Parameters of Siliciferous Substrate of Photocatalytic Composition Material as a Factor of Its Efficiency

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Abstract. The article presents the results of the determination of the properties of the photocatalytic composite material (PCM) of the “TiO₂ – SiO₂” system synthesized by the sol-gel method. The characteristics of siliciferous raw material - diatomite and silica clay, as substrates in the composition of PCM - mineral composition, microstructural features, composition and concentration of active centers on its surface are determined. The dependences of the elemental composition of the surface, the features of the microstructure and photocatalytic activity of PCM on the properties of siliciferous raw material are found. The research shows that the use of diatomite makes it possible to obtain PCM with better characteristics, which is caused by a higher content of the amorphous phase, a more developed and chemically active surface of the particles.

Keywords: Siliciferous raw material · Titanium dioxide ·
Sol-gel · Photocatalysis · Microstructure · Activity

1 Introduction

The production of photocatalytic composite materials (PCM) of the “TiO₂ – SiO₂” system is aimed at increasing the efficiency of photocatalytic decomposition of pollutants (Arai et al. 2006; Guo et al. 2016). The peculiarities of physical and chemical interaction of siliciferous and titanium-containing components in the synthesis and use of PCM directly affect its photocatalytic activity. In this regard, it is important to study the influence of the properties of siliciferous raw materials on the final characteristics of PCM.

2 Methods and Approaches

As a siliciferous raw material and as a substrate in the composition of the photocatalytic composite material, the Diasil diatomaceous fine dispersed powder (specific surface $S_s = 1.39 \text{ m}^2/\text{g}$) was used (Diamix, Ulyanovsk region, Russia); fine-ground silica clay ($S_s = 1.08 \text{ m}^2/\text{g}$) (Alekseevskii deposit, Mordovia, Russia) were used. The determination of the mineral composition of siliciferous raw materials was carried out using an

ARL 9900 WorkStation X-ray fluorescence spectrometer. The peculiarities of microstructure and elemental composition of the surface were studied with the help of TESCAN MIRA 3 LMU high resolution scanning electron microscope. The acid-base characteristics of the surface of siliciferous raw materials were studied using the indicator method (Nechiporenko 2017; Nelyubova et al. 2018).

The production of composite material of the $\text{TiO}_2 - \text{SiO}_2$ system was obtained by the sol-gel method using a titanium-containing organic precursor—titanium butoxide $\text{Ti}(\text{OC}_4\text{H}_9)_4$ (TBT) (TU 6-09-2738-89, “PROMHIMPERM”, Russia). It was dissolved in ethanol, and then the siliciferous substrate (SS) material was introduced into the resulting solution, in a ratio of “TBT/SS” - 4/1. After stirring it on a magnetic mixer, the material was dried and burned at 550 °C.

Then, the tablets were prepared from the obtained materials of the “ $\text{TiO}_2 - \text{SiO}_2$ ” system. White cements CEM I 52, 5 R (Adana, Turkey) was used as a binder. The ratio $\text{TiO}_2 - \text{SiO}_2/\text{cement}$ is 1.3/1. The photocatalytic activity was determined using the photocatalytic decomposition method of the organic pigment Rhodamine B (Rhodamine B , $\text{C}_{28}\text{H}_{31}\text{ClN}_2\text{O}_3$). The pigment was applied to the tablets at a concentration of $4 \cdot 10^{-4}$ mol/l. The samples were kept for 4 and 26 h under ultraviolet radiation (UV-A, 1.1 ± 0.1 W/m²). The evaluation of color change, as an indicator of the effectiveness of self-cleaning of the surface, was carried out according to the Lab color space (coordinate a) using software (Guo et al. 2016).

3 Results and Discussion

Diatomite is a sedimentary biogenic rock consisting of microscopic siliciferous shells of algae (diatoms) with a valve size of 5–200 μm . The presence of nanoscale pores and elements is shown on the Fig. 1a. Silica clay is of sedimentary biogenic and chemogenic origin, composed mainly of opal-cristobalite silica particles with a size of less than 5 μm . It is a microporous rock and the content of organic fragments is insignificant (Fig. 1b). The mineral composition of the raw material is similar; a higher content of the amorphous phase is found in the composition of diatomite (Table 1).

Fig. 1. Microstructure of siliciferous raw materials: a – diatomite, b – silica clay

Table 1. Mineral composition of siliciferous raw material

<i>Siliciferous raw material</i>	<i>α-Quartz</i>	<i>Cristobalite low</i>	<i>Tridimite low</i>	<i>Illite 2M1</i>	<i>Albite</i>	<i>Amorphous</i>
Diatomite	9.35 ± 0.72	40.57 ± 4.22	4.21 ± 0.90	2.44 ± 0.89	0.53 ± 0.20	42.90
Silica clay	17.36 ± 0.72	31.63 ± 1.42	14.63 ± 1.31	3.42 ± 0.65	0.54 ± 0.12	32.42

The presence of a high concentration of acid sites characterized by proton acidity (Brønsted) is noted on the surface of diatomite (Table 2).

Table 2. The composition and concentration of active centers on the surface siliciferous raw materials ($q \cdot 10^{-3}$, mEq/g)

<i>Siliciferous raw material</i>	<i>pK_a</i>				
	−0.29	+0.80	+7.15	+12.00	+12.80
	Lewis bases	Bronsted acids		Bronsted bases	
Diatomite	53.11	490.43	54.09	47.95	55.80
Silica clay	115.90	No data	20.51	98.68	13.41

The photocatalytic activity of PCM based on diatomite (Table 3) is high and close to the control specimen – the industrial nano-sized Aeroxide TiO₂ P25 photocatalyst.

Table 3. Elimination of Rhodamine B, %

<i>Time</i>	<i>Aeroxide TiO₂ P25</i>	<i>Diatomite</i>	<i>TiO₂–SiO₂ (diatomite)</i>	<i>Silica clay</i>	<i>TiO₂–SiO₂ (Silica clay)</i>
4 hours	29	9	29	1	5
26 hours	91	61	86	43	68

The analysis of the peculiarities of the microstructure and elemental composition of the surface of synthesized PCM based on diatomite (Fig. 2a) and silica clay (Fig. 2b) shows that the silica particles are partially covered with titanium-containing new formations. The surface of PCM particles based on diatomite is more developed; the distribution of the titanium-containing phase is more even.

Fig. 2. Microstructure of PCM on the basis of: a – diatomite, b – silica clay (with mapping by elements)

4 Conclusions

The siliciferous raw material differs in morphology, concentration of acid-base centers and content of the amorphous phase: the surface of the diatomite is more developed, characterized by a high concentration of proton acid centers; it has a higher content of the amorphous phase in its composition. As a result, the photocatalytic activity of PCM synthesized on the basis of diatomite is higher by 20% in comparison with PCM on the basis of silica clay. In order to improve the efficiency, it is advisable to consider the possibility of pre-activation of silica clay, which will allow using this waste (by-product) rock to produce modern self-cleaning materials.

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