TALC PROPERTIES AFTER ACID TREATMENT AND MECHANICAL PROCEDURES

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Abstract

The effect of different mechanical treatments in combination with inorganic/organic acid treatments on the structure of natural talc was purpose of this work. The mechanically and chemically treated samples were investigated by measurement of specific surface area, X-ray diffraction and Infrared spectroscopy. Mechanical procedures and inorganic/organic acid treatment led to reduction of particle size and to increase of the specific surface area. The value of SSA increased three-times (31.83 m²/g) for sample TvsH in comparison to initial talc (T) sample (10.10 m²/g). The sample TvsH was prepared from talc (T) by combination grinding (v) and sonication (s) and subsequent acid activation with strong hydrochloric acid (H). The sample TvsH showed the smallest particle size 0.067 μm among all prepared samples which reduced from initial particle size 0.212 μm of T.

Keywords: talc, mechanical and acid treatment, inorganic/organic acids

1. INTRODUCTION

Layered silicates (phyllosilicates) represent an important group of natural materials, including clay minerals, which can be used in various technological applications. Talc belongs to the 2:1 phyllosilicates widely used for a large number of applications such as in paper, ceramics, polymers, paints, cosmetics and pharmaceuticals. The ideal structural formulae of talc is Mg₆Si₈O₂₀(OH)₄ with a interlayer space d = 0.91 – 0.94 nm. Talc 2:1 structure contains one central octahedral (O) sheet between two parallel tetrahedral (T) sheets connected via T silica oxygen apices to octahedral OH hydroxyl planes [1]. The layer structure is electrically neutral and therefore no charge-balancing cation is present in the interlayer space. Contiguous layers are held together by van der Waals interactions [2].

Talc exhibits a small surface area thanks to the difficulty of its delamination and therefore particle size reduction methods have to be used to increase the surface area for eventual applications [3]. The reduction of the particle size of phyllosilicates require particular importance in material science because affect properties of the end products. For example, nano-sized talc attracts attention especially as a filler application in order to reinforce materials in nanocomposites [4].

Mechanical treatments of clay minerals create important changes and influence their behavior in further processing step. Grinding and sonication represent common techniques for particle size reduction of clay minerals by the mechanical way. Besides particle size reduction, the milling causes the increase of reactivity the particles. The influence of grinding [5, 6, 7, 8, 9] and sonication [10, 11, 12, 13] treatments on the talc structure has been extensively studied.

Chemical modifications performed by inorganic/organic acids, bases or organic molecules involve alteration of structure, surface functional groups and surface area [14]. Acid activation of clay minerals belongs to one of the most common chemical modification. By the acid activation is possible to prepare in part dissolved material with increased specific surface area, porosity and surface acidity [15]. The extent of dissolution of structure depends on clay mineral type and used reaction conditions [16]. The various types of acids can be used for acid treatments including inorganic acids (hydrochloric, sulfuric and nitric) and organic acids (acetic, citric, oxalic). However, hydrochloric and sulfuric acids are probably the most widely used due to their preferable results in specific surface area, porosity and adsorption capacity [14].
Talc is very resistant to acids. Distortion of the talc structure caused by mechanical activation promotes its leaching behavior [12, 17]. Moreover, the combination of mechanical milling and subsequent acid treatment lead to preparation of porous silica from talc. Yang et al. (2006) successfully prepared porous silica via ball milling and subsequent hydrochloric acid. Temuujin et al. (2002) prepared also porous material from talc by milling and then leaching with sulfuric acid. Castillo et al. studied talc samples of different origins and composition in order to assess the effects of inorganic/organic acid treatments. Authors used hydrochloric acid, acetic and formic acid. Talc after hydrochloric acid treatment was purified with silanol groups onto its surface. Organic acids caused the grafting carboxylic groups onto the surface of talc.

The purpose of this work was to assess the effect of different inorganic/organic acid treatments on the structure of natural talc. Talc was treated with different inorganic or organic acid such as hydrochloric acid (HCl) and oxalic acid ((COOH)₂) at 80 °C for 4 h. The characterization of changes in the structure of talc before and after acid treatments was performed using the methods of X-ray diffraction (XRD) and Infrared spectroscopy (IR) and specific surface measurement (SSA).

