Abstract

The precise determination of sulfur in nanomaterials is an important task with respect to quality control of nanomaterials production as well as in the course of research and development of new nanocomposites. Composites based on nanostructured sulphides deposited on surface of suitable substrates and nanomaterials prepared with help of substances containing sulfur are typical examples of materials where the sulfur content has to be precisely determined. Combustion techniques are used for the determination of carbon and sulfur in a wide range of inorganic materials. These methods are based on heating of samples in a ceramic crucible placed in an induction furnace in flow of oxygen. During the heating the samples are decomposed and carbon and sulfur are released in the form of carbon and sulfur dioxides. Both these gases are detected in infrared cells. The advantage of combustion techniques is a small amount of sample needed for the analysis as well as a large concentration range of sulfur and carbon, which can be determined.

The aim of this work was to verify the combustion technique for the determination of sulfur in nanostructured composites based on metal sulfides and metal oxides deposited on kaolinite and montmorillonite. The samples with low (<1 wt.%) and high (>1 wt.%) contents of sulfur were analyzed.

Keywords: Nanocomposite materials, clay minerals, chemical analysis, combustion techniques

1. INTRODUCTION

The growing number of research activities in nanotechnology is connected with the development of new materials that has to be precisely characterized by the means of chemical, phase and structural analysis. Chemical analysis of the developed materials commonly represents the first step of the characterization and reveals both the yield of given synthesis method as well as the presence of impurities in final reaction products.

Recently we introduced newly developed composite materials based on the: i) TiO$_2$ nanostructured particles captured at the surface of kaolinite or quartz via the hydrothermal synthesis with titanylsulphate [1, 2] and ii) CdS nanoparticles captured at the surface of montmorillonite [3]. Both kinds of composites show the application potential in the area of photocatalysis [4, 5]. In the case of the composites based on the sulfides the sulfur is present in a form of sulfide ion and its content is in direct relation with Cd content and gives the information about the yield of the synthesis. In the case of TiO$_2$ particles captured at the surface kaolinite and quartz prepared using titanyl sulphate the sulfur is presented in a form of sulfate ions and its amount is in direct relation with degree of washing treatment and has the influence on the structural changes of TiO$_2$ during the heat treatment. Although the role of sulfur present in above-mentioned composites is significantly different, the precise determination of its content is important task in the course of characterization of both composites.

There are a number of methods used for chemical analysis of materials. X-ray fluorescence spectroscopy (XRFS) is fast instrumental analytical technique used for determination of elemental composition of different kinds of materials in a form of powders, solid samples or even in a form of liquids [6]. For the powdered samples XRFS utilized generally three methods of the sample preparation. In the first method the powdered samples are placed in cuvettes, the second is based on the preparation of pressed pellets and the third is based on the preparation of fused pearls. The non-destructive character and low amount of sample required for the analysis are the main pros of cuvette technique. On the other hand, precision and accuracy are the often-discussed cons of this technique. XRFS performed on the pressed pellets offer more precise results in
comparison to cuvette technique, but it is destructive and requires higher amount of sample. Preparation of borate pearls requires lower amount of sample, but it is destructive and thermally less stable compounds can decompose during the preparation of pearls by fusion technique.

Scanning electron microscopy (SEM) is powerful technique used for the study of the surface morphology of samples and the modern SEM is also equipped with e.g. EDS or WDS (or both) detectors, which enable to perform local chemical analysis [7]. This method requires very low amount of sample but its ability to provide representative results is in the case of local analysis limited.

For total sulfur content determination combustion technique is fast non-labor method and requires lower amount of sample in comparison to XRFS. The method is based on the combustion of sample at high temperatures in presence of fusion ingredients (wolfram, pure iron) in a stream of oxygen. During the heating of the sample (most often induction heating) all of the forms of the sulfur are converted to sulfur dioxide which is then detected in infrared cell [8]. The combustion technique is most often utilized for analysis of metallic samples. The adaptation of this technique for analysis of sulfur in other matrices has to be carefully considered and tested.

