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PHYSICOCHEMICAL AND PHOTOCATALYTIC INVESTIGATIONS OF MECHANOCHEMICALLY TREATED TiO_2-ZnO COMPOSITES

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Abstract

The nanodimensional TiO_2-ZnO composites in different weight ratios 1:1; 1:2 and 2:1 were prepared by mechanochemical activation. As starting materials were used ZnO synthesized by precipitation and commercial TiO_2. The phase composition and structure of obtained mechanochemically activated nanosized TiO_2-ZnO samples were confirmed by X-ray diffraction analysis and Fourier transform infrared spectroscopy. The produced materials were examined as catalysts for degradation of Reactive Black 5 dye under UV light. The results show the relation between photocatalytic activity of prepared samples TiO_2-ZnO and stoichiometric ratio of TiO_2 and ZnO in the mixture. The rate constants of dye degradation increase as follows TiO_2-ZnO (1:2) ($2.16x10^{-2}$ min^{-1}) < TiO_2-ZnO (2:1) ($2.45x10^{-2}$ min^{-1}) < TiO_2-ZnO (1:1) ($2.60x10^{-2}$ min^{-1}).

Key words: *TiO_2-ZnO composites, mechanochemical activation, photocatalytic properties*

1. INTRODUCTION

The polycrystalline TiO_2 and ZnO in pure form and as a mixture are semiconductor oxides widely used in liquid-solid and gas-solid photocatalytic reactions (Marcì et al. 2001). The various pollutants such as, dyes, pesticides, detergents and volatile organic compounds can be degradate under UV light irradiation through the photocatalytic ability of such semiconductors. Both oxides TiO_2 and ZnO are classified as wide band-gap semiconductors and have similar band-gap energies around 3.2 eV. When the semiconductor surfaces interact with UV-light, electron/hole pairs are generated. Photoexcitation of an electron from valence band to conduction band leaves a hole behind (Konyar et al. 2010). The mechanochemical activation of solids is promising method for synthesis of catalysts with novel properties and improved catalytic activity and selectivity (Buyanov et al. 2009, Baláž et al. 2013). Nanodimensional powders $(TiO_2)_x(ZnO)_{1-x}$ were prepared by mechanochemical processing and their photocatalytic activity was tested by measuring hydroxyl radical yield following exposure to UV-light using the spin-trapping technique with electron paramagnetic resonance spectroscopy (Dodd et al. 2010). Mechanochemical activation was used as preparation method for compositions as $95ZnO\text{-}5Ti_nO_m$ (Dimitriev et al. 2011). TiO_2/ZnO nanocomposites were synthesized by the sol–gel method (Liao et al. 2008, Janitabar-Darzi and Mahjoub, 2009), a nonhydrolytic route (Stoyanova et al. 2013), a solvothermal method and ultrasonic precipitation followed by heat treatment (Ming Ge et al. 2009). Mixed oxide nanoparticles TiO_2-ZnO were obtained by precipitation of zinc nitrate and titanium tetrachloride as precursors and then heat treated using two techniques: hydrothermal and calcination. The prepared particles were investigated for their ability to induce the photocatalytic oxidation and adsorption of Procion Red MX-5B dye (William L. Kostedt et al. 2008). The nanostructured TiO_2-ZnO powders synthesized using an ultrasonic precipitation method indicated high photocatalytic activity towards the decolorization of C.I. Basic Blue 41 in water under solar irradiation and a Ti/Zn molar ratio of 1:1 showed highest photocatalytic activity (Jiang et al. 2008). Large number of researchers have investigated photocatalytic properties of TiO_2-ZnO systems for degradation of different dyes such as Methyl orange, Congo red, Malachite green, Brilliant golden yellow, Orange II (Liao et al. 2008, Ge et al. 2009, Janitabar-Darzi and Mahjoub, 2009, Stoyanova et al. 2013, Bansal et al. 2009, Md Ahsan Habib, Md Tusan Shahadat et al. 2013, Houšková et al. 2008).

