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Effect of the duration of mechanochemical treatment on the photocatalytic activity under UV light irradiation of nano-sized zinc oxide synthesized by precipitation

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The influence of mechanochemical treatment on the photocatalytic properties under UV light irradiation of nano-sized zinc oxide is investigated in the present paper. The zinc oxide was synthesized by classical precipitation procedure with starting reagents $ZnCl_2$, NaOH and following thermal treatment. As-prepared zinc oxide was mechanochemically treated under different milling conditions. The phase composition and structure of the initial and of the mechanochemically activated nanodimensional zinc oxide samples were determined by X-ray diffraction analysis (XRD) and Fourier transform infrared spectroscopy (FTIR). The photocatalytic properties of all prepared zinc oxide samples were tested in the reaction of oxidative photocatalytic degradation of Reactive Black 5 dye as model pollutant under UV light irradiation. Calculations were performed using XRD data establishing that the mechanochemically treated ZnO photocatalysts were ground to smaller average crystallite size (9.9 nm) than that of the starting zinc oxide (14.6 nm). The obtained results show that the photocatalytic activities (rate constants) of precipitated and mechanochemically treated nano-sized zinc oxides decrease in the following order: ZnO (15 min) ($35.5x10^{-3}min^{-1}$) > ZnO ($30.4x10^{-3}min^{-1}$) > ZnO (30 min) ($26.4x10^{-3}min^{-1}$) > ZnO (4 h) ($19x10^{-3}min^{-1}$). The milling time interval of 15 min is optimal for obtaining nanostructured zinc oxide photocatalyst with the highest photocatalytic activity ($k=35.5x10^{-3}min^{-1}$) compared to the other investigated samples.

Key words: mechanochemical treatment, nanodimensional zinc oxide, photocatalytic activity, Reactive Black 5.

INTRODUCTION

ZnO is a semiconductor with a wide band gap (3.37eV) at room temperature, and a large exciton binding energy of 60 meV [1–3]. Zinc oxide finds application in production of rubber, inks, cosmetics, pharmaceutical, ceramic industry, etc due to its electronic and surface properties [3]. In particular, nano-sized ZnO possesses excellent optical, photoelectric and piezoelectric properties, which can be applied in the design of varistors, solar cells, gas sensors and acoustic wave resonators [2]. The different synthetic methods have been described in literature for preparation of ZnO such as precipitation [4–6], sol-gel technique [7], sonochemical method [8], hydrothermal procedure [9, 10], using microwave irradiation [11], spray pyrolysis [12], mechanochemical treatment [13, 14] and others. The precipitation is one of the most often used preparation methods and plays an important role in the field of bulk nanoparticle synthesis because of its high degree of flexibility enabling the possibility to create pure materials with homogeneous distributions [15]. Zinc oxide (ZnO) is highly efficient photocatalysts in degradation of organic pollutants dissolved in water and other solvents because of its impressive catalytic activity and quantum efficiency compared to widely used TiO_2 nanomaterials [16, 17]. Investigations on the use of ZnO as photocata-

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lyst for photodegradation of different dyes such as Methylene Blue [18–21], Methyl Orange [22, 23], Reactive Black 5 [24], Pararosaniline chloride [25], Mordant Black 11 [26], Reactive Orange 4 [27], Rhodamine B [28], Acid Bright Yellow G [29] have been carried out.

The study on the effect of the duration of mechanochemical treatment on the photocatalytic activity under UV light irradiation of nano-sized zinc oxide is the main aim of the present work. For this purpose the nanodimensional zinc oxide, prepared by precipitation procedure, followed by thermal treatment, was mechanochemically treated using different milling conditions. The physicochemical characterization of the so prepared zinc oxide samples was done by X-ray diffraction analysis and FTIR spectroscopy. In order to determine the changes in the photocatalytic activity of precipitated and mechanochemically treated ZnO, all the prepared samples were tested in the reaction of oxidative degradation of Reactive Black 5 dye (RB5) under UV irradiation.

EXPERIMENTAL

The ZnO, was synthesized by the well-known classical precipitation procedure using aqueous solutions of 1M $ZnCl_2$ and 4.6M NaOH as precipitating agent. The sodium hydroxide was slowly added drop-by-drop. After the precipitation procedure the residual was filtered. The obtained white precipitate was washed with distilled water several times and then heated at 150 °C. The prepared ZnO was then treated mechanochemically to obtain nano-sized ZnO particles. The mechanochemical treatment was performed on a high-energy planetary ball mill model PM 100, Retsch, Germany. The milling time interval was varied for the different samples – 15, 30 min or 4 hours using agate or stainless steel milling container at rotational velocity of 300 or 600 rpm and mass ratio sample : balls = 1:6 or 1:13.