Gravimetric determination of total sulfur content is based on the transforming of all of the sulfur forms into sulfate ions followed by precipitation of barium sulfate [9]. This technique is generally accepted to provide precise and accurate results, but requires higher amount of sample and is quite labor and time consuming.

The aim of this contribution is to analyze the total sulfur content at kaolinite/TiO₂ and montmorillonite/CdS composite using combustion method and to compare the results with the amounts of sulfur obtained using EDS and gravimetric analysis.

2. MATERIALS AND METHODS

2.1 Composites

Kaolinite/TiO₂ composites
The procedure for the kaolinite/TiO₂ (KATI) composites preparation is based on thermal hydrolysis of suspension of kaolinite in titanylsulfate. The preparation procedure was firstly introduced in [1] and revised in [10]. The titanylsulphate was obtained from Precheza a.s. and kaolinite KKAF from L.B. Minerals s.r.o. For the studies in present research the composite with 20 wt.% of TiO₂ dried at 100 °C was selected.

Montmorillonite/CdS composite
CdS nanoparticles were precipitated by the reaction of cadmium acetate and sodium sulphide in the presence of the stabilizing cationic surfactant cetyltrimethylammonium bromide. The originated CdS nanodispersion was shaken with montmorillonite (MMT) for 24 hours. The resulting nanocomposite of CdS and montmorillonite was then filtered and dried at 60-70 °C.

2.2 Methods for total sulfur content determination

Energy dispersive microanalysis
Morphological investigations of the composite particles were carried out with SEM Quanta FEG 450 (FEI) with EDS analysis (APOLLO X - EDAX). Samples were coated with Au/Pd film and the SEM images were obtained using a secondary electron detector. Point chemical analysis was performed in 5 independently selected particles.

Combustion analysis
Total sulfur content was determined using ELTRA CS 2000 combustion analyzer and analysis was conducted in an induction furnace. The weighted samples were placed in alumina crucible then wolfram
powder was added as an accelerator and high purity iron as a fusion agent. To assess the reproducibility of this method three parallel analyses of each sample were performed.

Gravimetric analysis

The gravimetric method of the analysis of sulfur content was performed according to ČSN 44 1379 [9]. In the first step the sample is melted at 820 °C with Eschka's mixture for 2 hours. After the cooling down of the mixture, hot distilled water and 1 ml of H₂O₂ (30 wt.%) is added. Then the mixture is heated up to 80 °C and kept 30 min at this temperature. Then it is heated up till the mixture starts to boil. After these steps the suspension is filtrated and filter cake is washed several times with distilled water whereas all of the liquid portions are collected in a baker. Next step comprises acidification of filtrate using HCl and sulfate ions are coagulated with approx. 10 ml of aq. solution of BaCl₂ (10 wt.%) while the BaSO₄ is precipitated. After the 12 hours long aging the suspension with precipitated BaSO₄ is filtered and several times washed with hot distilled water. Filter paper with filter cake is then calcinated at 850 °C for 2 hours in previously weighted annealing crucible. The difference of the weights of annealing crucible after the calcinations and empty annealing crucible used for the calcinations gives the weight of the BaSO₄, which is in direct relation to total amount of sulfur. With respect to amount of the sample needed for gravimetric method only composite kaolinite/TiO₂ was analyzed. To assess the reproducibility of this method two parallel analyses of the sample were performed.

3. RESULTS AND DISCUSSION

The morphology of both composites was studied using SEM. The image of the particles of kaolinite/TiO₂ composite is shown in Figure 1, while the morphology of the particles of the montmorillonite/CdS sample is shown in Figure 2.