The aim of present investigations is to prepare by mechanochemical activation nanodimensional TiO_2-ZnO composites with different mass ratio as 1:1; 1:2 and 2:1 of TiO_2 and ZnO which can be used as potential photocatalysts for removal of organic pollutants as dyes. The physicochemical characterization of the prepared

samples is made in order to study phase composition and structure of mechanochemically treated TiO_2-ZnO materials. The photocatalytic properties of TiO_2-ZnO composites are tested for degradation of Reactive Black 5 dye under UV irradiation.

2. EXPERIMENTAL

2.1. Mechanochemical activation of TiO_2-ZnO composites

The commercial TiO_2 and ZnO prepared by precipitation using aqueous solutions of $ZnCl_2$ and NaOH as precipitant in appropriate amounts were mechanochemically treated in different mass ratio as 1:1; 1:2 and 2:1 in order to prepare TiO_2-ZnO composites. The mechanochemical activation was performed on a Highenergy planetary ball mill type PM 100, Retsch, Germany. The TiO_2-ZnO samples were mechanochemically treated in an agate milling container of 80 ml volume for milling time of one hour and milling speed 300 rpm using air atmosphere.

2.2. Physicochemical methods for structural studies of TiO_2-ZnO composites

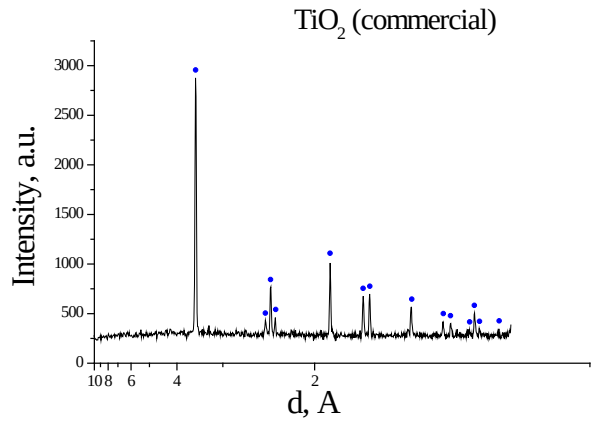
The phase composition of obtained TiO_2-ZnO composites was examined by X-ray diffraction (XRD) technique on a TUR M62 apparatus with PC management and data accumulation, using HZG-4 goniometer and CoKα radiation. JCPDS database (Powder Diffraction Files, Joint Committee on Powder Diffraction Standards, Philadelphia PA, USA, 1997) was used to determine the presence of phases. FTIR spectroscopy was carried out with a Fourier infrared spectrometer Bruker-Vector 22 and spectra were registered in the 400-4000 cm^{-1} region by KBr tablets.

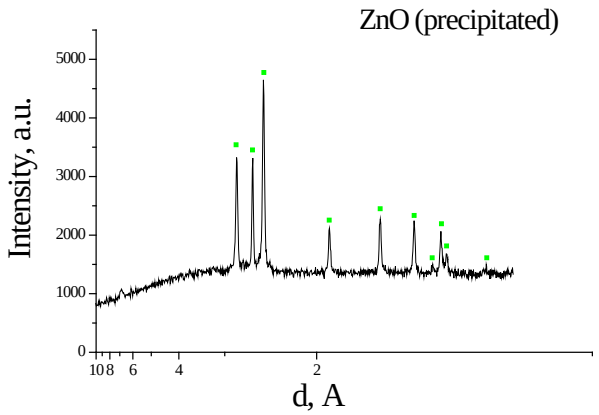
2.3. Photocatalytic investigations of TiO_2-ZnO composites

