

Photocatalytic activity of nanostructure zinc ferrite-type catalysts in degradation of Malachite green under UV-light

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Series of nanostructured zinc ferrite-type materials $Zn_xFe_{3-x}O_4$ ($x=0.25, 0.5, 1$) with average crystallite size about 8 nm prepared by co-precipitation or co-precipitation and mechanochemical treatment were tested for photocatalytic degradation of Malachite green oxalate as model contaminant in aqueous solution under UV-light. The performed experiments determined that co-precipitated zinc ferrite-type powders show the higher photocatalytic activity than the mechanochemically treated samples: $ZnFe_2O_4$ ($k=13.7 \times 10^{-3} \text{min}^{-1}$) > $Zn_{0.5}Fe_{2.5}O_4$ ($k=10.7 \times 10^{-3} \text{min}^{-1}$) > $Zn_{0.25}Fe_{2.75}O_4$ ($k=9.4 \times 10^{-3} \text{min}^{-1}$) > $Zn_{0.5}Fe_{2.5}O_4$ (MCT-2hours) ($k=8.1 \times 10^{-3} \text{min}^{-1}$) > $ZnFe_2O_4$ (MCT-1hour) ($k=6.3 \times 10^{-3} \text{min}^{-1}$). The results established that the increase in the degree of substitution of iron ions by zinc ones leads to higher photocatalytic activities for the synthesized ferrite-type samples by co-precipitation. The mechanochemical treatment of co-precipitated zinc ferrite-type materials leads to obtaining of catalyst with higher photocatalytic activity $Zn_{0.5}Fe_{2.5}O_4$ (MCT-2hours) ($k=8.1 \times 10^{-3} \text{min}^{-1}$) with increasing the milling time and decrease the content of zinc ions incorporated in magnetite host structure. Mössbauer spectroscopy was performed in order to study the changes in catalytic behavior of used zinc ferrite-type photocatalysts during the photodegradation process of the dye.

Key words: zinc ferrite-type materials, photocatalysis, Malachite Green.

INTRODUCTION

Photocatalysis find application in various fields including purification of contaminants from water [1]. The presence of industrial wastewater containing dyes in environment generate significant problems due to its high toxicity and possible accumulation in the environment. The most dangerous pollutants in water are synthetic dyes. The presence of even very low concentrations of dyes in water reduces light penetration through the water surface, precluding photosynthesis of the aqueous flora. A large number of these dyes are mutagenic, teratogenic and carcinogenic. These pollutants are toxic to human beings, microorganisms, and fish species and therefore their removal from polluted waters is essential for environmental protection [2]. Many investigations are

carried out about obtaining of effective photocatalyst for degradation of organic contaminants in the past decades [3]. Iron oxides possess catalytic properties for different reactions such as decomposition of hydrogen peroxide and discoloration of synthetic dyes, decomposition of alcohols, selective oxidation of carbon monoxide. The environmental applications of these oxides are widely investigated [4]. The photocatalysts with semiconductor properties are extensively used for degradation of the organic contaminants for the remediation of hazardous wastes and polluted groundwater, and the control of toxic air pollutants [5]. The advantages of using the spinel $ZnFe_2O_4$ in photocatalysis are displaying the desirable optical absorption for the narrow band gap of $\sim 1.9 \text{eV}$, electronic structure, outstanding photochemical stability, strong magnetism and low cost [6, 7]. The zinc ferrite ($ZnFe_2O_4$) photocatalyst was used for degradation of different dyes such as Brilliant Red M5B under UV irradiation [1], methyl orange under UV-irradiation [8], methylene blue under real sunlight irradiation [9] or visible light ir-

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radiation [10], Rhodamine B under the irradiation of simulated solar light [11] or visible light irradiation [6, 12, 13], Acid Orange II in H_2O_2 /visible light system [14], Procion red dye in the presence of H_2O_2 /visible irradiation [15], Reactive Red 198 and Reactive Red 120 in the presence of H_2O_2 and UV-light [16].

The present paper is focused on the investigations of photocatalytic activity of nanosized zinc ferrite-type materials obtained by different methods as co-precipitation or co-precipitation and mechanochemical activation. The catalytic activity of prepared ferrite-type materials is tested about photocatalytic degradation of Malachite green dye as model contaminant in aqueous solution under UV-light at different irradiation intervals. The sorption ability of ferrite materials are studied also. The Mössbauer spectroscopy was used to study the behavior of nanodimensional zinc ferrite-type photocatalysts after photocatalytic reaction.