The physicochemical methods X-ray diffraction (XRD) and FTIR were used to characterize the structural properties of precipitated and mechanochemically treated zinc oxides. The XRD analysis was performed on a TUR M62 apparatus with PC control and data acquisition, 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 identify the present phases. FTIR spectra were recorded with a Fourier infrared spectrometer Bruker-Vector 22 in the range 400–4000 cm^{-1}. The KBr tablets were used to register the spectra of zinc oxide samples.

Reactive Black 5 (RB5), a toxic azo dye was used as a model waste water pollutant for the evaluation of the photocatalytic activity. The course of the photodegradation oxidative reaction of Reactive Black 5 (RB5) was monitored in the photoreactor using 150 mg of ZnO sample and 150 ml of dye aqueous solution (Reactive Black 5 initial concentration, 20 ppm giving pH=7), which was then stirred continuously with a magnetic stirrer at a constant magnetic stirring rate (400 rpm) under oxidative conditions (bubbling air through two frits to achieve water saturation in oxygen) to form suspension at room temperature. The degree of photocatalytic oxidative degradation of RB5 has been carried out using polychromatic UV-A lamp (Sylvania BLB, 18 W), with wavelength range 315-400 nm (with a maximum of the irradiation at wavelength 365 nm). The light power density at 2 cm distance of illumination was 0.66 $mW.cm^{-2}$. The concentrations of dye after regular time intervals were determined, after the powder was separated from the suspension by centrifugation, using a UV-Vis absorbance single beam spectrophotometer CamSpec M501 (UK) on the basis of the absorbances operating in the wavelength range from 190 to 800 nm. After dark adsorption 30 min, the lamp was switched on to initiate the photocatalytic reactions.

RESULTS AND DISCUSSION

The X-ray diffractograms of prepared zinc oxide photocatalysts are represented in Figure 1. As it can be seen the presence of single zinc oxide (ZnO) phase (PDF-89-0510) is registered in the XRD spectra of precipitated and mechanochemically treated ZnO samples for 15 and 30 minutes. The mechanochemical treatment of ZnO sample for 4 hours leads to formation of ZnO and additional iron nickel (Ni, Fe) (PDF-12-0736) phase. The content of iron nickel phase in sample is due to the continuous vigorous contact between stainless steel milling container, balls and ZnO sample during the mechanochemical process of milling. The average crystallite size, the lattice microstrain parameter and the unit cell parameter of investigated ZnO phases were determined using PowderCell for Windows Version 2.4 program [30]. The calculated values are given in Table 1. The precipitated and mechanochemically treated ZnO samples possess mean crystallite size about 11.1 nm. The obtained results show that the mechanochemical process of milling reduces the average partical size (9.9 nm) compared to the initially prepared ZnO (14.6 nm).

The presence of ZnO is also confirmed by FTIR measurements. Figure 2 illustrates the FTIR spectra of the investigated ZnO samples. In the mid-infrared spectral region absorption peaks are registered at about 422–536 cm^{-1}, characteristic of the Zn-O

