PHOTOCATALYTIC ACTIVITY OF COMPOSITE MATERIALS BASED ON ZEOLITES AND TiO_2 NANOPARTICLES

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ABSTRACT

The photocatalytic degradation of an organic dye Acid Orange 7 (AO7) was investigated over composite materials based on zeolites, natural (clinoptilolite) and synthetic (ZSM-5 and 13X), and TiO_2 nanoparticles under simulated solar irradiation. The composites were prepared by the ultrasound assisted solid state dispersion method. Obtained materials were characterized by X-ray powder diffraction, FT-IR and UV-Vis diffuse reflectance spectroscopy. Successful degradation of AO7 was confirmed for all investigated composite materials. The best photocatalytic efficacy was achived using composite made of ZSM-5 zeolite and 10 wt% of TiO_2 nanoparticles, which degraded 93 % of organic dye after 30 min of irradiation.

Keywords: zeolite, TiO_2 nanoparticles, photocatalytic activity.

INTRODUCTION

The rapid industrial growth has caused serious environmental problems by release of urban, industrial and hospital waste waters containing various organic pollutants to the surface waters [1]. For this reason, various technologies have been developed for the treatment of waste waters and among them a heterogeneous photocatalytic degradation has emerged as very promissing because it is environmentally friendly and inexpensive [2]. Applications of TiO_2 semiconductor for water purification have been widely studied [3,4]. Its advantageous properties are low cost and toxicity, good physical and chemical stability and high photocatalytical efficiency for degradation of different harmful organic compounds. In order to improve the photocatalytic activity of TiO_2 nanoparticles and to overcome the costly process of its filtering in the wastewater treatment applications, TiO_2 is deposited on solid supports like zeolite, glass, silica [5-7]. Moreover, the tendency of TiO_2 nanoparticles to agglomerate is reduced by using support, like zeolites, with a large surface area. The zeolites also possess photochemical stability, high adsorption capacity and transparency to ultraviolet/visible radiation which is important for the application in photocatalysis [8].

In this study, composite materials based on zeolites and TiO_2 nanoparticles were synthesized by simple preparation procedure and characterized by X-ray powder diffraction (XRPD), FT-IR and UV-vis diffuse reflectance (DR) spectroscopy. Photocatalytic activity of obtained materials was tested by degradation of dye Acid Orange 7 (AO7) in water. Our aim was to study the role of zeolites in composites with nanosized TiO_2, by comparing different zeolitic structures of synthetic zeolites, ZSM-5 and 13X, and cheap and abundant natural zeolite, clinoptilolite, in order to produce efficient photocatalyst.

EXPERIMENTAL

Natural zeolite clinoptilolite (Cli) from Zlatokop mine, Serbia, and two synthetic zeolites, NH_4-ZSM-5 (Si/Al = 40) from Zeolyst and 13X (Si/Al = 1,2) from Union Carbide were used as support for Degussa P25 TiO_2 nanoparticles (70 % anatase and 30 % rutile phase). Prior to composite synthesis, NH_4-ZSM-5 was transformed to HZSM-5 form by

calcination at 500 ^{o}C for 5 h. The different amounts of TiO_2, 5, 10 and 20 wt%, were thoroughly mixed with investigated zeolites in an agate mortar. Then, in a 10:1 ratio (ethanol ml/solid powder g), samples were mixed with ethanol, used as a dispersing agent, and sonicated for 4 h at 80 ^{o}C by RK52H with a frequency of 35 Hz and power of 240 W. Obtained samples were dried overnight at 80 ^{o}C and calcinated in air at 500 ^{o}C for 5 h. The synthesized composites were denoted as e.g. TCli-5, TZSM5-5 and T13X-5, where T indicates TiO_2,Cli, ZSM5 and 13X indicate type of starting zeolite, and number corresponds to wt% of used TiO_2.

XRPD patterns were collected on RigakuUltima IV diffractometer in Bragg-Brentano geometry, using Cu Kα radiation (λ=1.54178 Å) from 4° to 50° 2θ in 0.020° step with acquisition rate of 1°/min. The phase identification was made based on JCPDS tables. UV-Vis DR spectra were recorded on Agilent Cary Uv-Vis-NIR 5000 spectrophotometer equipped with an integrated sphere in the range from 200 to 600 nm. FT-IR spectra were recorded on Nicolet 6700 spectrometer in the wavenumber range from 4000 cm^{-1} to 400 cm^{-1} by using KBr pellets technique.