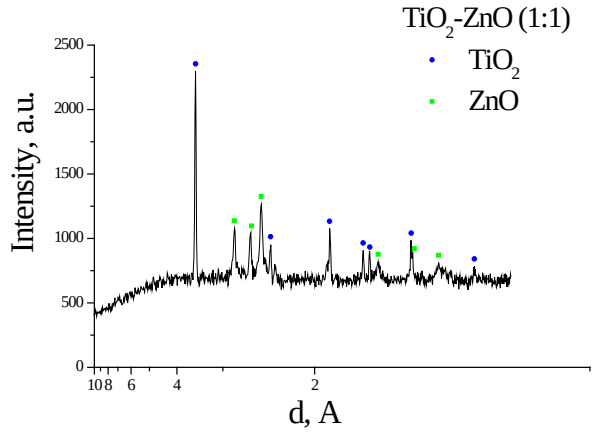
The textile industry is producing considerable amounts of wastewaters, containing di-azo dyes as textile coloring agents. Such wastes are posing a threat for the environment because of the benzene or naphthalene groups, which have carcinogenic effect. In the present research work we selected Reactive Black 5 dye (RB5) as model waste water contaminant. The photocatalytic activity test of RB5 oxidative degradation involved a volume of 150 ml dye aqueous solution having 20 ppm starting concentration (the pH factor value was 7). Polychromatic UV-A light lamp (Sylvania BLB, 18 W) irradiation was applied (wavelength range 315-400 nm with a maximum at 365 nm). The light power density upon the photocatalytic material was 0.66 $mW.cm^{-2}$. The degree of decoloration was followed as a function of the time interval of illumination spectrophotometrically (BOECO S26) in the wavelength range from 200 to 800 nm. A batch suspension photocatalytic reactor blowing air through two frits to saturate the solution in oxygen. All photocatalytic activity tests have been carried out at one and the same agitation velocity (400 rpm) at room temperature. The samples reach adsorption-desorption equilibrium in the dark for half an hour before turning on the lamp. To test the photocatalytic activity of TiO_2-ZnO (1:1), TiO_2-ZnO (1:2) and TiO_2-ZnO (2:1) powders, sample aliquots of the suspension have been taken out of the reaction vessel after regular time intervals. The powder was then separated from the aliquot solution by centrifugation before the UV–Vis spectrophotometric measurement of dye concentration. After that, the aliquot solution, together with the photocatalyst powder, were returned back into the reaction vessel. The degree of discoloration is expressed as $-\ln (C/C_0)$ (where C_0 and C are initial concentration before switching on the illumination and residual concentration of the solution after illumination for selected time interval at 599 nm absorbance maximum, corresponding to the peak of the diazo bond (-N=N-).

3. RESULTS AND DISCUSSION

X-ray diffractograms of commercial TiO_2, precipitated ZnO and mechanochemically treated nanostructured TiO_2-ZnO materials are displayed on Fig. 1. In the X-ray patterns of starting materials TiO_2 and ZnO are indexed the diffraction lines due to anatase of TiO_2 (PDF-21-1272) and ZnO (PDF-03-0888) phases. The presence of different amount of anatase (PDF-21-1272) and ZnO (PDF-03-0888) phases are observed in the X-ray spectra of mechanochemically activated TiO_2-ZnO samples with different weight ratio of TiO_2 and ZnO as 1:1; 1:2 and 2:1. All X-ray patterns present the higher crystallinity degree of investigated materials.


TiO2 (commercial)
Intensity, a.u.
3000
2500
2000
1500
1000
500
0
10 8 6 4 2
d, A


ZnO (precipitated)
Intensity, a.u.
5000
4000
3000
2000
1000
0
10 8 6 4 2
d, A


TiO2-ZnO (1:1)
TiO2
ZnO
Intensity, a.u.
2500
2000
1500
1000
500
0
10 8 6 4 2
d, A

