscopic vermiculites (Ver) from different exploited deposits were investigated regarding their chemistry and structural transformation stage from mica (phlogopite), and compared with selected raw vermiculites and “hydrobiotites” known from literature, in which the chemical analyzes verified the existence of iron as Fe³⁺ and Fe²⁺. Subsequently prepared vermiculite/ceria (Ver/CeO₂) nanoparticles composites were compared from the point of view of the fixation of ceria nanoparticles by using stability test and regarding their photocatalytic activity in the decomposition of N₂O. The experimental methods used for these studies were X-ray fluorescence spectrometry, atomic emission spectrometry, X-ray powder diffraction, infrared (FR-IR) and Raman spectroscopy and transmission electron microscopy with high resolution (HRTEM). Negative layer charge of vermiculites produced by the local charge balance and distribution of Fe³⁺ in tetrahedral and octahedral sheets were related to the CeO₂ nanocrystals fixation and orientation. Among the four Ver/CeO₂ nanoparticles composite samples, the vermiculite in sample Ver-C/CeO₂ exhibited the highest negative layer charge. The CeO₂ crystallites were the smallest among all four samples. HRTEM found separated CeO₂ nanocrystallites and CeO₂ agglomerates of differently oriented nanocrystallites. Such forms of CeO₂ nanocrystals influenced the position of the Raman CeO₂ F_{2g} and suppressed ability for photocatalytic N₂O conversion.

1. Introduction

The macroscopic and microscopic types of raw vermiculites are major categories of clay mineral vermiculite occurring in ultrabasic and basic rocks of raw vermiculite deposits (Basset, 1963). Large crystalline plates of the macroscopic vermiculites are of secondary origin, as they are formed by weathering, hydrothermal action or percolating ground water from biotites, chlorites, pyroxenes, amphiboles, etc. In pyroxenites and amphibolites, vermiculites were found together with biotite minerals, mainly phlogopite. On the contrary, vermiculites appearing in the carbonate type deposits together with magnesium and calcium salts are materials different from biotites showing interlayer basal d-value 1.4 nm in their X-ray diffraction patterns. Boettcher (1966) explored the chemical conditions necessary for the conversion of biotite to vermiculite, both occurring in the Rainy Creek alkaline-ultramafic igneous complex near Libby, Montana, USA. The author concluded that biotite and biotite pyroxenite were the first zoned body crystallizing from the original ultramafic magma. Such a large amount of altered coarse-

grained biotite pyroxenite is the major source of commercial vermiculite in the world.

The considerations in literature suggest that trioctahedral biotite could weather to vermiculite under acid conditions and to vermiculite plus montmorillonite under neutral and alkaline conditions (Latimer, 1952). The oxidation of Fe²⁺ to Fe³⁺ under alkaline conditions causes a large decrease of the clay mineral surface charge and expansion of the crystal lattice that predetermines conditions for the formation of montmorillonite. Based on the analysis of vermiculites and “hydrobiotites”, Foster (1963) concluded that the composition, charge relation and cation exchange capacity in these vermiculites can be derived from phlogopite or magnesian biotite by replacement of K⁺ by Mg²⁺. The term “hydrobiotite” was interpreted as regular 1:1 interstratification of biotite (or interlayer-deficient biotite) and vermiculite (Rieder et al., 1998).

Vermiculites were classified as 2:1 phyllosilicates with clay mineral layer charge $0.6 < x < 0.9 \text{ eq}/(\text{Si,Al})_4\text{O}_{10}$, arising mostly from the tetrahedral substitution of Si⁴⁺ by Al³⁺ (Bailey, 1980; Guggenheim

* Corresponding author.

E-mail address: marta.valaskova@vsb.cz (M. Valášková).

<http://dx.doi.org/10.1016/j.clay.2017.10.006>

Received 30 June 2017; Received in revised form 31 August 2017; Accepted 8 October 2017
0169-1317/ © 2017 Elsevier B.V. All rights reserved.

et al., 2006). The two-layer ordered structure of Mg-vermiculite from the Llano, Texas, where alternating layers were displaced relative to one another by displacement of $+b/3$ and $-b/3$ parallel to the y-axis have been refined by Shirozu and Bailey (1966). The authors claimed that this two-layer structure is different from the structure of Mg-vermiculite from Kenya refined by Mathieson and Walker (1954) and Mathieson (1958). Subsequent studies have revealed various possible layer-stacking sequences depending on the nature of the interlayer cation and relative humidity (de la Calle et al., 1975; de la Calle and Suquet, 1988).

