RAMAN STUDY OF CLAY/TiO$_2$ COMPOSITES

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Abstract

Isolated nanoparticles are generally known to have negative impact on living organisms. Some types of engineered nanoparticles, e.g. titanium dioxide nanoparticles (TiO$_2$), show photocatalytic activity after UV light exposure and if they are tightly anchored to suitable type of matrix, they demonstrate their photodegradable properties together with lower environmental risk due to decreased mobility of nanoparticles. TiO$_2$ nanoparticles are able to eliminate organic pollutants from air, as well as from waste water, however the photocatalytic properties are highly influenced by parameters such as particle size and phase modifications. TiO$_2$ occurs in three basic phase modifications, anatase, brookite and rutile. The anatase modification shows the highest photoactivity after UV light exposure compared to the other forms of TiO$_2$.

The work deals with study of two clay composites bentonite/TiO$_2$ (BETI) and vermiculite/TiO$_2$ (VETI). These composites were prepared with different content of TiO$_2$ were calcined at different temperatures and for different time. Therefore, the effects of temperature, as well as time on transformation of anatase to rutile were studied. Both types of the composites were studied by Raman microspectroscopy, which shown that VETI composite is more stable for anatase phase as well as that larger content of TiO$_2$ allows higher conversion to rutile phase.

Keywords: Raman microspectroscopy, bentonite, vermiculite, titanium dioxide, composite

1. INTRODUCTION

TiO$_2$ is widely studied because of its promising applications in many fields including photovoltaic cells, electronic devices, sensors, etc. Photocatalysis is the main application of TiO$_2$, especially degradation of environmental contaminants. Its importance as photocatalyst is related to its low cost, reduced toxicity and high chemical stability [1]. TiO$_2$ occurs in three basic modifications, i.e. anatase, rutile and brookite. Rutile is the most stable form, whereas anatase and brookite are metastable and could be transformed to rutile by calcination. Temperature of the phase transition is highly dependent on conditions of the TiO$_2$ preparation. Pure brookite without rutile and anatase is very difficult to prepare [2]. Many papers have studied the photocatalytic application of TiO$_2$ and it is generally accepted that anatase is more efficient as photocatalyst than rutile or brookite [3].

Although nanoparticles may be potentially very useful, they may also pose a risk to the environment and to the living organisms. They are capable of entering the biogeochemical cycles and to the food chain finally. Due to the fact, it is desirable to prepare anchored nanoparticles to the suitable type of matrix. Phyllosilicates have been found as a suitable matrix, because clays are abundant natural materials with a wide scale of practical applications. Impregnation of clays with TiO$_2$ shows thermal stability and larger pore sizes [4-6].

The work is focused to two selected clay minerals: bentonite and vermiculite.

The composites were prepared with different content of TiO$_2$ and effects of temperature, as well as time on transformation of anatase to rutile have been studied. Nanocomposites were studied by Raman spectroscopy, which may provides information about molecular vibrations, which are specific to the chemical bonds and symmetry of molecules. Such kind of information can be used for sample identification as well as to determine the phase composition.
2. EXPERIMENTAL

2.1 Sample preparation

Samples were prepared from vermiculite – Letovice (Czech Republic) and from bentonite – Ankerpoort NV (Maastricht, Netherlands). Titanyl sulfate (TiOSO₄) was obtained from Precheza a.s Přerov (Czech Republic) and contains 102 g of TiO₂ in 1 liter of suspension. 30 g of appropriate clay matrix was mixed with appropriate volume of TiOSO₄ to give the desired amount of TiO₂ in the final composite. This suspension was treated by shaking for 24 hours in vertical shaker at room temperature. After 24 hours the mixture was heated to 80°C and the suspension was stirred for 5 hours. After hydrolysis using 150 ml of distilled water, which lasted for 90 min, the solid phase was left to settle and decant. After rinsing with distilled water for several times the conductivity of supernatant liquor was less than 5 mS/cm².

The prepared composites BETI and VETI were dried at 105°C and then calcined at 400, 600, 800 and 1000°C for 1 hour. The BETI composite with 20 wt.% TiO₂ was calcined for 0.5, 1, 2 and 3 hours at temperature 800°C. The prepared samples were assigned as follow: BETI12, VETI12 for composite dried to 105°C with 20 wt.% TiO₂, BETI15 for composite with 50 wt.% TiO₂ and dried at 105°C. BETI (VETI) 4x, 6x, 8x and 10x indicates calcination temperature 400, 600, 800 and 1000°C, x means the TiO₂ content: 2...20 wt.% of TiO₂, 5 ... 50 wt.% of TiO₂.

2.2 X-ray fluorescence spectroscopy

Phase composition of samples BETI12, BETI15 and VETI12 was determined using XRFS SPECTRO XEPOS (SPECTRO Analytical Instruments, Germany) equipped with 50 W Pd X-ray tube. The samples were prepared in the form of fused discs.

2.3 Raman spectroscopy

Raman spectra of all samples were measured using a Smart Raman Microscopy System XploRA™ (HORIBA Jobin Yvon, France). Raman spectra were acquired with 532 nm excitation laser source, 50x objective and using 1800 gr./mm grating in the range from 80 to 4000 cm⁻¹.