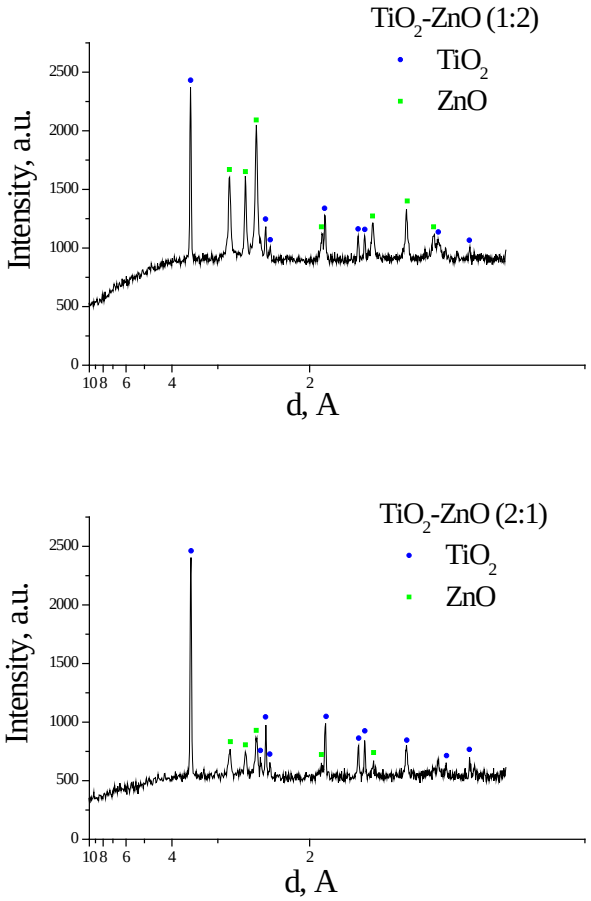


Fig. 1. XRD patterns of commercial TiO_2; precipitated ZnO and TiO_2-ZnO composites.

In the Table 1 are illustrated the mean crystallite size, lattice strain and unite cell parameter of TiO_2 and ZnO phases calculated by Williamson–Hall equation using PowderCell program (Williamson and Hall, 1953). The results show that the determined values of average particle size of TiO_2 and ZnO are about 9.3 and 8.7 nm.

Table 1. Mean crystallite size (D), lattice strain (**ε**) and unit cell parameter (a) of TiO_2-ZnO composites.

Sample	Phase	D, nm	ε, a.u	a, A
TiO_2-ZnO (1:1)	TiO_2	11,8	$3,5.10^{-3}$	3.7906
	ZnO	8,8	3.10^{-3}	3.2544
TiO_2-ZnO (1:2)	TiO_2	8	$3,4.10^{-3}$	3.7882
	ZnO	9,2	$3,3.10^{-3}$	3.2519
TiO_2-ZnO (2:1)	TiO_2	8	$3,3.10^{-3}$	3,7818
	ZnO	8,1	$3,1.10^{-3}$	3,2494

The FTIR spectra of mechanochemically activated TiO_2-ZnO materials are illustrated on Fig. 2. In the infrared region below 700 cm^{-1} are registered peaks corresponding to the metal oxide vibrations of TiO_2 and ZnO (Viswanatha et al. 2012, Zuas and Hamim 2013, Gao et al. 2003). The vibration peak at about 1200 cm^{-1} also is registered by Hamza et al. 2013 in FTIR spectra of pure TiO_2. The observed broad bands of absorption at around

3422 cm^{-1} attributed to the frequencies of O–H group on the surface (Keyes et al. 2005, Hsieh 2007). The absorption bands at about 2923 and 2850 cm^{-1} could be due to the hydrocarbon impurities (Keyes et al. 2005). The FTIR studies confirmed the results obtained by X-ray diffraction analysis.

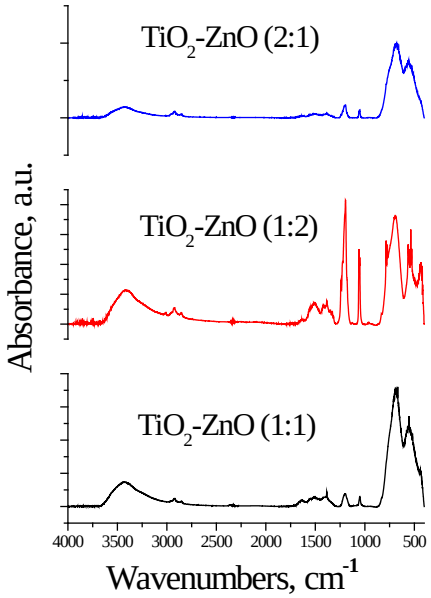


Fig. 2. FTIR spectra of obtained TiO_2-ZnO composites.

