



Effect of low frequency ultrasound on the surface properties of natural aluminosilicates



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ABSTRACT

Structural and surface properties of different natural aluminosilicates (layered, chain and framework structural types) exposed of 20 kHz ultrasound irradiation (0–120 min) in aqueous and 35 wt% aqueous H₂O₂ dispersions were studied by X-ray diffraction (XRD), dynamic light scattering (DLS), nitrogen adsorption–desorption, thermal analysis, and Fourier transform infrared spectroscopy (FTIR) techniques. It was confirmed that sonication caused slight changes in the structure of investigated minerals whereas their textural properties were significantly affected. The aqueous dispersions of montmorillonite (Mt), clinoptilolite (Zlt), glauconite (Glt) and palygorskite (Pal) were represented by several particles size fractions according to DLS-study. Ultrasound irradiation produced a decrease of the average particle diameter by 4–6 times in water and by 1.3–5 times in H₂O₂ dispersions except for Pal, which underwent strong agglomeration. A significant increase of total pore volume and pore diameter was observed for Glt sonicated in H₂O₂ dispersions whereas for Pal mainly micropore volume sharply increased in both aqueous and H₂O₂ dispersions.

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1. Introduction

Currently it is required from a chemical production processes to be as much as possible safe to the natural environment. For that, the “green chemicals”, i.e. those having less toxic effect on the environment, and the “eco-technologies” are being actively developed. Natural aluminosilicates can contribute to the “eco-friendly chemical processes” as they are widespread materials of natural origin, possessing various surface active sites, e.g. hydroxyls, exchangeable and structural cations, as well as micro- and mesoporous structure that allows their application in ion-exchange, adsorption and catalytic processes [1].

Another environmental measure for intensification of technological/chemical processes getting an increasing interest during the past few decades is the use of ultrasound [2–4]. Indeed, ultrasound irradiation of materials can lead to disaggregation and deagglomeration of particles, improve dispersing and emulsification effects in various phases, as well as activates chemical reactions

by improving the mass transfer, prevent sedimentation and coagulation, and cause running of cavitation driven reactions [5].

In case of aluminosilicates, low frequencies ultrasonic irradiation significantly shortens the time of nucleation and synthesis [6–8], enhances accessibility of internal pores of aluminosilicates, reduces time of adsorption equilibrium [9,10] as well as intensifies the intercalation processes [11,12], etc. Besides, short ultrasound irradiation is usually applied during purification of natural clay samples as promoting deagglomeration of clay minerals phases and non-clay admixtures [13,14]. Sometimes, a combined use of clays and ultrasonic irradiation may have a synergetic effect on reaction time and yield of products in several catalytic organic reactions [4,15,16]. However, depending on the choice of ultrasonic parameters (power, frequency, irradiation time, etc), the nature of a solvent or an electrolyte present in dispersion and the type of the structure of aluminosilicate itself, sonication may severely affect properties [17,18] and behavior of aluminosilicate dispersions [19–21].

Detailed investigations of aqueous dispersions of montmorillonite, palygorskite and kaolinite under ultrasound irradiation [22,23] observed that short sonication times (<7.5 min at 19.5 kHz) breaks natural aggregates of clay minerals enhancing their dispersing and increasing stability of suspensions due to

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formation of a new coagulation structure with an increased surface energy [22]. As a result, viscosity and ξ -potential of dispersions increased [23,24].

The longer sonication of clay suspensions lead to enlargement of particles (autocoagulation) due to their strong interaction. In some cases, particles with high surface energy complete the structure so that further ultrasound irradiation cannot destroy them. The crystal structure of particles continues improving that may lead to formation of a new phase, such as montmorillonite arising by sonication (>7 min) of palygorskite suspensions [22]. Aqueous dispersions of kaolinite, hydromica and montmorillonite mainly disaggregate [25] and undergo more slight changes of crystal structure.

Applying the ultrasound treatment for 40–100 h in aqueous or acid (1 M HCl) media, it is possible to reach severe delamination of minerals (talc), reduce plate diameters in lateral dimensions and sharply abate the degree of crystallinity, especially in acid media where magnesium is easily leached [26].

Nevertheless, despite the increased spreading of ultrasound treatment in processes with clay minerals and aluminosilicates, there is no uniform procedure for the treatment, including type of equipment applied, ultrasonic parameters, duration of irradiation and other experimental conditions [4]. As a consequence, the data on ultrasound effect on physico-chemical properties of aluminosilicates are rather scattered, not systematic, that makes them difficult to generalize trends and reproduce the results.

The present research was aimed at studying the effect of ultrasound treatment of aqueous and hydrogen peroxide (H_2O_2) dispersions on structural and physical–chemical properties of natural aluminosilicates. The data obtained by applying XRD, DLS, nitrogen adsorption, TGA, FTIR techniques allow comparing the stability of the aluminosilicates towards ultrasonic treatment (20 kHz) in aqueous media and in the presence of aqueous H_2O_2 considered as a benign oxidant. Indeed, we reported in our recent review on the combination between clay science and sonochemistry that aqueous oxidants should be used in these conditions, to develop clay-based catalyst materials to be applied in oxidation reactions involving H_2O_2 [4]. Some studies are performed in our laboratories to investigate the catalytic activity, but the goal of the current paper is to characterize the effects of ultrasound on clay structures and composition, in these aqueous oxidative conditions, to further better understand the reactivity and chemical mechanisms.