EXPERIMENTAL

The zinc ferrite-type samples *Sample 1* – $Zn_{0.25}Fe_{2.75}O_4$, *Sample 2* – $Zn_{0.5}Fe_{2.5}O_4$, *Sample 3* – $ZnFe_2O_4$ were prepared by co-precipitation procedure using initial materials $ZnCl_2$, $FeCl_2 \cdot 4H_2O$ and/or $FeCl_3 \cdot 6H_2O$ represented to [17]. The other zinc ferrite-type materials as *Sample 4* – $Zn_{0.5}Fe_{2.5}O_4$ and *Sample 5* – $ZnFe_2O_4$ were synthesized using co-precipitation and mechanochemical treatment for 2 and 1 hours. The mechanochemical activation process was carried out on Highenergy planetary ball mill type PM 100, Retsch, Germany. The phase composition, structure and magnetic behavior of co-precipitated and mechanochemically activated zinc ferrite-type materials were investigated and determined by various physicochemical techniques such as Powder X-ray diffraction analysis, Mössbauer and FT-IR spectroscopy [17].

The photocatalytic tests were performed in a slurry containing 1g zinc ferrite-type catalyst/l and using a $10^{-5}M$, aqueous solution of Malachite green dye as model pollutant. After 60 min “dark”-period in order to establish the equilibrium of the sorption process, the system was UV-illuminated by lamp (Sylvania 18 W BLB T8, emission in the 345–400 nm region with maximum at 365 nm) situated at 9.5 cm distance above the slurry, under continuous magnetic stirring (350 min^{-1}) and bubbling with air (45 l/h). Periodically 7 ml aliquot was taken from the solution and filtered through a 20 μm HPLC filter membranes. The dye concentration was determined spectrophotometrically using Specol 11 by the band at 622 nm. The data obtained were plotted in coordinates $(C/C_0)/t$ and $-\ln(C/C_0)/t$ (where C_0

is the concentration after the “dark” period and C is the concentration after t min of irradiation), and apparent rate constants were determined assuming pseudo first- order kinetic.

In order to investigate the behavior of zinc ferrite-type catalysts after photocatalytic reaction, the Mössbauer spectra were recorded using apparatus Wissenschaftliche Elektronik GmbH, working with a constant acceleration mode, $^{57}Co/Rh$ source (activity $\approx 50 \text{ mCi}$) and α -Fe standard. The computer fitting of the Mössbauer spectra was made to determine the Mössbauer parameters of hyperfine interactions of spectral components: isomer shift (IS), quadrupole splitting (QS), hyperfine effective magnetic field in the site of iron nuclei (H_{eff}), line widths (FWHM) and component relative weights (G).

RESULTS AND DISCUSSION

The Powder X-ray diffraction investigations determined the presence of the single non-stoichiometric spinel zinc ferrite phase $Zn_xFe_{3-x}O_4$ (PDF-01-1109) for *Sample 1* – $Zn_{0.25}Fe_{2.75}O_4$. The ferrite and additional akaganeite phase (PDF-34-1266) were observed in co-precipitated *Sample 2* – $Zn_{0.5}Fe_{2.5}O_4$, *Sample 3* – $ZnFe_2O_4$. The mechanochemical treated *Sample 4* – $Zn_{0.5}Fe_{2.5}O_4$ and *Sample 5* – $ZnFe_2O_4$ contain ferrite phase (PDF-01-1109) and metal iron (PDF-87-0721). The PXRD patterns are presented in study [17]. The calculated mean crystallite size of obtained nanodimensional zinc ferrite-type materials is about 8 nm.

The catalytic results for photocatalytic degradation of Malachite green oxalate as model pollutant in aqueous solution under UV-light irradiation are shown on Figures 1 and 2. The highest decrease-

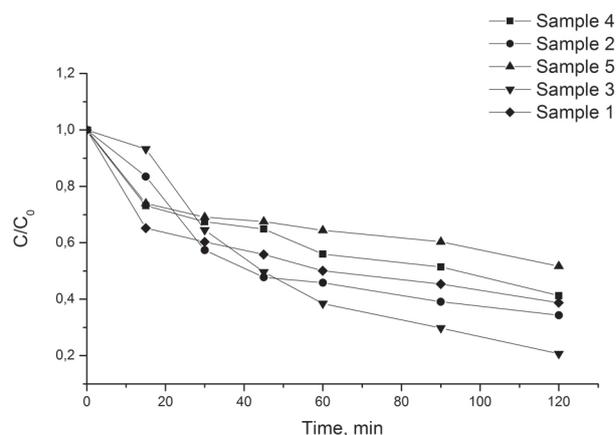


Fig. 1. Concentration changes of Malachite green dye under UV irradiation time using different zinc ferrite-type photocatalysts

