PREPARATION AND CHARACTERIZATION OF ZIRCONIUM-TALC FOR ITS POSSIBLE USE TO THE ZIRCON-ENSTATITE CERAMIC

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Abstract

Effect of milling process in combination with hydrochloric acid treatment on the structure of talc was studied in terms of ability to bind the zirconium in the zirconium-talc composite. Zirconium-talc was prepared from the natural powdered talc from Egypt and aqueous solution of zirconyl chloride. The mechanically and chemically modified talc was investigated by the chemical analysis of elements (XRF), X-ray diffraction (XRD), scanning electron microscopy (SEM) and the measurement of specific surface area (SSA). Combination of procedures of milling with acidification contributed to the increase in SSA of talc from 10.1 to the 17.3 m²/g. The maximum content of zirconium bound in a zirconium-talc was 0.65 wt.%.

Keywords: talc, milling, hydrochloric acid, zirconium-talc

1. INTRODUCTION

Clay minerals are important industrial minerals. Pyrophyllite and talc are the most common clay minerals applied for raw materials in the production of ceramics [1].

Talc, having a chemical formula Mg₃Si₄O₁₀(OH)₂, is the clay mineral whose structure consists of the 2:1 layers which are composed from the tetrahedral-octahedral-tetrahedral sheets [2]. In the ideal case, no interlayer material exists in the structure of talc because 2:1 layers are electrically neutral [2, 3]. Van der Waals interactions and the weak cohesion hold adjacent 2:1 layers together and account for the very soft nature talc [3]. The softness of talc is due to the easy displacement of the 2:1 layers [4].

The use of talc is derived from its unique structural, physical and chemical properties, which are reflected by its softness, surface properties, particle size and morphology [5]. The paper industry is the major consumer of talc (as a loading agent). Talc is very often used as a filler in rubber, paints, plastic and composites [6]. Talc is also a significant raw material in the preparation of magnesium ceramics (steatites, cordierites, enstatites and forsterites) [7].

The mechanochemical treatments of the most structurally inactive clay minerals bring many benefits such as reduced annealing and sintering temperature, accelerated rate of densification rate in ceramics powder, production of porous materials, reduction in phase transformation temperature, enhanced leaching process, decreased thermal decomposition temperature and increased particle reactivity [8]. The mechanochemical treatments of inorganic solids constitute promising way for achieving control of the reactivity in the solid state and for the preparation of metastable phases with new and useful properties. This activation often allows a significant lowering in reaction temperature and times of thermal processing [9].

Mechanical grinding leads to random delamination of the silicate layers and the surface area increase [10]. The high-energy or long time of grinding causes the amorphization of material [11]. The most common chemical activation of clay minerals to increase their specific surface area and porosity is treatment with solutions of the strong inorganic acids [12].

The study deals with solution of two issues. The first topic was the performance of modification of talc by milling and by acidification with hydrochloric acid and evaluation of samples by the X-ray fluorescence spectrometry (XRF), the X-ray diffraction (XRD), the specific surface area (SSA) measurement and scanning
electron microscopy (SEM). The second step was to determine how modified talc affected the ability to bind zirconium.

2. MATERIALS AND METHODS

2.1 Materials

The natural powdered talc from Egypt was selected as starting material for the samples preparation. The chemical composition of raw talc in wt.% from the elemental analysis was: 51.49 SiO$_2$, 35.71 MgO, 2.91 CaO, 0.29 Fe$_2$O$_3$, with loss of ignition 9.31.

An aqueous solution of 37 % hydrochloric acid (HCl), from Sigma Aldrich, was used, for the acid activation of talc. Zirconyl chloride (ZrOCl$_2$), 30 % solution in hydrochloric acid, supplied by Sigma Aldrich, was chosen as a source of zirconium.

2.2 Characterizations methods

The specific surface area (SSA) was determined with Sorptomatic 1990 (Termi-Finnigan) at liquid nitrogen temperature. Nitrogen gas was used as an adsorbate.

The X-ray powder diffraction (XRD) patterns were obtained using a diffractometer INEL CPS 120 with a 120° curved position-sensitive detector and Ge-monochromatized CuKα radiation.

The chemical composition of talc was determined by the X-ray fluorescence spectrometer (XRF) SPECTRO X-LAB. The samples were mixed with the wax and pressed into the form of the pellets.

The particle morphologies of talc were observed on a scanning electron microscope (SEM Philips XL 30) using a secondary electron detector equipped with energy dispersive spectroscopy analysis (EDS) for elemental analysis and mapping.

2.3 Samples preparation

The sample of talc (T) was ground in planetary ball mill (FRITSCH) for 20 min, then passed through a 0.045 mm sieve and labeled T1. The samples T and T1 (always 10 g) were treated with 200 ml of 6M HCl at 80°C for 2 h. The resulting suspensions were washed with demineralized water to remove chlorides, then centrifuged, dried at 80°C and designated as T6 and T16, respectively. The samples T6 and T16 after milling in a planetary micro mill (FRITSCH pulverisette 7) for 15 min were labeled as T61 and T161, respectively.