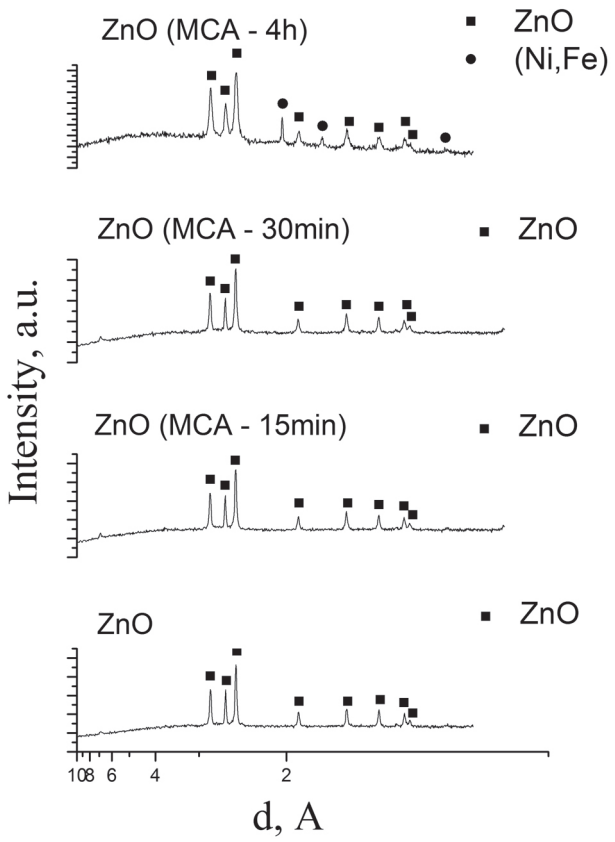

Fig. 1. XRD patterns of obtained ZnO powders

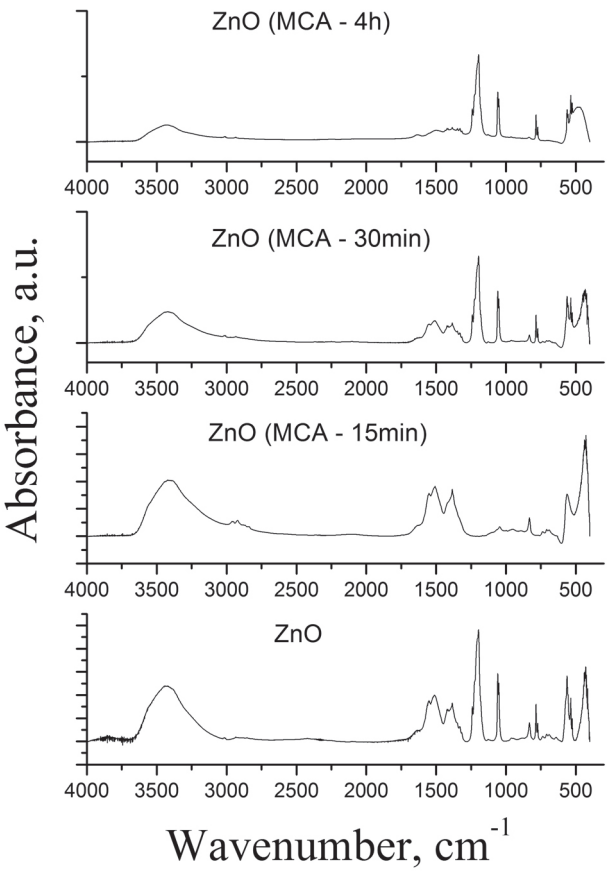

Fig. 2. FTIR spectra of prepared ZnO powders

Table 1. Calculated values of mean crystallite size (D), lattice strain (**ε**) and unit cell parameter (a) of ZnO phase

Sample	D, nm	ε, a.u	a, Å
ZnO	14.6	2.7. 10^{-3}	3.2493
ZnO (MCA – 15 min)	9.9	2.9. 10^{-3}	3.2511
ZnO (MCA – 30 min)	9.9	2.9. 10^{-3}	3.2503
ZnO (MCA – 4 h)	9.9	3. 10^{-3}	3.2495

bond stretching vibrations [31–34]. According to the literature data the broad band at frequencies about 3440 cm^{-1}, 3422 cm^{-1} and 3429 cm^{-1}, observed in the spectra, can be attributed to the O-H vibration mode of water molecules, adsorbed on the zinc oxide surface [11, 25, 33–35]. The bending vibrations of the two OH groups in the adsorbed water molecule are corresponding to the peaks at 563 cm^{-1} and the band of low intensity positioned at 1638 cm^{-1} [7, 36]. The vibration bands at wave numbers about 785 cm^{-1}, 832 cm^{-1}, 1045–1051 cm^{-1}, 1058 cm^{-1}, 1196 cm^{-1}, 1384 cm^{-1}, 1507–1511 cm^{-1} and 1551 cm^{-1} could be the result from the presence of carbonate (CO_3^{2-}) and hydrocarbonate (HCO_3^-) groups, respectively [37, 38]. The existence of (hydro)carbonates is possibly due to carbonization of prepared samples, when exposed to the air. The FTIR results are in agreement with obtained XRD data.

The concentration changes (C/C_0) and degree of degradation (%) of Reactive Black 5 dye during the photocatalytic process under UV light using precipitated and mechanochemically treated zinc oxide photocatalysts are displayed in Figures 3 and 4. The obtained experimental data show that the highest photocatalytic efficiency, based on conversion, is reaching up to 96% for the mechanochemically activated ZnO powder for 15 minutes. Similar values for the photocatalytic degradation (95%) amd (94%) for RB5 dye were established for the mechanochemically treated for 30 minutes and precipitated ZnO materials. The lowest degree of degradation (82%) for Reactive Black 5 dye is observed in the presence of ZnO photocatalyst mechanochemically treated for 4 hours.

