



Preparation and characterization of photoactive composite kaolinite/TiO₂

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ABSTRACT

Preparation of nanocomposite kaolinite/TiO₂, using hydrolysis of titanyl sulfate in the presence of kaolin was addressed. A variable (kaolin)/(titanyl sulfate) ratio has been used in order to achieve the desired TiO₂ content in prepared nanocomposites. Calcination of the composites at 600 °C led to the transformation of the kaolinite to metakaolinite and to origination of metakaolinite/TiO₂ composites. The prepared samples were investigated using X-ray fluorescence spectroscopy, X-ray powder diffraction, Fourier transform infrared spectroscopy, scanning electron microscopy, thermogravimetry and diffuse reflectance spectroscopy in the UV–VIS region. Structural ordering of TiO₂ on the kaolinite particle surface was modeled using empirical force field atomistic simulations in the *Material Studio* modeling environment. Photodegradation activity of the composites prepared was evaluated by the discoloration of Acid Orange 7 aqueous solution.

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1. Introduction

Nanosized titanium dioxide (TiO₂) is the most frequently studied photocatalyst currently. The surface and structural properties of TiO₂ were summarized in detail by Diebold [1]. Titanium dioxide may occur in three modifications according to ambient conditions – anatase, brookite and rutile. Among these modifications, the anatase form is a material with promising properties due to its high photocatalytic activity. The principle of the photodegradation mechanism of TiO₂ can be found in the review article published by Carp et al. [2].

Many techniques are utilized for TiO₂ nanoparticles synthesis and the article published by Xiabo and Mao [3] offers

Abbreviations: E_{ad} , adhesion energy [kcal]; E_{tot} , total energy of the nanocomposite [kcal]; $E_{tot,KLT}$, total energy of the kaolinite substrate [kcal]; E_{tot,TiO_2} , total energy of the TiO₂ nanoparticle [kcal]; K, kaolin; K6, kaolin calcined at 600 °C; KATI, titanium oxide nanoparticles/kaolinite nanocomposite; KATI12, composite dried at 105 °C and containing 20 wt.% of TiO₂; KATI14, composite dried at 105 °C and containing 40 wt.% of TiO₂; KATI16, composite dried at 105 °C and containing 60 wt.% of TiO₂; KATI62, composite calcined at 600 °C and containing 20 wt.% of TiO₂; KATI64, composite calcined at 600 °C and containing 40 wt.% of TiO₂; KATI66, composite calcined at 600 °C and containing 60 wt.% of TiO₂; KLT, kaolinite; M, muscovite; MKLT, metakaolinite; MS, Accelrys Materials Studio modeling environment; Q, quartz; QEq, charge equilibration method; TiO₂(1), pure TiO₂ powder dried at 105 °C; TiO₂(6), pure TiO₂ powder calcined at 600 °C; UFF, universal force field.

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their overview. The sol–gel procedure is among the most frequently used methods and the common precursors are titanium(IV) alkoxides, mainly titanium(IV) tetraisopropoxide, and titanium(IV) *n*-butoxide (or titanium(IV) tert-butoxide) [4,5]. In spite of numerous advantages connected with these precursors, the unquestionable fact is that they are too expensive to be employed for preparation of large scale samples. Consequently a large effort has been devoted towards use of low cost intermediates: mainly titanylsulfate (TiOSO₄) [6] and titanium tetrachloride (TiCl₄) [7], which are obtained during the sulfate or the chloride procedure of TiO₂ white-pigment manufacturing.

The main application of anatase is in the field of photocatalysis, especially degradation of environmental contaminants. Photodegradation activity of TiO₂ is proven with degradation of model substances presented in liquid as well as in gaseous phase. The anatase may allow for degradation of organic dyes [8], phenol [9], pesticides [10] in liquid phase, e.g., in contaminated waters. In a gaseous phase the degradation of nitric oxides [11], toluene [12] and formaldehyde [13] was observed. Photodegradation test with organic dyes represents an easy and fast estimation of TiO₂ photodegradation activity. The rate of the degradation can be monitored by the change in the absorption of the dye solution by the UV–VIS spectrometry. In the case when TiO₂ forms a finely dispersed suspension in a dye solution, the photocatalyst has to be removed by filtration or ultracentrifugation before a measurement of UV–VIS absorption. The complete separation of TiO₂ is almost impossible if its size is in the order of nanometers. If the TiO₂

nanoparticles are fixed on the surface of the suitable particulate substrate, then separation of the photocatalyst can be accomplished easily by filtration or, in the case of bigger carrier particles, by sedimentation.

Despite the fact that TiO_2 is referred as a material with very low toxicity [14,15], there are many studies dealing with possible hazards of TiO_2 nanoparticles [16]. This issue becomes important during entire life cycle of a material containing TiO_2 nanoparticles, which can be potentially released to the environment during manufacturing, usage or disposal. Paints containing nanosized photocatalysts, as well as the polymer/ TiO_2 nanocomposites, represent possible danger by the means of releasing of nanosized particles due to the deterioration of material cohesion [17,18]. Growing and anchoring of the nanosized TiO_2 particles on the surface of a suitable substrate prevents the release of nanoparticles to the environment, whereas the substrates can represent an inert part [19], or can bring additional functions at final composite [20,21]. A number of substrates has already been studied for anchoring of the TiO_2 on their surface. Preparation of a TiO_2 thin layer on glass substrates by dip or spin coating is widely investigated [22,23]. The resulting glass shows superhydrophilicity which is reflected in anti-fogging and self-cleaning properties. Silica particles were also studied as a matrix for TiO_2 growth and many authors showed, that the prepared $\text{SiO}_2/\text{TiO}_2$ composites have improved photodegradation activity against model pollutants [24,25].