**Fig. 1** Character of the particles of kaolinite/TiO₂ composite

**Fig. 2** Character of the particles of montmorillonite/CdS composite
The kaolinite particles are covered with consistent smooth layer of TiO$_2$ as evident in Figure 1, while in the case of montmorillonite/CdS composite the surface of montmorillonite particles is covered by CdS particles (Figure 2). The point EDS analysis was performed at the independent randomly selected particles for both samples and the obtained amounts of sulfur in each point are listed in Table 1. Taking into account the character of EDS point analysis it can be concluded that the measured values of sulfur in the case of composite kaolinite/TiO$_2$ do not show significant scatter and only the value 0.60 wt.% is outlying. Comparing the same data for composite montmorillonite/CdS (see Table 1) higher scatter is observed but taking account of significantly higher amount of sulfur in this composite, we can again conclude good agreement of the results. Point EDS analysis is very good method for determination of chemical composition of the powdered samples, but requires higher number of spots to be analyzed. Other benefit of SEM-EDS is also the possibility to obtain the information about the particles morphology. The disadvantage of the EDS method is the necessity for the performing of higher number of point analysis at the surface of different particles, and there is still the question about the representativeness of this analysis because only a negligible part of the sample is often analyzed.

**Table 1** The values of sulfur content (wt.%) in kaolinite/TiO$_2$ and montmorillonite/CdS composite determined using EDS analysis, combustion method and gravimetric method (only for kaolinite/TiO$_2$ composite)

<table>
<thead>
<tr>
<th>No. of measurement</th>
<th>kaolinite/TiO$_2$</th>
<th>montmorillonite/CdS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>EDS</td>
<td>combustion</td>
</tr>
<tr>
<td>1</td>
<td>0.37</td>
<td>0.423</td>
</tr>
<tr>
<td>2</td>
<td>0.39</td>
<td>0.438</td>
</tr>
<tr>
<td>3</td>
<td>0.60 -</td>
<td>0.412</td>
</tr>
<tr>
<td>4</td>
<td>0.40</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>0.34</td>
<td>-</td>
</tr>
<tr>
<td>Average</td>
<td>0.42 (0.38)</td>
<td>0.424</td>
</tr>
</tbody>
</table>

Although the weight of the sample used for combustion method depends on the total sulfur content and for the samples studied within this research it was 0.04 g, this amount of the sample is in contrast to EDS analysis significantly higher. The contents of the sulfur determined using combustion technique for both composites is listed in Table 1. The scatter of the values is low and in the case of kaolinite/TiO$_2$ composite the values of sulfur content are slightly higher in comparison to sulfur content analyzed using EDS. In the case of montmorillonite/CdS composite the values of sulfur content analyzed by combustion method fall into interval of the values analyzed using EDS. The combustion technique is fast and with respect to amount of the sample used for this analysis is more representative in comparison to EDS. This method is especially suitable if large sets of samples have to be analyzed, e.g. in the case of study of the effect of thermal treatment of the composite kaolinite/TiO$_2$ on the amount of the sulfur (see Fig. 3).
The most precise technique for total content of sulfur determination is gravimetric analysis [9]. Due to the requirement of the high amount of the sample this technique was used only for the determination of total sulfur content in composite kaolinite/TiO\(_2\). The results of two parallel analyses are listed in Table 1 and it is evident that the values are almost the same and average content of sulfur is very close to the average content of sulfur analyzed using combustion technique as well as EDS method (in the case of EDS it holds true if the outlying value 0.60 wt.% is also included). This agreement clearly shows all of the three methods as suitable for the determination of the sulfur content in the nanocomposites based on the nanosized metal oxides and metal sulfides captured at the surface of clay minerals.

4. CONCLUSIONS

Precise determination of the sulfur content in the composites based on metal oxides and metal sulfides nanoparticles captured at the surface of clay minerals can be achieved using all of the tested methods of chemical analysis. EDS analysis is labor, time consuming and expensive method and even if high numbers of spots are analyzed the representativeness of the results is still arguable. Gravimetric analysis is precise but labor and time consuming and it also requires high amount of the sample. Combustion technique is precise, representative, fast and requires lower amount of sample in comparison to gravimetric analysis.

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REFERENCES