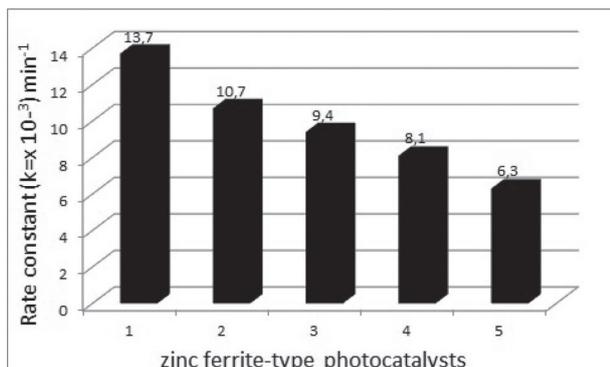


Fig. 2. Apparent rate constants of obtained zinc containing ferrites: 1 – Sample 3; 2 – Sample 2; 3 – Sample 1; 4 – Sample 4; 5 – Sample 5.

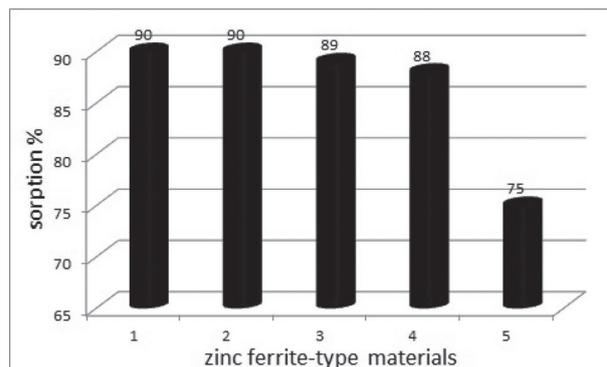


Fig. 3. Sorption abilities of obtained zinc ferrite-type materials: 1 – Sample 3; 2 – Sample 4; 3 – Sample 2; 4 – Sample 1; 5 – Sample 5

ing of initial concentration of Malachite green dye solution during photocatalytic degradation process using UV-illumination was achieved by using co-precipitated *Sample 3* – ZnFe_2O_4 photocatalyst (see Figure 1). The apparent rate constants of prepared nanosized zinc ferrite-type materials were determined by linear slopes using pseudo-first-order kinetic equation $-\ln(C/C_0) = k.t$. The comparison of calculated rate constants is presented on the Figure 2. As can be seen the co-precipitation method leads to formation of zinc ferrite-type catalysts with the higher photocatalytic activity than that of the mechanochemically treated ferrite samples: ZnFe_2O_4 ($k=13.7 \times 10^{-3} \text{ min}^{-1}$) > $\text{Zn}_{0.5}\text{Fe}_{2.5}\text{O}_4$ ($k=10.7 \times 10^{-3} \text{ min}^{-1}$) > $\text{Zn}_{0.25}\text{Fe}_{2.75}\text{O}_4$ ($k=9.4 \times 10^{-3} \text{ min}^{-1}$) > $\text{Zn}_{0.5}\text{Fe}_{2.5}\text{O}_4$ (MCT-2hours) ($k=8.1 \times 10^{-3} \text{ min}^{-1}$) > ZnFe_2O_4 (MCT-1hour) ($k=6.3 \times 10^{-3} \text{ min}^{-1}$). The photocatalytic investigations show that photocatalytic activity of zinc ferrite-type materials depends on the preparation technique, milling time of mechanochemical treatment and degree of substitution of iron ions by zinc ones in magnetite host structure. The increase in the degree of substitution of iron ions by zinc ones leads to the enhancement of photocatalytic activities for the co-precipitated ferrite-type samples. The increase of activation time during the milling treatment of nanostructured zinc ferrite-type photocatalysts and decreasing amount of Zn^{2+} ions incorporated in magnetite host lattice leads to obtaining of mechanochemically treated zinc-ferrite-type catalyst with the higher photocatalytic activity as $\text{Zn}_{0.5}\text{Fe}_{2.5}\text{O}_4$ (MCT-2 hours) ($k=8.1 \times 10^{-3} \text{ min}^{-1}$).

The prepared nanodimensional zinc ferrite-type samples demonstrate good sorption ability of the dye after the dark period varying in the range 75–90% and such materials could be used as sorbents for organic dye pollutants (Figure 3). The sorption abilities of investigated zinc containing ferrite photocatalysts increase in the following order: *Sam-*

ple 5 – ZnFe_2O_4 (75%) < *Sample 1* – $\text{Zn}_{0.25}\text{Fe}_{2.75}\text{O}_4$ (88%) < *Sample 2* – $\text{Zn}_{0.5}\text{Fe}_{2.5}\text{O}_4$ (89%) < *Sample 4* – $\text{Zn}_{0.5}\text{Fe}_{2.5}\text{O}_4$ (90%) ~ *Sample 3* – ZnFe_2O_4 (90%).