The rate constants of all studied zinc oxide photocatalysts are determined using logarithmic linear dependence of the rate constant k (min^{-1}): $-\ln(C/C_0) = k.t$ [27]. The changes in photocatalytic activities of precipitated and mechanochemically treated for dif-

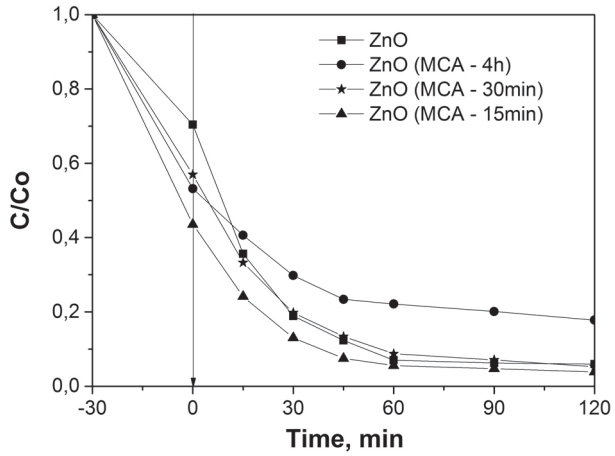

Fig. 3. Concentration decrease in the course of photocatalytic oxidative degradation of a starting solution concentration (C_0) of RB5 dye, observed as changes in the intensity of the absorption peak, corresponding to azo bond (-N=N-) at 599 nm as a dependence of the time interval of UV illumination.

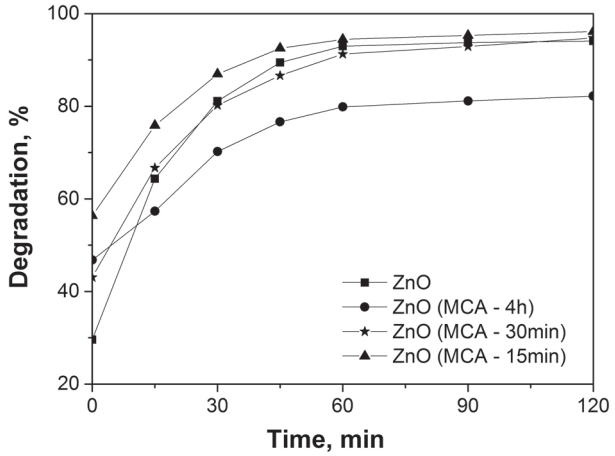

Fig. 4. Degree of degradation of the RB5 dye expressed as $[(C_0\text{-}C)/C_0]$x100, % (where Co and C are initial concentration before switching on the illumination and current concentration of the solution based on changes in the intensity of the peak, corresponding to azo bond (-N=N-) at 599 nm with the course of time

ferent milling time intervals, nano-sized ZnO photocatalysts are shown in Figure 5. The calculations established that the mechanochemical activation of ZnO photocatalyst for 15 minutes shows the highest photocatalytic activity ($k=35.5x10^{-3}$ min^{-1}). The precipitated nanodimensional ZnO powder possesses a higher rate constant ($k=30.4x10^{-3}$ min^{-1}) than that of ZnO (MCA – 30min) ($k=26.4x10^{-3}$ min^{-1}) and of ZnO (MCA – 4 h) ($k=19x10^{-3}$ min^{-1}). The photocatalytic investigation established that 15 min-

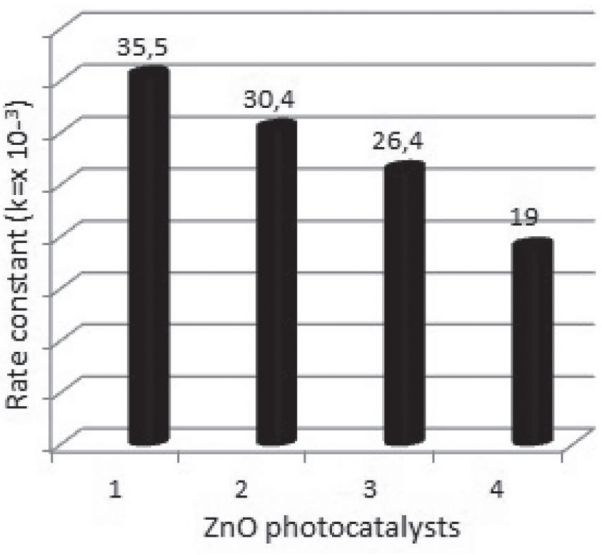

Fig. 5. Comparison data of calculated rate constants of precipitated and mechanochemically treated for different milling time intervals nano-sized zinc oxide photocatalysts in photodegradation of RB5 dye under UV irradiation, 1 – ZnO (MCA – 15 min); 2 – ZnO; 3 – ZnO (MCA – 30 min); 4 – ZnO (MCA – 4h)

utes is optimal milling time interval for activation of ZnO photocatalyst. The longer milling intervals – 30 minutes and 4 hours decrease the photocatalytic activity of ZnO photocatalysts, compared to that of initially precipitated ZnO.