Phyllosilicates are abundant natural materials with a wide scale of practical applications (among others, as sorbents for cations of heavy metals Cd, Zn, Pb, etc. [26]). Due to their unique crystallochemical properties, phyllosilicates represent a suitable matrix for anchoring of TiO_2 nanoparticles [27–29]. Montmorillonite belonging to the 2:1 phyllosilicate group is mentioned more often as a matrix for TiO_2 nanoparticles than other phyllosilicates like vermiculite, kaolinite, saponite, hectorite, etc. In most cases the preparation procedure uses titanium alkoxides as the precursors for clay/ TiO_2 composites preparation. Kameshima et al. [30] described preparation of montmorillonite/ TiO_2 composite using titanium(IV) tetra iso-propoxide and demonstrated enhanced photodegradation activity of the prepared composite against 1,4-dioxane in comparison to pure photoactive anatase. Machado et al. [31] used exfoliated vermiculite (also belonging to 2:1 group) particles with size in the range of 0.2–0.5 mm and titanium tetraisopropoxide for preparation of the vermiculite/ TiO_2 composite. Prepared composite floats on the water surface and shows enhanced photodegradation activity against textile dye Drimaren Red. Kaolinite (1:1 group) as a substrate for nanosized TiO_2 growing was used by Chong et al. [32]. They described a two-step procedure for the KATI composite preparation using titanium(IV) butoxide. Prepared composite showed enhanced photodegradation ability against dye Congo Red.

In this work we focused on the preparation and characterization of the KATI composites using thermal hydrolysis of kaolin and TiOSO_4 suspension. Using a simple hydrothermal procedure the composites containing 20 wt.%, 40 wt.% and 60 wt.% of TiO_2 were prepared. Prepared samples were characterized by X-ray powder diffraction method (XRPD), X-ray fluorescence spectroscopy (XRF), Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). Specific surface area was characterized using the Brunauer–Emmett–Teller (BET) method, thermal properties were studied with thermogravimetric analysis (TG), and UV–VIS diffuse reflectance spectroscopy (UV–VIS DRS) was used for characterization of optical properties of composites prepared. Photoactivity of the prepared composites was evaluated by means of photodegradation of Acid Orange 7 (AO7) model solution. Atomistic simulations using an empirical force field in the *Materials Studio* (MS) modeling environment have been carried out in order to study structure and adhesion forces in the KATI composite.

Table 1

Chemical composition of raw K and prepared composites KATI12, KATI14 and KATI16 (in wt.%). LOI, lost on ignition.

Sample	Al_2O_3	SiO_2	SO_3	K_2O	TiO_2	Fe_2O_3	LOI
K	32.4	52.1	<0.00050	1.450	1.15	0.640	10.9
KATI12	21.8	37.4	1.56	1.070	25.8	0.532	12.5
KATI14	15.0	25.6	3.13	0.707	42.5	0.288	14.9
KATI16	9.1	16.1	4.53	0.433	57.2	0.144	16.0

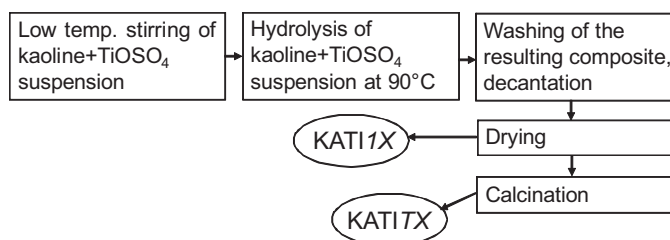


Fig. 1. The scheme of synthesis procedure for composites KATI.

2. Materials and methods

2.1. Sample preparation

Kaolin (K) sample SAK47 (LB MINERALS s.r.o.) was dried for 3 h at 105 °C in order to remove the adsorbed water, and the chemical composition of dried sample K is shown in Table 1. TiOSO_4 (PRECHEZA a.s.) containing 102 g of TiO_2 per 1 dm³ of suspension was used as a TiO_2 precursor. In a typical experiment 50 g of K is mixed with an appropriate volume of TiOSO_4 to give the desired amount of TiO_2 in the final composite. The composites are denoted as KATI1X or KATI6X, where symbol 1 means that the composite was dried at 105 °C, symbol 6 shows the calcination temperature (600 °C for 2 h), symbol X denotes the amount of TiO_2 in the final composite (2 for 20 wt.%, 4 for 40 wt.%, 6 for 60 wt.%). The procedure scheme is shown in Fig. 1.

As a reference sample the pure TiO_2 powder was prepared in the same way as presented in Fig. 1 and denoted as $\text{TiO}_2(1)$ and $\text{TiO}_2(6)$, respectively.

2.2. Characterization methods

2.2.1. X-ray fluorescence

Chemical composition of the prepared samples was determined using energy dispersive fluorescence spectrometer (XRFS) SPECTRO XEPOS (SPECTRO Analytical Instruments GmbH) equipped with 50 W Pd X-ray tube. The samples analyzed were prepared in the form of pressed tablets (wax was used as binder) for this measurement.

2.2.2. Combustion method (determination of sulfur content)

Sulfur content was determined using the CS244 carbon/sulfur analyzer (LECO Corporation) equipped with an induction furnace HT1000. Combustion process was realized in ceramic crucibles filled with 1 g of flux LECOCEL (tungsten particulates) and 1 g of iron chip accelerator.

2.2.3. Scanning electron microscopy

The morphology of composite particles was observed by SEM Philips XL 30 (PHILIPS). Samples were coated with an Au/Pd film and the SEM images were obtained using a secondary electron detector. Elemental composition of samples was determined using energy dispersive X-ray analysis (EDS).

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