Raw vermiculites are classified as mixed-layer phyllosilicates or interstratified phyllosilicates. Interstratified clay minerals can have ordered or regular mixed-layer structures, if different layers alternate along the c^* direction (Brigatti et al., 2006). Mixed-layer clay minerals with any appreciable degree of randomness show an irregular series of basal reflections. The mixed-layer biotite-vermiculites are derived in most cases from the degradation of pre-existing clay minerals. The charge of the vermiculite layers is heterogeneous due to variations in the degree of substitution within the individual layers (Lagaly, 1982; de Haro et al., 2005). The interlayer cations balancing the net charge deficiency may occur at a zero-water-layer hydration state (0-WLHS) or higher hydration states like 1-WLHS and 2-WLHS (Suzuki et al., 1987).

Vermiculites are very abundant and much cheaper in comparison with other clays. Therefore, they are extensively investigated for various industrial applications. For example, the treatment of vermiculites with mineral acids resulted in an increase of specific surface area and porosity (Pérez-Maqueda et al., 2012; Kupková et al., 2015; Komadel, 2016). The acid activated vermiculites have various applications as selective adsorbents (Hashem et al., 2015; Klika et al., 2017) and selective catalysts for NO_x reductions (Chmielarz et al., 2010). The combination of clay mineral matrices with metal-oxide nanoparticles is very remarkable. Gorobinskii et al. (2007) stabilized ceria nanoparticles and fixed them on montmorillonite using calcination at 550 °C. In previous studies, we presented the ceria nanoparticles on the matrix of vermiculite from the Paraíba region (Brazil) that were prepared using the same method as in this work and tested for photocatalytic decomposition of N_2O (Valášková et al., 2015, 2016).

The aim of this work was to perform new experiments on different vermiculites and to obtain important information from the comparison of their properties that may be interesting from the point of view of applications. Four commercial macroscopic vermiculites from different exploited deposits were investigated regarding their chemistry and structural transformation stage from mica (phlogopite), and compared with selected raw vermiculites and “hydrobiotites” known from literature, in which the chemical analyzes verified the existence of iron as Fe^{3+} and Fe^{2+} . Subsequently prepared vermiculite/ceria nanoparticles composites are compared from the point of view of the fixation of ceria nanoparticles on different vermiculite matrices by using stability test and regarding their photocatalytic activity in the decomposition of N_2O . The central experimental methods used for these studies were X-ray fluorescence spectrometry (XRF), Atomic Emission Spectrometry with Inductively Coupled Plasma (AES-ICP), X-ray powder diffraction (XRD), Infrared (FR-IR) and Raman spectroscopy, and high-resolution transmission electron microscopy (HRTEM).

2. Experimental

2.1. Materials and samples

Four commercial vermiculites (Ver) from the Village Belitsa in northwestern region of Bulgaria (named Ver-B), from the Paraíba region of Brazil in the Santa Luzia mine (Ver-S), from the Palabora mine in the Limpopo province of South Africa (Ver-P) and from the Qieganbulak apatite-vermiculite deposit in Xinjiang, China (Ver-C) were obtained from Grena Ltd., Czech Republic. The particle size fraction < 0.04 mm was prepared by milling the starting powders in a

vibratory mill VM4 (OPS Přerov, Czech Republic) at 1500 rpm for 2.5 min and subsequent sieving. The cation exchanged capacity (CEC) in the samples was determined using an ion exchange procedure with Cd^{2+} (Klika et al., 2016) as follows: $\text{CEC(Ver-B)} = 110 \text{ cmol(+)}/\text{kg}$, $\text{CEC(Ver-S)} = 86 \text{ cmol(+)}/\text{kg}$, $\text{CEC(Ver-P)} = 80 \text{ cmol(+)}/\text{kg}$ and $\text{CEC(Ver-C)} = 126 \text{ cmol(+)}/\text{kg}$.