The results presented in this paper indicated that UV/TiO_2-ZnO process could be efficiently used to degrade the Reactive Black 5. For all of the TiO_2-ZnO samples the photodegradation efficiency reached up 90% at irradiation time of 120 minutes and resulted in the appearance of growing of photocatalytic ability. The sample TiO_2-ZnO (1:1) shows the highest photocatalytic ability for degradation of Reactive Black 5 under UV light compared to TiO_2-ZnO (1:2) and TiO_2-ZnO (2:1) (see Fig. 3 and Fig. 4).

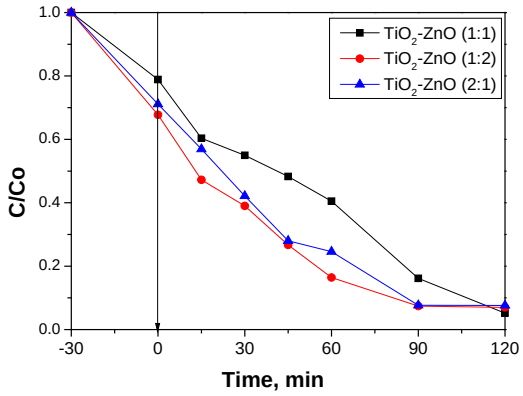


Fig. 3. Concentration ratio varying during the photocatalytic oxidative degradation of an initial concentration (C_0) of 20 ppm RB5 dye, based on changes in the intensity of the absorbance peak, corresponding to azo bond (-N=N-) as a function of the time interval of illumination.

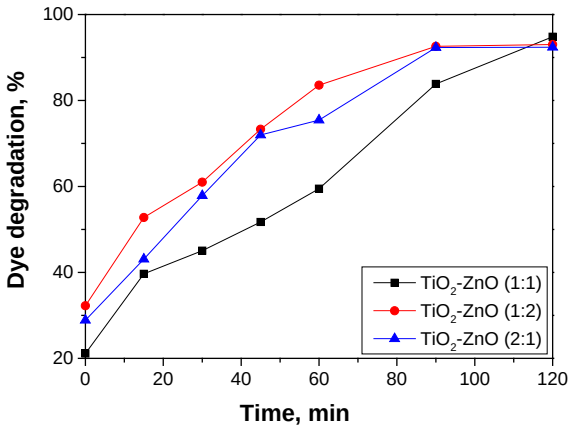


Fig. 4. Degree of discoloration of the dye solution after 120 minutes of UV-A illumination over TiO_2-ZnO (1:1), TiO_2-ZnO (1:2) and TiO_2-ZnO (2:1) samples.

The first-order kinetic decolorization of Reactive Black 5 dye using nanosized TiO_2-ZnO composites as photocatalysts are illustrated on Fig. 5-7 in coordinates $-\ln (C/C_0)/t$.

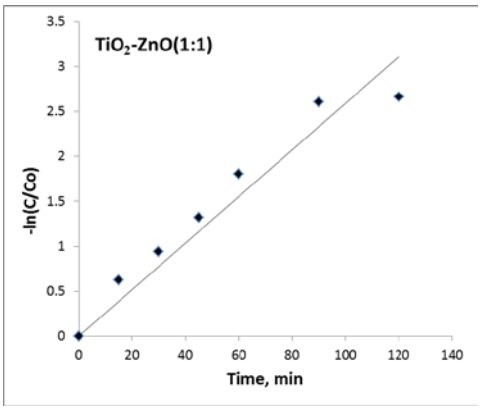


Fig. 5. Reaction course as a linear dependence of the illumination time $-\ln (C/C_0)$ of TiO_2-ZnO (1:1) powders; where C_0 is initial concentration of the dye, C is the dye concentration after illumination.