In present investigations the structural changes of nanosized zinc ferrite-type materials, after the photocatalytic degradation of Malachite green

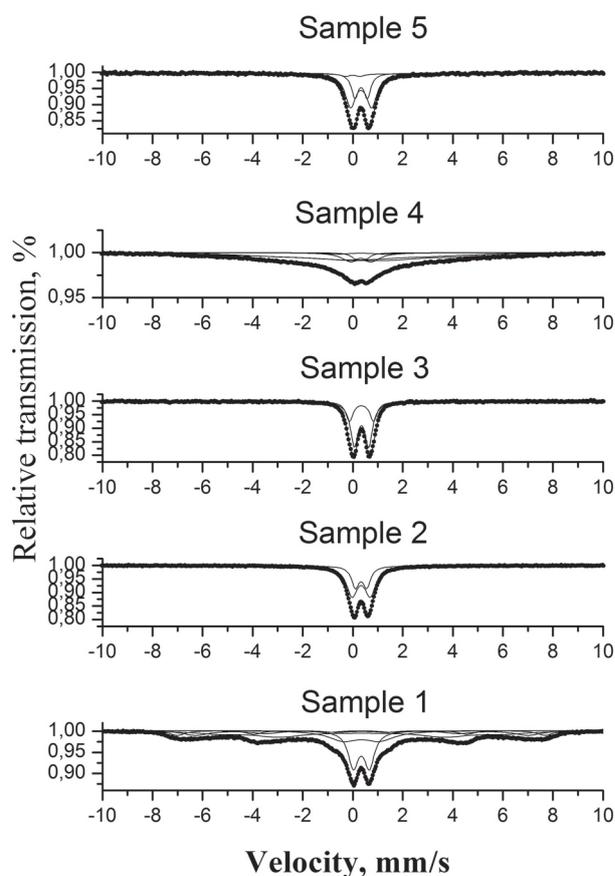


Fig. 4. Mössbauer spectra of synthesized nanosized zinc ferrite-type catalysts after photocatalytic tests

Table 1. Mössbauer parameters of nanodimensional zinc ferrite-type samples at RT after photocatalytic tests

Sample	Components	IS, mm/s	QS, mm/s	H _{eff} , T	FWHM, mm/s	G, %
Sample 1	Sxt 1 – Fe ³⁺ -tetra, spinel	0.32	0.03	45.6	0.77	10
	Sxt 2 – Fe ³⁺ -octa, spinel	0.36	–0.01	41.2	1.27	16
	Sxt 3 – Fe ions spinel	0.36	0	35.4	2.45	31
	Dbl 1 – SPM, core	0.34	0.65	0	0.49	24
	Dbl 2 – SPM, shell	0.35	1.46	0	1.46	19
Sample 2	Dbl 1 – SPM, core	0.33	0.46	0	0.37	33
	Dbl 2 – SPM, shell	0.34	0.73	0	0.54	67
Sample 3	Dbl 1 – SPM, core	0.35	0.58	0	0.37	70
	Dbl 2 – SPM, shell	0.35	0.97	0	0.35	30
Sample 4	Sxt 1 – Fe-Me	0	0	21	3.66	37
	Sxt 2 – Fe ^{2.5+} -octa, spinel	0.62	0	36	3.28	44
	Sxt 3 – Fe ³⁺ -tetra, spinel	0.33	0	37.3	0.89	3
	Dbl 1 – SPM, shell	0.33	0.86	0	0.83	12
	Dbl 2 – SPM, core	0.32	0.42	0	0.43	4
Sample 5	Sxt 1 – Fe-Me	0	0	11.7	4.80	15
	Dbl 1 – SPM, core	0.33	0.50	0	0.33	27
	Dbl 2 – SPM, shell	0.33	0.85	0	0.51	58

