NITROGEN DOPPED COMPOSITE KAOLINITE/TiO₂

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Abstract

Photocatalysis over the nanosized titanium dioxide (TiO₂) is induced by ultraviolet irradiation, having the wavelength typically less than 380 nm. Only 5% of sunlight fulfill this demand what represents main limitation with respect to photocatalytic efficiency of TiO₂ under irradiation using day light. To avoid this limitation the TiO₂ doped with suitable elements is often prepared. One of the most promising procedures represents doping of TiO₂ with nitrogen. The capturing of the nanosized TiO₂ on the surface of clay minerals (e.g. kaolinite) brings several advantages whereas one of the most important is avoiding of the environmental risk related to nanodimension of bare TiO₂ nanoparticles. In this work the composites KATI16 (kaoline/TiO₂ composite containing 60 wt.% of TiO₂) were doped with nitrogen by the means of thermal treatment of the mixture of KATI16 and urea. Photocatalytic activity of the nitrogen doped KATI16 composite was proved by photodegradation of acid orange 7 after irradiation using light source with absence of UV component.

Keywords: TiO₂, anatase, photocatalysis, kaolinite, doping

1. INTRODUCTION

Titanium dioxide is a non-toxic semiconductor photocatalyst showing high photocatalytic activity. Its photoactivity is induced after activation with UV irradiation with energy approx. higher than 3.2 eV (band gap energy of pure anatase) whereas the electron-hole pair is generated [1, 2]. Photoactivated TiO₂ is able to degrade organic or anorganic impurities, but also viruses and bacteria, ideally up to carbon dioxide, water and other harmless products. Photocatalytically active nanosized TiO₂ is mainly used in a form of i) powder for cleaning of waste water and air and is also utilized for liquidation of toxic materials or ii) in a form of thin layers or films applied on various surfaces where the photodegradation activity of the surfaces is followed with antibacterial properties and superhydrophilic character. The photoinduced superhydrophilic character of the surfaces covered with TiO₂ cause also self-cleaning properties and resistance against fogging and thus these layers find wide application in a modern life [3].

Wavelength of photon required for activation of photocatalyst is about 380nm and lower, what corresponds to UV region of electromagnetic radiation. However this radiation makes up only 4-5% of the spectrum of incident sunlight and thus for effective photodegradation process the artificial sources of UV light are commonly used [1, 2]. From this reason the research activities focus on modifying the structure of TiO₂ with appropriate dopants, which shift photoactivity of TiO₂ into the visible zone (so-called red shift). Together with the shift of band gap to lower energies emphasis is put on the preparation of more efficient photocatalyst [4]. The most popular is doping TiO₂ with ions [1, 2], which leads to the band gap narrowing, increasing the separation of electrons and holes and improving efficiency in the visible light photoactivation. Doped ions, such as anions of nitrogen, sulphur or carbon, change the conductivity and optical properties caused by overlapping of p orbitals of anions with the 2p orbitals of oxygen [1].

In this paper, N-doped composite kaolinite/TiO₂ with 60 wt.% of TiO₂ (N-KATI16) was prepared via thermal treatment of the mechanically homogenized mixture of composite KATI16 and urea. The mixture was calcinated at temperatures 300, 400, 500 and 600°C and prepared samples were characterized using
infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX). Determination of photoactivity of prepared N-KATI16 composites and undoped KATI16 composites (thermally treated at the same conditions as N-KATI16) was conducted using degradation of organic dye acid orange 7 in a liquid phase under irradiation with visible light.

2. EXPERIMENTAL

2.1 Materials
Kaolinite (Al₂O₃·2SiO₂·2H₂O) is a clay mineral, whose surface can be used as a matrix to grow nanostructured TiO₂ particles whereas new kind of composite material kaolinite/TiO₂ (KATI) is obtained. The synthesis of this composite is described in work published by Mamulova Kutlakova et al. [5].

Urea ((NH₂)₂CO) is an organic compound and in our work served as a source of nitrogen. Deionized water was used for preparation of all the solutions for measurement of photodegradation activity.

2.2 Samples preparation
Milled and dried urea was mechanically homogenized with dried composite KATI16 in the ratio weight 1:1. The mixture was divided (approx. 2.0000 g) into the ceramic crucibles with ceramics covers and calcinated in muffle furnace. Calcination took place at temperatures 300, 400, 500 and 600 °C, with a rise time of 2 hours and delay time 1 hour at given temperature. During the calcination the colour of all of the mixtures changed from white to yellow as shown in Fig. 1.

Undoped samples KATI16, for which the calcinations in a crucible with a cover carried out at the same conditions, were prepared simultaneously with the mixtures KATI16 and urea. The samples were assigned KATI76 for undoped composites and N-KATI76 for nitrogen doped composites, where T is an shortcut for the calcination temperatures (3…300, 4…400, 5…500 and 6…600 °C).

2.3 Characterization methods

2.3.1 Infrared spectroscopy
The structure and the composition of samples N-KATI16 calcinated at different temperatures, original kaoline and powderized and dried urea were analyzed by infrared spectrometer (Nicolet 6700) with Fourier transform (FTIR) with a diamond ATR attachment working in the middle infrared region (4000 – 400 cm⁻¹).

2.3.2 Scanning electron microscopy, energy-dispersive X-ray spectroscopy
The morphology of the particles of samples KATI46 and N-KATI46 was observed using SEM QUANTA FEG 450 (3D). Samples were coated with Au/Pd film and the SEM images were obtained using a secondary electron detector. The composition of the samples was determined by EDX analysis.
2.3.3 Elemental analysis
Determination of total nitrogen in selected composites was performed using CHNSO Microanalyzer Flash 1112 from Carlo Erba company. This analysis was performed at the Institute of Rock Structure and Mechanics ASCR, v.v.i..