2. EXPERIMENTAL

2.1. Starting materials

The starting material used for the mechanical and chemical treatments was natural raw talc from Egypt. Table 1 shows the chemical compositions of raw talc which was determined from XRF analysis.

Table 1 The chemical compositions of original talc

<table>
<thead>
<tr>
<th>Compositions</th>
<th>SiO₂</th>
<th>MgO</th>
<th>CaO</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>L.o.I.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass %</td>
<td>57.5</td>
<td>28.7</td>
<td>2.9</td>
<td>0.6</td>
<td>0.3</td>
<td>9.3</td>
</tr>
</tbody>
</table>

L.o.I. Loss on ignition

For acid activation were used chemicals: aqueous solutions of 35 % hydrochloric acid (HCl), supplied from Lach-Ner, Czech Republic, and oxalic acid dihydrate (C₂H₂O₄·2H₂O), supplied from Mach-chemicals, Czech Republic.

2.2. Characterization techniques

The chemical elemental composition of origin talc was determined by the energy dispersive X-ray fluorescence spectrometer (XRF) SPECTRO X-LAB. The sample was mixed with wax and pressed into the form of the pellet.

The X-ray powder diffraction (XRD) patterns were taken on the diffractometer Ultima IV Rigaku (CuKα radiation, scintillation counter, reflection mode, Bragg-Brentano configuration) under working conditions 40 kV and 40 mA. The XRD patterns were recorded in the rage of 2 – 60° with a scanning rate of 2.1 °/min.

The specific surface area (SSA) of powder samples was measured with a Sorptomatic 1990 (Thermo Electron Corporation, USA) at liquid nitrogen temperature. Nitrogen gas was used as adsorbate. The SSA was calculated by the software according to the BET isotherm. The spherical diameter (SD) was calculated from the following expression (1):

\[ D = \frac{6}{\rho S} \]  

where \( \rho \) is the density of talc (2.8 g.cm⁻³) and S is measured value of the specific surface area (m².g⁻¹).

The Fourier-transform infrared (FTIR) spectra were measured with spectrometer Nicolet 6700 FT-IR (Thermo Nicolet, USA) by ATR technique with diamond crystal. FTIR spectra were recorded in the range from 400 to 4000 cm⁻¹.
2.3. Sample preparation

Mechanical treatments
Talc was treated as follows: raw talc (T) was milled for 3 min in a laboratory vibration mill (VM4) and sieved though a 0.040 mm sieve. The obtained fraction was named Tv. Ultrasonic modification was performed with an ultrasonic processor UP100H (Hielscher-Ultrasound Technology) (100 W, 30 kHz) with sonotrode (MS3). Samples T and Tv (1.5 g) were mixed with 50 ml of demineralized water to form the slurry, then subjected to ultrasounds for 30 min and dried at 80 °C overnight. The prepared samples were designated as Ts and Tvs, respectively.

Chemical treatments
The chemical activation was carried out by adding 10 g of samples Tv, Ts and Tvs to 200 ml of solution of 6 mol.l⁻¹ hydrochloric acid (H) and/or 0.5 mol.l⁻¹ oxalic acid (O). Action of acids on the samples was carried out in suspensions at 80 °C for 4 h. Then, the samples were centrifuged and several times washed with demineralized water and dried at 80 °C overnight. The prepared samples were designated as TvH, TsH, TvsH; TvO, TsO, TvsO.

3. RESULTS AND DISCUSSION

3.1. Specific surface area measurement
The values of specific surface area (SSA) and the spherical diameter (SD) of mechanically and chemically treated samples are in Tab. 2. The SSA of raw talc increased from the 10.86 m²/g to the 13.21 m²/g after sonication and to the 17.19 m²/g after vibrating milling. The highest value of SSA (20.33 m²/g), obtained by mechanical way, was achieved for sample Tvs when the combination of milling and sonication was used. The increase in SSA was observed also for all samples after inorganic/organic acid action. The maximum value of SSA (31.83 m²/g) was achieved by combination milling and sonication and following hydrochloric action.

The value of SD decreases from 0.212 μm for original talc to 0.162 μm for Ts, 0.124 μm for samples Tv and 0.105 μm for Tvs. The SD decreases also after acidification. The smallest value of SD (0.067 μm) was determined for sample TvsH. These results confirm earlier findings from the literature [12, 13] that mechanical and chemical processes produce significantly particle size reduction. The relation between the SSA and SD presented in Fig. 2 shows the particle size reduction after mechanical and chemical action.