The photocatalytic activities of all investigated materials were evaluated by measuring the degradation of test dye molecule AO7. The reaction was performed with 30 ml of $2{,}85x10^{-5}$ $molL^{-1}$ of dye aqueous solution containing 1 gL^{-1} of catalyst under constant stirring, illumination and O_2 flow. In order to establish adsorption-desorption equilibrium, the suspensions were stirred in the dark for 15 minutes, before illumination. The light source was a lamp (Osram Vitalux 300 W) that simulated solar irradiation. The distance between lamp and experimental dispersion was 30 cm [9]. Aliquots (1 mL) were taken both before and after illumination at designated time intervals, and centrifuged (11000 rpm, 15 min) in order to remove particles of photocatalyst. The concentration of AO7 dye in supernatant was measured as the maxima (λ = 486) in the absorption spectra. UV-Vis spectra of aliquots were recorded on Thermo scientific evolution 600 spectrophotometer in range from 350 to 750 nm.

RESULTS AND DISCUSSION

XRPD patterns of starting zeolites and composite materials with 10 wt% of TiO_2 are shown in Figure 1. The characteristic diffraction peaks of clinoptilolite mineral are present together with peaks originating from quartz (2θ=20.8^{o}, 26.68^{o}) and feldspar (2θ=21.9^{o}, 23.6^{o}, 27.7^{o}) phases. Also, crystal structures of starting zeolites ZSM-5 and 13X were confirmed by the detection of characteristic peaks. The XRPD patterns of all investigated composites displayed the characteristic peaks of used zeolites (Cli, ZSM-5, 13X) and peaks originating from TiO_2 anatase phase at 2θ=25.2^{o} and 48.1^{o} for TZSM5-10 and T13X-10, and at 2θ=25.3^{o}, 37.7^{o}, 48.1^{o} for TCli-10 composite. Thus, the XRD patterns of photocatalysts showed that structures of starting zeolites have not been affected by TiO_2 loading.

The UV-vis DR spectra of the TiO_2 nanoparticles, starting zeolites and composites are presented in Figure 2. The band gaps values for all investigated samples, calculated based on Kulbeka-Munk function and Tauc theory [10], are given in Table 1. These values were determined by drawing tangent through linear segment on Tauc plot (inset Figure 2), and extrapolating to x-axis intercept. The similar values for band gap energy were obtained for TiO_2 nanoparticles and composites. This finding shows that the preparation procedure did not affect significantly the optical properties of TiO_2 nanoparticles.

The results of dye AO7 photocatalytic degradation in the presence of composites based on ZSM-5 zeolite with different TiO_2 loading are presented in Figure 3. Clearly, composite TZSM5-10 showed the best photocatalytic activity. The analogous results were obatined for other investigated catalysts. The composites with 10 wt% of TiO_2 for all investigated zeolites showed the highest activity in comparison to composites with 5 wt% and 20 wt% of TiO_2.

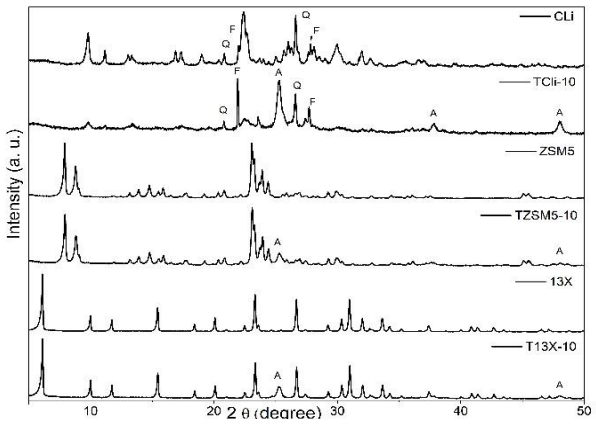

Figure 1. XRPD patterns of bare zeolites and synthesized photocatalysts. Abbreviations: A-anatase, Q-quartz and F-feldspar.

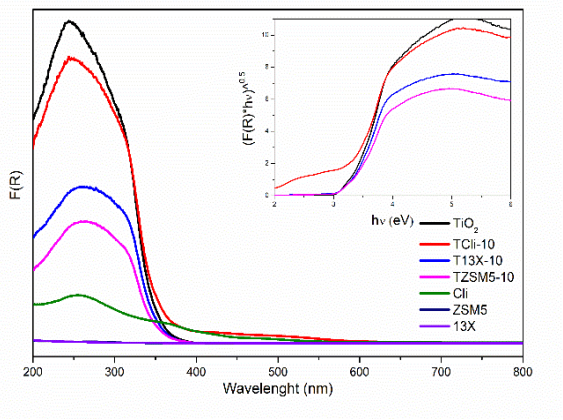

Figure 2. UV-Vis DR spectra of bare zeolites and synthesized photocatalyst; inset: the Tauc plots.

