X-RAY FLUORESCENCE SPECTROMETRY ANALYSIS OF CLAY/ZnO COMPOSITES

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Abstract

Zinc oxide is one of the most studied materials with very good photocatalytic properties which are used in the photodegradation of pollutants occurring in environment. Natural clay minerals (such as kaolinite, montmorillonite, vermiculite etc.) as carrier and e.g. ZnCl\(_2\) as the source of zinc are suitable for the preparation of clay/ZnO composites, whereas their ratio gives the final ZnO content in final composites. XRFS represents suitable technique for the analysis of these composites. The main problem connected to the XRFS analysis is verifying of the ZnO content because of the unavailability of the reference materials with high content of ZnO (in the order of tenth wt.%). To avoid this limitation we prepared our own set of standards, which consists of selected clay minerals and given amount of pure ZnO to obtain the samples with required content of ZnO and to utilize them for calibration of X-ray fluorescence spectrometer. This work deals with the preparation of various reference materials, evaluation of homogeneity, creation of calibration curves and especially the development of the method for precise determination of ZnO content in composites using commercial software.

Keywords: zinc oxide, kaolinite, montmorillonite, vermiculite, x-ray fluorescence spectrometry

1. INTRODUCTION

ZnO has been widely used as a photocatalyst showing high photoactivity, low cost and environmentally friendly feature [1]. Capturing of the ZnO nanoparticles on the surface of suitable substrate leads to formation of composite materials which brings new benefits in comparison to bare ZnO nanoparticles. Clay minerals are natural materials with a wide range of applications, e.g. sorbents for heavy metals cations as Cd, Zn, and Pb etc. [2,3]. Different precursors of ZnO have been already tested in combination with clay minerals for preparation of clay/ZnO composites (e.g. ZnCl\(_2\) · 2H\(_2\)O [4], ZnSO\(_4\) · 7H\(_2\)O [5], Zn(CH\(_3\)COO)\(_2\) · 2H\(_2\)O [6]) and as well as different carriers based on clay minerals (kaolinite [6], montmorillonite [7]).

After the composites are prepared several characterization techniques are often utilized for their characterization. X-ray fluorescence spectrometry (XRFS) is a suitable method for chemical analysis of these materials, using x-ray diffraction analysis (XRPD) the phase composition can be analyzed and using scanning electron microscopy (SEM) the morphology of the prepared composites can be observed.

One of the significant tasks after the composite materials synthesis is related to the determination of their chemical composition. In the case of clay/ZnO composites it is mainly determination of ZnO content also with the aim to determine the yield of the synthesis procedure. XRFS is an analytical method often used for determination of the chemical composition of numerous kind of materials (solid, liquid, powder, filtered and other forms). XRFS method is fast, accurate and in some cases also non-destructive. Range of XRFS analysis application is very broad including metal, cement, oil, polymer, plastic and food industries, as well as mining, mineralogy, geology and environmental analysis of water and waste materials. XRFS is also very useful technique for pharmacy research [8].

Although the XRFS technique is common instrumental analytical method and numerous standard procedures have been established for the purpose of analysis of different materials, the main problem
connected to its direct utilization for characterization of newly developed materials is unavailability of reference materials with certificated content of given elements. The same problem is related to the clay/ZnO composites with the ZnO content in the order of tens of wt.%. This limitation can be overcome by preparing of the standards based on the mechanical mixtures of given clay mineral with known amount of pure ZnO. The prepared samples can be used for calibration of X-ray fluorescence spectrometer.

Present work deals with the development of new accurate method for determination of real content of ZnO in clay/ZnO composites using XRFS method. Preparation of our own reference materials, assessment of the homogeneity of these reference materials as well as verification of the reproducibility of their preparation is also described and discussed in present paper.

2. EXPERIMENTALS

2.1 Materials and methods

2.1.1 Materials

Kaolinite (KKAF), montmorillonite Ivančice (MMT), vermiculite Brazil (VMT) and talc (M) were used for preparation of reference samples. Pure zinc oxide (ZnO p.a.) purchased from Lach-Ner, Czech Republic was used as a source of Zn. FLUX-lite tetraborate – dilitiumtetraborate (Li₂B₄O₇) (FLUXANA, GmbH & Co. KG, Kleve, Germany) was used as a flux for preparation of pearls. Hoechst wax C micropowder (Merck KGaA, Darmstadt, Germany) was used as a binder for preparation of pellets.