The same amount of the vermiculite samples Ver-B, Ver-S, Ver-P and Ver-C (5 g) was dispersed in 100 mL of distilled water. These aqueous dispersions, which had the pH values of 9.6, 10.0, 9.6 and 10.2, respectively, were added dropwise to a ceria precursor and stirred for 3 h at 50 °C. The cerium precursor was a solution of 80 mL aqueous cerium nitrate $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ($0.4 \text{ mol}\cdot\text{L}^{-1}$) and 13 mL of ammonia hydrate NH_4OH ($1.4 \text{ mol}\cdot\text{L}^{-1}$) (pH = 11) that was stirred for 15 min at room temperature. The slurries containing dispersed samples Ver-B/ CeO_2 , Ver-S/ CeO_2 , Ver-P/ CeO_2 and Ver-C/ CeO_2 had the pH values of 10.2, 10.5, 10.1 and 10.6, respectively. For comparison, CeO_2 nanoparticles were precipitated in water at corrected pH 9 and pH 11. The solid fractions of the samples were separated by centrifugation and washing with distilled water, until a NO_3^- -free material was obtained. Finally, samples were dried in an oven at 80 °C for 24 h. The aqueous filtrates were collected to determine not fixed cerium and elements releasing from the vermiculites structure.

2.2. Analytical methods

The chemical elemental analysis of the vermiculites and vermiculite/ceria nanoparticles composites was performed using the energy dispersive X-ray fluorescence (XRF) spectrometer SPECTRO XEPOS (Spectro Analytical Instruments, Germany). Each sample (4 g) in duplicate was mixed with the wax (0.9 g) and prepared in pellets using hydraulic pressing at 10 tons. The content of Fe^{2+} was subtracted from the total Fe, when it was determined using titration with 0.1 M solution of $\text{K}_2\text{Cr}_2\text{O}_7$ in sample decomposed in HCl and HF in a CO_2 atmosphere.

The elements Ce, Na, K, Ca, Mg and Al releasing from the vermiculite structure during the production of Ver/ CeO_2 nanoparticles composites were determined from aqueous solutions using an atomic emission spectrometer with and Ar/Ar inductively coupled plasma (AES-ICP, SPECTRO CIROS VISION EOP, Germany), a flow nebulizer and a CCD semiconductor detector. The calibration standards for each element were prepared on the basis of one-element certified standard (Merck, Germany) with a concentration of 1 g/L.

The X-ray powder diffraction (XRD) analyses of the vermiculites and the Ver/ CeO_2 nanoparticles composites were performed with $\text{CuK}\alpha$ radiation ($\lambda = 0.15418 \text{ nm}$) 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 $2^\circ/\text{min}$ at 40 kV and 40 mA using a scintillation counter as detector. The divergence of the primary X-ray beam was limited by a $2/3^\circ \times 10 \text{ mm}$ slit. In the diffracted beam, a $2/3^\circ$ scattering slit and a 0.45 mm receiving slit were inserted.

The infrared spectra of all samples were recorded with a FT-IR spectrometer (Nexus 470, ThermoScientific, USA) equipped with a DTGS detector. The following conditions were used for the acquisition of the IR spectra: spectral region $4000\text{--}400 \text{ cm}^{-1}$, spectral resolution 4 cm^{-1} , 64 scans and Happ-Genzel apodization. The pellets for analyses were prepared from 1.0 mg of the respective sample and 200 mg of dried potassium bromide by pressing at 8 tons for 30 s under vacuum. The measured IR spectra were first corrected for background (second order polynomial baseline was assumed). Subsequently, the IR spectrum of pure potassium bromide was subtracted.

Raman spectra were measured at dispersive Raman spectrometer DXR SmartRaman (ThermoScientific, USA) with CCD detector using a 180° degree measurement technique. The measurement parameters were as follows: the wavelength of the excitation laser was 780 nm, the grating 400 lines/mm, the aperture 50 μm , the exposure time 1 s, the

Download English Version:

<https://daneshyari.com/en/article/8046436>

Download Persian Version:

<https://daneshyari.com/article/8046436>

[Daneshyari.com](https://daneshyari.com)