2.3.4 UV-VIS spectroscopy
For absorbance measurement the fiber optics spectrometr USB4000 (OceanOptics) was used.

2.4 Measurement of photodegradation activity
The prepared N-KATIT6 and KATIT6 composites (0.05g) were mixed with deionized water (65ml) and organic dye acid orange 7 (5ml, c = 6.10^-4 mol/l). The mixtures were stirred for one hour in darkness to achieve adsorption equilibrium. Then approx. 3ml of colloid suspension was taken by syringe and filtered using syringe filter and an absorbance A_0 at 465nm was measured. The residue of the solution was placed under the lamp (Osram Blue 36 W) and irradiated using the source of visible light. Light spectrum of this lamp is showed in Fig. 2. Except of visible part of electromagnetic radiation the spectrum of the lamp also contains UVA radiation at λ = 370 nm, which may affect the photoactivity of undoped KATIT6. After one hour irradiation absorbance A_1 was measured in the same way as the absorbance A_0. Photoactivity of the composites was determined from these measured values.

3. RESULTS AND DISCUSSION

3.1 Morphology and composition of the prepared samples
Increasing of calcination temperature leads to weight loss of samples as shown in Fig. 3. This decrease is more pronounced for mixtures containing urea, because the thermal decomposition of urea. When urea is heated above its melting point (132 - 135 °C) firstly a large amount of gaseous ammonia is released, while the residue is transformed to organic products, such as biuret or isocyanate acid.

Infrared spectra of doped samples N-KATIT6 are compared with spectra of pure...
kaolinite and urea in Fig. 4. Characteristic bands of kaolinite are visible in areas 3800 – 3600 cm$^{-1}$ and represent the valence vibrations of hydroxyl groups. The infrared spectrum of urea is characterized by bands with wavenumbers in the range 3500 – 3100 cm$^{-1}$ and band centered at 1600 cm$^{-1}$, which shows three typical vibrational stretching of the amide anion $–$NH$_2$, the vibrational stretching of carbonyl group C=O is indicated by the presence of bands in the region 1700 – 1650 cm$^{-1}$ and the bands characterizing asymmetric N-C-N stretching vibration lies in region 1450 – 1500 cm$^{-1}$ [6]. It is evident, that the samples calcinated at temperatures higher than 500°C show a gradual transformation of kaolinite to metakaolinite what is proved by disappearing of band in region 3800 – 3600 cm$^{-1}$ (see Fig. 4). IR spectra of the samples N-KATI76 calcinated up to 400°C also revealed the presence of products of thermal decomposition of urea.

![Infrared spectra of pure kaolinite, urea and calcinated composites N-KATIT6](image)

**Fig. 4** Infrared spectra of pure kaolinite, urea and calcinated composites N-KATIT6

Scanning electron microscope (SEM) equipped with EDX analyzer (SEM-EDX) was used for observation of surface topography and chemical analysis of samples N-KATI46 and KATI46. The surface topography of the sample KATI46 and N-KATI46 is shown in **Fig. 5a)** and **5b)** respectively. Comparing the surface topography of both samples obtained at the same magnification there is not any significant difference.

The presence of nitrogen in the N-KATI46 sample was qualitatively proved using EDX analysis, which is indicated in **Fig. 6** by blue arrow.

![Images of SEM a) KATI46, b) N-KATI46](image)

**Fig. 5** Images of SEM a) KATI46, b) N-KATI46
Tab 1. Elemental analysis of N-KATI46 and KATI46

<table>
<thead>
<tr>
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<th>N-KATI46</th>
<th>KATI46</th>
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<tbody>
<tr>
<td>w(N) wt.%</td>
<td>1.35</td>
<td>0.03</td>
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The elemental analysis was performed for samples calcinated at temperature 400°C and the results are reported in the Tab.1. Obtained data revealed higher content of nitrogen in the case of nitrogen doped sample N-KATI46.

3.3 Determination of photodegradation activity

Photodegradation activity of both samples calcinated at selected temperatures was expressed as decrease in absorbance of AO7 solution after 1 hour irradiation. The decrease in absorbance was calculated according to equation (1).

$$\Delta A = \left(\frac{A_0 - A_1}{A_0}\right) \cdot 100 \,[\%]$$

where $A_0$ is an absorbance before irradiation and $A_1$ is an absorbance after 1 hour irradiation.

The progress of dye degradation after the exposure of the suspension to the visible light is shown in Fig. 7. All samples show photocatalytic properties, whereas the nitrogen doped composites shows higher activity in visible region if they are heat treated up to 500°C. It is evident that the highest photodegradation activity shows sample N-KATI46. Calcination of N-KATI16 composites at 600°C (sample N-KATI66) led to decrease in photodegradation activity to same level as was determined for undoped sample KATI66.
4. CONCLUSION

The mechanical homogenization of mixture of KAT16 composite and urea followed by calcination was successfully used for the preparation of nitrogen doped composite N-KAT176. The N-KAT176 samples show more efficient photocatalytic activity under visible light than the undoped KAT176 if the calcination temperature does not exceed 500°C. The nitrogen doped composite prepared in a crucible with a cover calcinated at 400 °C shows the highest photoactivity under visible light, whereas the extent of AO7 degradation is 4 times higher in comparison to undoped composite KAT146.

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LITERATURE