2.1.2 X-ray fluorescence spectrometry analysis

Energy dispersive fluorescence spectrometer (XRFS) SPECTRO XEPOS equipped with 50 Watt Pd X-ray tube was used to excite the samples. The target changer, with up to 8 polarization and secondary targets, offers many different excitation conditions ensuring optimum determination of all elements from sodium to uranium. Measurements are performed in helium atmosphere. The detector is a state-of-art silicon drift detector (SDD). A spectral resolution of less than 160 eV for Mn K-alpha is achieved. The maximum count rate is 120,000 cps. The analyzer can handle samples with diameters up to 32 mm, 40 mm. We used X-LAB Pro software to control spectrometer functions and to evaluate data. Nominal input voltage is 120V/230V AC ± 10%, 50/60Hz. Liquid or solid samples could be measured.

2.2 Preparation of pellets

Pellets were pressed from the mechanical mixture of powder samples (4 g) and wax (0.9 g) using manual hydraulic press with applied load 10 tons. Prepared pellets had diameter 32 mm.

2.3 Preparation of fusions

The advantage of fusions is the high reliability of results, removing of the heterogeneity, substantial decrease of interelement influence, next benefit is lower consumption of sample in comparison to pellet technique. Typically 1g of sample and 8g of flux (Li₂B₄O₇) are weighted with accuracy 0,0001g into previously cleaned crucible (cleaning was performed in 15% aq. solution of citric acid at of 60-80°C in ultrasonic bath). Fusions were prepared in gas melting furnace “VULCAN 5 mA” from company HD Electronic. The device includes one burner for samples decomposition by melting and two positions for preparing fusions at main burners. Fusion is automatically flipped into Pt – Au casting plate with diameter of 40mm and gradually cooled.
2.4 Preparation of reference materials

Mixtures of selected clays with successively increasing content of ZnO (10, 20, 30, 40, 50, 60, 70, 80 and 90 wt.%) were prepared. The exact concentration of individual elements in used clay minerals (montmorillonite, vermiculite, kaolinite or talc) was determined by XRFS, whereas the results were traced on available certified reference materials (CRM) of clay minerals. The measured intensity of individual spectral lines obtained for prepared samples (fusions and pellets) was latterly used for creation of new calibration model.

2.5 Assessment of homogeneity of reference materials and reproducibility of sample preparation

Test of the homogeneity in the context of the prepared reference samples is verification of regular distribution of individual elements on a fusion’s or pressed pellet’s surface and is very important in the assessment of our reference samples (materials) and this test was performed using universal Turbo Quant method. Test of the homogeneity of the fusions and pressed pellets was performed using the mechanical mixture of 20% of zinc oxide with different clays (20%ZnO_MMT, 20%ZnO_VMT, 20%ZnO_KKAF and 20%ZnO_M). These samples were analyzed and evaluated using universal Turbo Quant method, whereas the measurement proceeded in nine different positions and also nine times in one position. Standard deviation of the results was calculated and compared for both measurements. To assess the reproducibility of the procedure of reference samples preparation five fusions and five pressed pellets with 20% of ZnO were prepared by the same method and subjected to analysis with newly developed XRFS method. As a measure of reproducibility the standard deviation was used.

2.6 The development of the method for the XRFS analysis of clay/ZnO composites

New method for analysis of fusions and pressed pellets based on the modification of the original method Turbo Quant was created. Three targets were used for the modification of the primary radiation from the Pd X-ray tube in fusions method:

- Compton/secondary target – molybdenum, energy of 25keV
- Secondary target – cobalt, energy 12.5 keV
- Bragg crystal material slot HOPG (highly oriented pyrolitic Graphite), energy 12.5keV

Moreover for the method pellets corundum Barkla Scatter target was used.

Measured intensities of individual spectral lines were used to create a new calibration model. A calibration model was based on a combination of methods of fundamental parameters and empirical model. Calculated values of concentration of elements were loaded to a new calibration model, whereas calibration curves for all monitored elements were calculated using the company software. After the new method was proposed, our prepared reference samples were again analyzed and evaluated using newly developed method for the verification of trueness of the new calibration model.
3. RESULTS AND DISCUSSION

The relative standard deviation values calculated from the results of the XRFS analyses of the fusions with 20 wt. % of ZnO performed in nine different positions (RSD9) and nine times in one position (RSD1) are given in Table 1. The values of RSD9 and RSD1 obtained for fusions are comparable and confirm very good homogeneity of the prepared RM standards. RSD values are low for most of the elements and fall into the interval 0 - 4 %. Contrary to the fusions the homogeneity for the pressed pellets is rather worse as revealed by comparison of the RSD1 and RSD9 values. It can be concluded that the homogeneity and reproducibility of the analysis using the samples in the form of fusions is better in comparison with pressed pellets.

**Tab. 1** Values of RSD of given analytes for the pressed pellets and for the fusions of the content 20% of ZnO, measured nine times in one position (RSD1) and in nine different positions (RSD9).