Table 2 Specific surface area (SSA) and spherical diameter (SD) of treated talc samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>SSA [m²/g]</th>
<th>SD [μm]</th>
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<th>SD [μm]</th>
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<th>SSA [m²/g]</th>
<th>SD [μm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>10.10</td>
<td>0.212</td>
<td>T</td>
<td>10.10</td>
<td>0.212</td>
<td>T</td>
<td>10.10</td>
<td>0.212</td>
</tr>
<tr>
<td>Ts</td>
<td>13.21</td>
<td>0.162</td>
<td>TsH</td>
<td>18.73</td>
<td>0.114</td>
<td>TsO</td>
<td>13.73</td>
<td>0.156</td>
</tr>
<tr>
<td>Tv</td>
<td>17.19</td>
<td>0.124</td>
<td>TvH</td>
<td>24.10</td>
<td>0.089</td>
<td>TvO</td>
<td>24.54</td>
<td>0.087</td>
</tr>
<tr>
<td>Tvs</td>
<td>20.33</td>
<td>0.105</td>
<td>TvsH</td>
<td>31.83</td>
<td>0.067</td>
<td>TvsO</td>
<td>28.37</td>
<td>0.075</td>
</tr>
</tbody>
</table>

3.2. X-ray diffraction analysis
The XRD patterns presented in Fig. 1 shows a mild decrease of intensity of basal diffractions (002), (004), (006) for samples TvsH and TvsO in comparison with the untreated sample (T) but their positions were not affected. Therefore, based on the XRD patterns, their significant structural change can not be considered. XRD pattern of raw talc revealed the presence of admixtures of kaolinite (K) and dolomite (D). Dissolution of dolomite after exposure with strong HCl and also with organic oxalic acid at all prepared samples caused that resulted XRD patterns correspond to the pure talc.
3.3. Infrared spectroscopy

The FTIR spectra can be divided into two characteristics part. The bands in the range 3750 – 3400 cm\(^{-1}\) could be assigned to the surface structural hydroxyl groups as well as adsorbed water. A series of bands located at 1400 – 400 cm\(^{-1}\) could be assigned to lattice vibration of the clay minerals. The FTIR spectra of raw talc (T) and talc after exposure with oxalic acid are shown in Fig. 3.

The spectrum of raw talc (T) is characterized by bands at 3674 cm\(^{-1}\) (Mg-OH stretching vibration), 981 cm\(^{-1}\) (stretching vibration of Si-O-Si bonds), 666 cm\(^{-1}\) (Si-O-Mg bonds), 507 cm\(^{-1}\) (Al-OH bonds) and 460 cm\(^{-1}\)
(Mg-O bonds) [17]. The band at 1459 cm\(^{-1}\) was assigned to dolomite (CaMg(CO\(_3\))\(_2\)) that it was also identified by XRD analysis. The FTIR spectra of talc after milling and sonication treatments did not change.

The significant changes in the FTIR spectra are evident for samples after oxalic acid activation. The FTIR spectra of TsO, TvO and TvsO present a new bands in comparison with the initial talc sample (T). The broad band around 1635 cm\(^{-1}\) belongs to the stretching vibration of C=O. This band is composed of two contributions at 1621 cm\(^{-1}\) and 1657 cm\(^{-1}\). Moreover, the new sharp bands are observed at 1319 cm\(^{-1}\) and 780 cm\(^{-1}\). The first band is attributed to combined stretching vibration of C-C and C-O in COO and the second band belongs to bending vibration of O-C=O [22, 23].

4. CONCLUSIONS

The study of different mechanical treatments in combination with hydrochloric/oxalic treatment on natural talc brought the following observations:

- In comparison to initial talc, the combination of mechanical procedures (grinding and sonication) and acid treatment with hydrochloric or oxalic acids caused at prepared samples about three-fold increase of SSA.
- Particle size reduction after grinding was more intensive than after sonication.
- Particle size reduction after grinding and sonication and further action of acids was slightly greater after hydrochloric than oxalic acid.

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LITERATURE