Figure 4 shows the photocatalytic degradation of AO7 dye in the presence of TZSM5-10, TCli-10, T13X-10, and pure TiO_2. In order to compare photocatalytic activity of prepared composites and pure TiO_2, the amount of used TiO_2 in photodegradation experiment corresponded to 10 wt% of catalyst loading. Results presented in Figure 4 reveal that during photocatalytic experiments with starting zeolites neither adsorption nor photocatalytic degradation of AO7 dye occured.

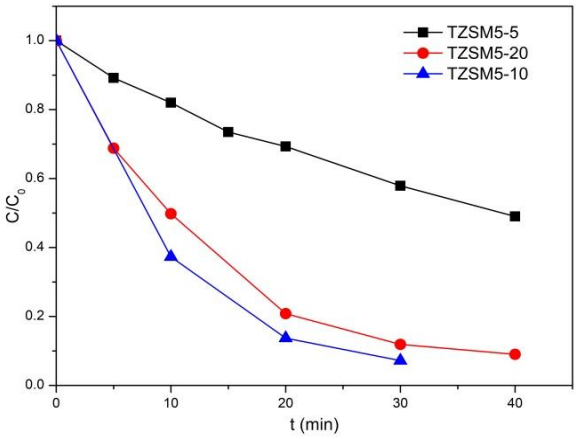

Figure 3.Photodegradation of AO7 dye over composites based on ZSM-5 zeolite and TiO_2.

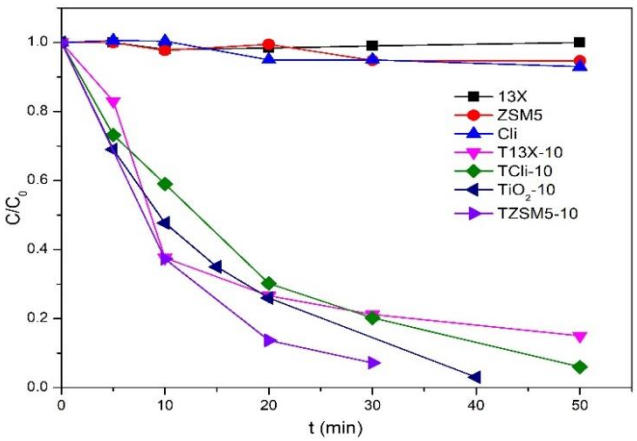

Figure 4. Photodegradation of AO7 dye in the presence of starting zeolites, composites and bare TiO_2.

Sample TZSM5-10 showed the maximum photocatalytic efficacy compared to all other investigated samples including the pure TiO_2 (Figure 4). TZSM5-10 degraded 93 % of dye after 30 minutes of irradiation. The photocatalyst TCli-10 showed slightly higher degradation activity (94 % after 50 min) compared to T13X-10 which degraded 85 % of AO7 for the same time of irradiation. The photocatalytic reaction of most organic compounds can be described by pseudo-first order kinetic model [2]. It is based on approximation that the concentration of used dye is low ($K_{ads}C_e < 1$), and following equation can be applied:

$$\frac{dC}{dt} = k_{app}K_{ads}C_e \qquad (1)$$

where k_{app} is rate constant, K_{ads} adsorption constant and C_e concentration [9]. The rate constants are calculated as slopes of straight lines for each sample and presented in Table 1.

Table 1. The degradation rate constants, percentage and time of AO7 degradation and bang gap values for pure TiO_2 and prepared composites.

Sample	k_{app} (min^{-1})	Degradation AO7 (%)	t (min)	Band gap (eV)
TiO_2	0.0488	97	40	3,33
TZSM5-10	0.0559	93	30	3,30
TCli-10	0.0559	94	50	3,25
T13X-10	0.0455	85	50	3,31

In FT-IR spectra of all investigated composites bands originating from stretching vibrations of Ti-O-Si and Ti-O-Al were not detected, indicating that TiO_2 nanoparticles were dispersed on the surface of zeolites. Performance of photocatalyst is highly affected by the crystal structure, size, shape, surface charge and optical properties of catalyst particles [2]. The used zeolites Cli, 13X and ZSM-5 are very different in terms of their structure and textural features. The best performance of TZSM5-10 composite can be attributed to the specific structure of ZSM-5 zeolite.

CONCLUSION

This study showed successful degradation of AO7 dye by prepared photocatalysts. Investigated zeolites have proven to be suitable support for TiO_2 nanoparticles. In order to create highly efficient photocatalysts, the future research will be focused on combining different sources of TiO_2 (colloidal and nanotubes) and zeolites, primarily low cost and abundant natural zeolite clinoptilolite.

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