<table>
<thead>
<tr>
<th>Oxide</th>
<th>20%ZnO_MMT RSD9 (%)</th>
<th>20%ZnO_VMT RSD9 (%)</th>
<th>20%ZnO_KKAF RSD9 (%)</th>
<th>20%ZnO_M oxide RSD9 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>1.96</td>
<td>1.92</td>
<td>1.86</td>
<td>1.75</td>
</tr>
<tr>
<td>SiO₂</td>
<td>1.96</td>
<td>1.94</td>
<td>1.88</td>
<td>1.77</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.65</td>
<td>1.13</td>
<td>0.83</td>
<td>0.85</td>
</tr>
<tr>
<td>CaO</td>
<td>0.54</td>
<td>0.73</td>
<td>0.66</td>
<td>0.67</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.55</td>
<td>0.76</td>
<td>1.62</td>
<td>2.44</td>
</tr>
<tr>
<td>MnO</td>
<td>0.52</td>
<td>0.62</td>
<td>1.14</td>
<td>0.71</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.47</td>
<td>0.75</td>
<td>1.08</td>
<td>0.66</td>
</tr>
<tr>
<td>ZnO</td>
<td>0.47</td>
<td>0.91</td>
<td>1.22</td>
<td>0.66</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Oxide</th>
<th>20%ZnO_MMT RSD9 (%)</th>
<th>20%ZnO_VMT RSD9 (%)</th>
<th>20%ZnO_KKAF RSD9 (%)</th>
<th>20%ZnO_M oxide RSD9 (%)</th>
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<tbody>
<tr>
<td>Al₂O₃</td>
<td>14.90</td>
<td>0.85</td>
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<tr>
<td>SiO₂</td>
<td>12.22</td>
<td>0.95</td>
<td>15.99</td>
<td>1.91</td>
</tr>
<tr>
<td>K₂O</td>
<td>4.09</td>
<td>1.24</td>
<td>13.71</td>
<td>1.01</td>
</tr>
<tr>
<td>CaO</td>
<td>2.71</td>
<td>1.09</td>
<td>12.18</td>
<td>1.07</td>
</tr>
<tr>
<td>TiO₂</td>
<td>1.95</td>
<td>0.66</td>
<td>11.84</td>
<td>1.27</td>
</tr>
<tr>
<td>MnO</td>
<td>1.62</td>
<td>0.80</td>
<td>5.76</td>
<td>0.59</td>
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<tr>
<td>Fe₂O₃</td>
<td>2.39</td>
<td>0.48</td>
<td>6.39</td>
<td>2.27</td>
</tr>
<tr>
<td>ZnO</td>
<td>4.24</td>
<td>0.41</td>
<td>5.78</td>
<td>0.43</td>
</tr>
</tbody>
</table>
The reproducibility of the sample preparation for fusions as well as pressed pellets method is demonstrated by the values of RSD which are pictured in Fig. 1. The RSD values were calculated from the values of given oxide content measured for five independently prepared samples supposing to have the same composition. Comparing the values of RSD in Fig 1 we can conclude that the reproducibility of sample preparation in a form of fusions is very good. RSD values for pressed pellets, which are shown also in Fig. 1, are higher than those values obtained for fusions. Although it means that the reproducibility of sample preparation in a form of pressed pellets is worse in comparison to sample preparation in a form of fusions the results are still acceptable.

Fig.1 Relative standard deviations values of results of determination of chosen elements in fusions and pressed pellets (with 20 wt. % of ZnO) prepared repeatedly five times by the same method.

Finally, new methods for fusions and for pressed pellets based on the modification of the calibration model included in the original Turbo Quant method were developed. Prepared reference samples with 20 wt. % of ZnO were analyzed using new calibration models to verify their trueness. Our known (calculated) concentrations of ZnO (assigned as KM) compared with concentrations measured by the new methods (assigned as RM), are shown in Fig. 2. From this figure it is evident that the results are better for the fusions than for pressed pellets.

Fig.2 Comparison of calculated concentrations of ZnO content (KM) and concentrations measured by the new method (RM)
4. CONCLUSIONS

Clay/ZnO composites as a set of suitable reference materials for analysis were prepared from selected clay minerals and pure ZnO. The reference materials were prepared in the form of fusions and pressed pellets and used for the calibration of X-ray fluorescence spectrometer. Homogeneity of prepared reference materials and reproducibility of sample preparation were assessed. The results showed that the preparation of the samples of the clay/ZnO composites in a form of fusions is better way for accurate receiving of the accurate results obtained using XRFS analysis.

ACKNOWLEDGMENTS

The study was supported by Ministry of Education, Youth and Sports of the Czech Republic within the project LH 12184. This paper has been also elaborated in the framework of the Nanotechnology – the basis for international cooperation project, reg. No. CZ.1.07/2.3.00/20.0074 supported by Operational Programme ‘Education for competitiveness’ and financed by the Structural Funds and from the state budget of the Czech Republic.

LITERATURE