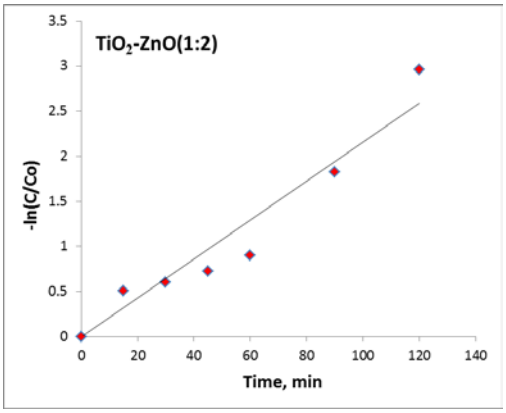


Fig. 6. Reaction course as a linear dependence of the illumination time $-\ln (C/C_0)$ of TiO_2-ZnO (1:2) powders; where C_0 is initial concentration of the dye, C is the dye concentration after illumination.

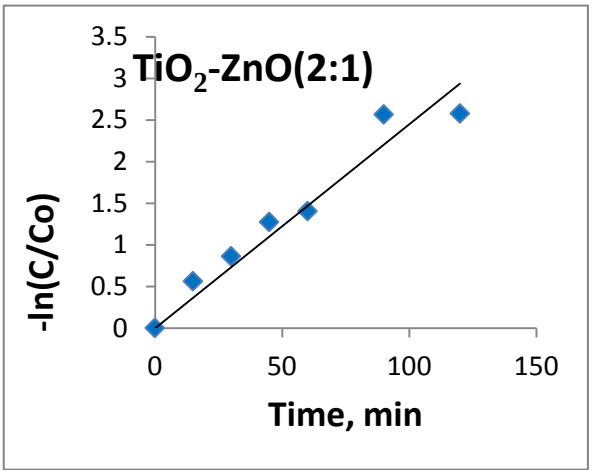


Fig. 7. Reaction course as a linear dependence of the illumination time –ln (C/C_0) of TiO_2-ZnO (2:1) powders; where C_0 is initial concentration of the dye, C is the dye concentration after illumination.

The determined data for rate constants of nanodimensional TiO_2-ZnO photocatalysts calculated by slopes using first order kinetic equation: $-\ln(C/C_0) = k.t$ are included in Table 2. The results show that sample TiO_2-ZnO (1:1) possesses the highest photocatalytic activity $2.60x10^{-2}$ min^{-1} about Reactive Black 5 photodegradation reaction than the other obtained samples TiO_2-ZnO (2:1) ($2.45x10^{-2}$ min^{-1}) and TiO_2-ZnO (1:2) ($2.16x10^{-2}$ min^{-1}). The made photocatalytic investigations established that different mass ratios of TiO_2 and ZnO in TiO_2-ZnO systems affect the photocatalytic activity of obtained composite materials and equal weight ratio leads to obtaining of catalyst with the highest photocatalytic activity.

Table 2. Rate constants of nanodimensional TiO_2-ZnO photocatalysts.

Sample	K ($x10^{-2}$ min^{-1})
TiO_2-ZnO (1:1)	2.60
TiO_2-ZnO (1:2)	2.16
TiO_2-ZnO (2:1)	2.45

According to the literature, increasing the photocatalytic activity of TiO_2-ZnO composites is due to effective charge separation. This process can be explained with the electron transfer realized from the conduction band of light-activated ZnO to the conduction band of light-activated TiO_2 and vice versa. The hole transfer can be achieved from the valence band of TiO_2 to the valence band of ZnO (Rauf et al. 2011).

4. CONCLUSIONS

In this study the nanodimensional TiO_2-ZnO composites are obtained successfully using mechanochemical treatment. The average particle size of TiO_2 and ZnO phases in TiO_2-ZnO materials are determined 9.3 and 8.7 nm. The obtained nanostructured TiO_2-ZnO samples exhibit high photocatalytic activity towards degradation of Reactive Black 5 dye under UV light especially TiO_2-ZnO (1:1) indicating a value of the rate constant $2,60x10^{-2}$ min^{-1}. The photocatalytic tests confirmed that photocatalytic properties are dependent on the weight ratios of TiO_2 and ZnO in prepared samples. The equal mass ratio of TiO_2 and ZnO leads to formation of catalyst with the highest photocatalytic activity. The good photocatalytic ability of synthesized nanosized TiO_2-ZnO systems allows them to be used as photocatalysts for purification of water containing organic dyes.

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