2. Materials and methods

As objects of investigation were chosen natural samples, containing aluminosilicates of varied structural types and belonging to different classes of minerals, i.e. clay minerals – (i) layered 2:1 mineral montmorillonite, 90% (Mt), deposit from Voronezh region, Russia; (ii) spherulite type mixed layered mineral glauconite (Glt) [27], collected on the area of Voronezh anticline, Russia [28]; (iii) chain-layered type mineral palygorskite (Pal) from S&B Industrial Minerals GmbH; and natural zeolite clinoptilolite (Zlt), Slovak deposit, with a hard-sphere framework structure. Part of the natural Mt-containing sample was fractionated (<2 μm) by sedimentation in osmosed water, converted to Ca-form and further used as a reference material (MtCa). The rest aluminosilicates were used as-received, being crushed and sieved into particle size fraction of less than 250 μm .

1 wt.% dispersions of the clay samples in deionized water (w) or in aqueous 35 wt.% H_2O_2 (hp) solution were exposed of ultrasound (US) for 60 and 120 min using a Digital Sonifier[®] S-250D from Branson (power of standby $P_0 = 27.0$ W, nominal electric power of the generator $P_{\text{elec}} = 8.2$ W). A 3.2 mm diameter tapered microtip probe operating at a frequency of 19.95 kHz was used and its

acoustic power in water ($P_{\text{acous.vol}} = 0.25$ W mL⁻¹) was determined by calorimetry using a procedure described in the literature [29]. Energy consumption was measured with a wattmeter (Perel[®]). The solvent and clay samples were inserted in a glass rounded cylindrical reactor (17 mm in interior diameter, 102 mm in height), thermostated at 19 °C using a Minichiller[®] cooler (Huber). In these rigorous conditions (same equipment, same ultrasonic parameters, and same amounts for treated samples), all the experiments are reproducible with exactly the same effects and results on irradiated clays.

Physical–chemical properties of natural and US-treated clay samples were studied by following methods: XRD, dynamic light scattering (DLS); nitrogen adsorption–desorption; DTA/TGA; FTIR.

XRD analysis. Materials were characterized with PANalytical XpertPro equipment using Cu radiation source (40 kV, 40 mA) and Xccelerator detector allowing a cumulative count on $2^\circ 2\theta$ range. Analytical conditions were recording ranges (2–65 $^\circ 2\theta$ and 2–35 $^\circ 2\theta$) and equivalent counting times (0.017 $^\circ 2\theta/0.75$ s and 0.033 $^\circ 2\theta/1.5$ s) for powder and oriented preparations respectively.

Particle size measurements. Suspensions of clay mineral aggregates (1%) in pure water or in 35 wt.% H_2O_2 solutions were employed. DLS method was applied for measuring the size of clay mineral aggregates using a Zetasizer Nano Malvern Instrument. 1.5 mL of suspensions before and after a definite time of US irradiation (0–120 min) were placed into a polystyrene cell and PSZ was measured using a red laser ($\lambda = 632.8$ nm).

Nitrogen adsorption measurements. N_2 adsorption–desorption isotherms at -196 °C were studied using a TRISTAR 300 gas adsorption system for samples of investigated aluminosilicates in natural form and after exposure of US in aqueous and hydrogen peroxide media. Outgassing conditions included 2 h at 90 °C followed by 8 h at 250 °C. BET-method was applied for calculation of specific surface area (SSA); BJH method for mesopores volume, and *t*-plot analysis were used for assessment of micropores volume.

Thermal analysis. The sample were characterized by thermogravimetric analyses (DTA/TGA) using a Q600 TA Instrument, under a dry air flow (100 mL/min, 10 °C/min)

FTIR-measurements of aluminosilicates samples in natural and US-treated form were carried out on Nicolet MAGNA-IR 760 spectrometer E.S.P. equipped with an IR source, DTGS detector and KBr Beam splitter. The KBr pressed-disc technique was used for preparing a solid sample. Samples of 0.5 mg were dispersed in 100 mg of KBr to record spectra within the 4000–400 cm⁻¹ transmission range. Discs were kept overnight in an oven at 150 °C to prevent water adsorption.

3. Results and discussion

3.1. XRD characterization of aluminosilicates samples before and after ultrasound irradiation

3.1.1. Mineralogical characterization of natural aluminosilicates samples

The XRD-patterns obtained for powder samples of investigated natural aluminosilicates are represented in Fig. 1.

As follows from XRD-pattern of Mt sample, it was essentially composed of a dioctahedral smectite of montmorillonite–beidellite series with (001) and (060) reflections located at 15.1 Å and 1.49 Å (Fig. 1). This clay mineral is associated with quartz and very little amounts of illite, kaolinite, chlorite and plagioclase. For MtCa sample prepared by sedimentation of <2 μm fraction, a relatively slight decrease in quartz content and a disappearance of chlorite and plagioclase reflections were observed (Fig. S1, ESI).

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