At the second step, ability of three samples to bind zirconium was tested. The 5 g of each sample T16, T161 and T61 were heated and stirred with 50 ml of 5 % aqueous solution ZrOCl$_2$ in closed flask at 80°C for 2 h. The obtained samples were named as T16Zr, T161Zr and T61Zr, (Table 1). All samples were then washed with demineralized water, centrifuged and dried at 80°C. This procedure was repeated twice.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Procedure of preparation</th>
<th>$S_{BET}$ [m$^2$/g]</th>
<th>Zr [wt.%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>raw talc (T)</td>
<td>10.1</td>
<td>0</td>
</tr>
<tr>
<td>T1</td>
<td>T milled</td>
<td>12.5</td>
<td>0</td>
</tr>
<tr>
<td>T16</td>
<td>T1 with 6M HCl</td>
<td>14.6</td>
<td>0</td>
</tr>
<tr>
<td>T161</td>
<td>T16 milled</td>
<td>17.3</td>
<td>0</td>
</tr>
<tr>
<td>T6</td>
<td>T with 6M HCl</td>
<td>11.9</td>
<td>0</td>
</tr>
<tr>
<td>T61</td>
<td>T6 milled</td>
<td>17.1</td>
<td>0</td>
</tr>
<tr>
<td>T61Zr</td>
<td>T61 with ZrOCl$_2$</td>
<td>not measured</td>
<td>0.32</td>
</tr>
<tr>
<td>T16Zr</td>
<td>T16 with ZrOCl$_2$</td>
<td>not measured</td>
<td>0.65</td>
</tr>
<tr>
<td>T161Zr</td>
<td>T161 with ZrOCl$_2$</td>
<td>not measured</td>
<td>0.59</td>
</tr>
</tbody>
</table>

Table 1 List of samples, preparation procedures, specific surface area ($S_{BET}$) and content of zirconium (Zr).
3. RESULTS AND DISCUSSION

3.1 Specific surface area

The main task of acid activation of clay minerals is to obtain partly dissolved material of increased specific surface area, porosity and surface acidity [12]. The SSA of clay minerals is one of their most important properties controlling surface phenomena. In the case of non-swelling clay minerals, the most widely used technique for determining SSA is based on gas adsorption, notably of nitrogen gas at 77 K [13].

The surface area of raw talc (T) after milling (T1) slightly increased from the 10.1 m$^2$/g to the 12.5 m$^2$/g. A slightly higher SSA 11.9 m$^2$/g of talc after treatment with the hydrochloric acid (sample T6) significantly increased by milling to the 17.1 m$^2$/g (sample T61). Also the procedure grinding in the first step and then the action of acid led to a corresponding increase in SSA to the 17.34 m$^2$/g (sample T161).

3.2 X-ray diffraction analysis

The XRD reflection patterns (Fig. 1.) of raw milled talc (T1) revealed admixtures of other crystalline minerals kaolinite (K) and dolomite (D). Diffraction of dolomite (D) expired after acid activation.

The XRD transmission patterns allowed to observed non-basal reflection. The comparison of diffraction patterns in Fig. 2. showed that acid activation and milling very slightly reinforced the intensity of non-basal reflection of talc.

![Fig. 1 XRD patterns of milled talc: T1 – reflection and T1tr – transmission.](image)

3.3 Modified talc and binding Zr

The mechanochemically activated talc samples T16, T161 and T61 after treatment with aqueous solution showed slightly smaller particles in comparison to the original talc. The modified talc sample with Zr showed a similar trend. The SEM images in Fig. 3. allow the comparison of the particles morphology in the samples T and T16Zr and the mapping of the distribution of the elements Mg and Zr on the surface of the sample T16Zr. The elemental XRF analysis revealed that the sample T16Zr contained 0.65 wt.% Zr by a similar amount 0.60 wt.% Zr in the sample T161Zr. It is surprising that a sample of talc T61Zr, which has first subjected to acid exposure and then grinding was able to bind only 0.32 wt.% Zr (Table 1).
4. CONCLUSION

Analysis of results gave the following facts:

1. The same increase in SSA of talc from the 10 m$^2$/g to 17 m$^2$/g occurred after procedures in which talc was first acidified and then milled or first milled, then acidified and re-milled.

2. Acid action and milling of talc did not affect significantly the XRD patterns.

3. First modification of talc by milling and then acid treatment was positive for binding zirconium. Conversely, considerably smaller amount of zirconium was bound in talc, which was first acidified before milling.

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LITERATURE


Fig. 3 SEM image of sample T and EDS elements distribution of Mg and Zr in the sample T16Zr.
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