3. RESULTS AND DISCUSSION

The chemical compositions of BETI12, BETI 15 and VETI12 are shown in Table 1. The chemical analysis revealed low yield of the proposed synthesis procedure, which has to be modified for applications in common practice.

Table 1 Phase composition of prepared composites (LOI - loss on ignition).

<table>
<thead>
<tr>
<th>Sample Parameter</th>
<th>BETI12</th>
<th>BETI15</th>
<th>VETI12</th>
<th>Sample Parameter</th>
<th>BETI12</th>
<th>BETI15</th>
<th>VETI12</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂O (wt.%)</td>
<td>0,931</td>
<td>0,617</td>
<td>0,863</td>
<td>K₂O (wt.%)</td>
<td>0,354</td>
<td>0,210</td>
<td>0,015</td>
</tr>
<tr>
<td>MgO (wt.%)</td>
<td>2,232</td>
<td>1,346</td>
<td>10,99</td>
<td>CaO (wt.%)</td>
<td>0,285</td>
<td>0,281</td>
<td>0,070</td>
</tr>
<tr>
<td>Al₂O₃ (wt.%)</td>
<td>13,95</td>
<td>8,840</td>
<td>7,222</td>
<td>TiO₂ (wt.%)</td>
<td>18,28</td>
<td>35,06</td>
<td>13,66</td>
</tr>
<tr>
<td>SiO₂ (wt.%)</td>
<td>46,29</td>
<td>26,95</td>
<td>40,35</td>
<td>MnO (wt.%)</td>
<td>0,010</td>
<td>0,002</td>
<td>0,044</td>
</tr>
<tr>
<td>P₂O₅ (wt.%)</td>
<td>&lt;0,0012</td>
<td>&lt;0,0012</td>
<td>&lt;0,0012</td>
<td>Fe₂O₃ (wt.%)</td>
<td>2,298</td>
<td>1,385</td>
<td>4,912</td>
</tr>
<tr>
<td>SO₃ (wt.%)</td>
<td>3,675</td>
<td>7,412</td>
<td>3,875</td>
<td>LOI (%)</td>
<td>10,7</td>
<td>16,9</td>
<td>17,0</td>
</tr>
</tbody>
</table>

Raman spectra of the BETI12 composite shows only one characteristic band of anatase at position 161 cm⁻¹ [7]. Its intensity in spectrum of BETI12 is much lower than intensities of the same band detected for other calcined BETI composites (see Fig. 1). Other three characteristic bands were not detected, due to the fluorescence background of the bentonite [8]. At spectrum of BETI42 fluorescence of the clay is still detectable, but all the characteristic bands are clearly visible at positions 156, 400, 520 and 642 cm⁻¹. Rutile phase appears at spectrum of BETI102, which was confirmed by bands at positions 247, 450 and 617 cm⁻¹.
Phase transformation was not complete because all anatase bands are still detectable. Small shift of anatase band at position 149-156 cm$^{-1}$ is noticeable.

**Fig. 1** Raman spectra of the BETI composite with 20 wt.% of TiO$_2$ calcined at different temperatures.

Fluorescence is less noticeable for BETI15 composite, which may be due to higher content of TiO$_2$ (see Fig. 2). All anatase characteristic bands are seen at all spectra of BETI composites at positions 148-158, 400, 519 and 642 cm$^{-1}$. Transformation of rutile phase is confirmed in spectra of BETI105. Rutile characteristic bands are at positions 245, 449 and 614 cm$^{-1}$. However anatase is still present what shows only one band at 149 cm$^{-1}$, but the intensity is lower, what indicates small content of anatase phase.

**Fig. 2** Raman spectra of the BETI composite with 50 wt.% of TiO$_2$ calcined at different temperatures.

Raman spectra of VETI composites have higher noise than spectra of BETI composites (see Fig. 3.), which may be caused by higher fluorescence background of vermiculite and lower content of TiO$_2$. All characteristic anatase bands are again detectable at positions 148-168, 397, 520 and 644 cm$^{-1}$. Small content of TiO$_2$ caused less transformation to rutile phase, which confirmed spectrum of VETI102. Only band at 250 cm$^{-1}$, which is one of the characteristic bands of rutile, was detected.
Fig. 3 Raman spectra of the VETI composite with 20 wt.% of TiO₂ calcined at different temperatures.

Composite BETI85 was calcined for 0.5, 1, 2 and 3 hours. But even 3 hours of calcination did not cause transformation to the rutile phase (see Fig.4). Therefore all the Raman spectra of BETI85 were observed to have only characteristic anatase bands at positions 148 (151), 400, 520 and 644 cm⁻¹.

Fig. 4 Raman spectra of the BETI85 composite calcined for different time (0.5, 1, 2 and 3 hours).

4. CONCLUSIONS
- From the measured Raman spectra it is evident that the rutile transformation at VETI composite is restricted in comparison to BETI composite.
- Higher content of TiO₂ caused less fluorescence background of the clays presented at the composites.
- The larger content of TiO₂ is favorable for the higher conversion to rutile phase, which was confirmed by spectra of BETI102 and BETI105 composites.
- Longer time of calcination of BETI 15 at 800°C have no effect on transformation of anatase to rutile.

ACKNOWLEDGMENTS
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LITERATURE