According to Panthi et.al. [39] the photocatalytic activity of ZnO tested in photodegradation of dye pollutants can be explained by the following sequence of four principal steps as the generation of the charge carrier (1), the trapping of the charge-carrier (2), the recombination of the charge carrier (3), and the decomposition of the dye pollutants (4) [39].

CONCLUSIONS

The effect of duration of mechanochemical treatment on the photocatalytic properties of precipitated ZnO powders was investigated. The mechanochemical treatment leads to a decrease in the mean crystallite size of ZnO phase (9.9 nm), compared to the initially obtained nanostructured ZnO (14.6 nm). The so prepared precipitated and mechanochemically treated ZnO powders were tested successfully as photocatalysts in the photocatalytic oxidative degradation of Reactive Black 5 dye under UV irradiation. The obtained results give evidence that the time interval of mechanochemical treatment causes some changes in the photocatalytic

activity of ZnO samples due to size changes. The ZnO treated mechanochemically for 15 min manifests the highest rate constant, based on the slope of the linear dependence –ln(C/Co)=kt compared to those of the others samples decreasing in the following order of photocatalytic activities: ZnO (15 min) ($35.5x10^{-3}min^{-1}$) > ZnO ($30.4x10^{-3}min^{-1}$) > ZnO (30 min) ($26.4x10^{-3}min^{-1}$) > ZnO (4 h) ($19x10^{-3}min^{-1}$). The conversion degree of RB5 dye degradation over the ZnO samples after 120 minutes of illumination is varying within the range 82–96%. The photocatalytic studies show that precipitated and mechanochemically treated zinc oxides are promising photocatalysts for degradation of textile azodyes under UV irradiation especially the mechanochemically treated ZnO powder after optimal mechanochemical activation for 15 min.

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ВЛИЯНИЕ НА ПРОДЪЛЖИТЕЛНОСТТА НА МЕХАНОХИМИЧНА ОБРАБОТКА ВЪРХУ ФОТОКАТАЛИТИЧНАТА АКТИВНОСТ ПРИ ОБЛЪЧВАНЕ С УВ СВЕТЛИНА НА НАНОРАЗМЕРЕН ЦИНКОВ ОКСИД, ПОЛУЧЕН ЧРЕЗ УТАЯВАНЕ

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(Резюме)

В настоящата статия е изследвано влиянието на времетраенето на механохимичната обработка върху фотокаталитичните свойства при облъчване с УВ-светлина на наноразмерен цинков оксид. Цинковият оксид е синтезиран чрез класическа процедура на утаяване, с изходни реагенти $ZnCl_2$, NaOH и последваща термична обработка. Полученият цинков оксид е механохимично обработен при различни условия на смилане. Фазовият състав и структурата на изходния и механохимично активираните проби на наноразмерен цинков оксид бяха определени чрез рентгенофазов анализ и инфрачервена спектроскопия с Фурие трансформация. Фотокаталитичните свойства на всички приготвени проби на цинков оксид бяха тествани във фотокаталитичното окислително разграждане при облъчване с УВ-светлина на багрилото Реактивно Черно 5 като моделен замърсител. Направените изчисления, използвайки данните от рентгенофазовия анализ, установиха, че механохимично третираните ZnO фотокатализатори са с по малък среден размер на кристалитите (9,9 nm) в сравнение с изходния цинков оксид (14,6 nm). Получените резултати показват, че фотокаталитичните активности (скоростни константи) на утаения и механохимично третираните наноразмерни цинкови оксиди намалява в следния ред: ZnO (15 min) ($35{,}5 \times 10^{-3} min^{-1}$) > ZnO ($30{,}4 \times 10^{-3} min^{-1}$) > ZnO (30 min) ($26{,}4 \times 10^{-3} min^{-1}$) > ZnO (4 h) ($19 \times 10^{-3} min^{-1}$). Оптималното времетраене на смилане, при което се получава наноструктурен ZnO фотокатализатор с най-висока фотокаталитична активност ($k=35{,}5 \times 10^{-3} min^{-1}$) в сравнение с другите изследвани образци, е 15 минути.