dye are studied with Mössbauer spectroscopy. The Mössbauer results determined nonsignificant changes of the materials when compared with the Mössbauer study of the initial nanostructure zinc ferrite-type samples $Zn_xFe_{3-x}O_4$ ($x=0.25, 0.5, 1$) discussed in [17]. As it is known the stationary composition of the catalyst is formed during the reaction so that it is possible to observe changes in the composition before and after the reaction. The Mössbauer spectra at room temperature (RT) of the ferrite samples after the catalytic tests are displayed on the Figure 4. The spectrum of *Sample 1* is superposition of three sextet and two doublet components. The doublet lines only are registered in Mössbauer spectra of *Samples 2* and *3*. The calculated Mössbauer parameters of hyperfine interactions after the best computer fitting of spectra are given in Table 1. The calculated hyperfine parameters of *Sample 1* established that sextet components can be related to tetrahedrally coordinated Fe³⁺ ions in a spinel phase – Sxt1, octahedrally coordinated Fe³⁺ in a spinel phase – Sxt2 and iron ions in a spinel phase with smaller size – Sxt3. The doublet components could be assigned the presence of ferrite particles with superparamagnetic (SPM) behaviour and sized below 10 nm for *Sample 1*. In the Mössbauer spectra at RT of *Samples 2* and *3* contain two superparamagnetic doublets attributed to the presence of ferrite particles with superparamagnetic (SPM) behaviour and intermediate phase (akaganeite) are observed. The

superposition of three or one sextet and two doublet components was registered in the Mössbauer spectra of mechanochemically treated nanodimensional zinc ferrite-type photocatalysts *4* and *5*. The calculated hyperfine parameters of doublet components could be relate to the presence of ferrite particles with superparamagnetic (SPM) behaviour. The Sxt 1 component belonging to the metal iron phase, Sxt 2 and Sxt 3 to the octahedrally coordinated Fe^{2.5+} and tetrahedrally coordinated Fe³⁺ in a spinel structure respectively.

CONCLUSIONS

The synthesized zinc ferrite-type materials used about photodegradation of Malachite green oxalate dye under UV irradiation showed good photocatalytic activity especially co-precipitated $ZnFe_2O_4$ ($k=13.7 \times 10^{-3} \text{min}^{-1}$). The investigated zinc ferrite-type photocatalysts possess good sorption ability of the dye after the dark period in the range 75–90%. The performed study determined that photocatalytic activity of zinc ferrite-type materials depends on the degree of incorporation of Zn²⁺ ions in magnetite host structure, preparation method and milling time of mechanochemical treatment. The increasing of Zn²⁺ content in magnetite host structure of powder synthesized by co-precipitation leads to formation of photocata-

lyst with higher rate constant than the other coprecipitated ferrite-type materials. The photocatalytic tests about mechanochemically treated zinc ferrite-type samples determined that photocatalytic activity increase with activation time and decreasing amount of Zn²⁺ ions incorporated in magnetite host lattice. The presence of superparamagnetic nanodimensional zinc-ferrite particles and stable catalytic behavior of tested ferrite-type materials was confirmed by Mössbauer study made after photocatalytic measurements.

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ФОТОКАТАЛИТИЧНА АКТИВНОСТ НА НАНОСТРУКТУРИРАНИ ЦИНКОВИ ФЕРИТЕН ТИП КАТАЛИЗАТОРИ ПРИ РАЗГРАЖДАНЕ НА МАЛАХИТОВО ЗЕЛЕНО ПОД УВ-СВЕТЛИНА

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(Резюме)

Серия наноструктурирани цинкови феритен тип материали $Zn_xFe_{3-x}O_4$ ($x=0,25, 0,5, 1$) със среден размер на кристалита 8 nm, получени чрез съутаяване или съутаяване и механохимична обработка, бяха тествани за фотокаталитичното разграждане на Малахитово зелено оксалат като моделен замърсител във воден разтвор при облъчване с УВ светлина. Проведените експерименти установиха, че сътаените цинкови феритен тип прахове показват по-висока фотокаталитична активност в сравнение с механохимично обработените проби: $ZnFe_2O_4$ ($k=13.7 \times 10^{-3} \text{min}^{-1}$) > $Zn_{0.5}Fe_{2.5}O_4$ ($k=10.7 \times 10^{-3} \text{min}^{-1}$) > $Zn_{0.25}Fe_{2.75}O_4$ ($k=9.4 \times 10^{-3} \text{min}^{-1}$) > $Zn_{0.5}Fe_{2.5}O_4$ (МХТ-2hours) ($k=8.1 \times 10^{-3} \text{min}^{-1}$) > $ZnFe_2O_4$ (МХТ-1hour) ($k=6.3 \times 10^{-3} \text{min}^{-1}$). Резултатите установиха, че нарастването на степента на заместване на железните йони с цинкови води до по-високи фотокаталитични активности на синтезираните феритен тип проби чрез съутаяване. Механохимичната обработка на сътаените цинкови феритен тип материали води до получаване на катализатор с по-висока фотокаталитична активност $Zn_{0.5}Fe_{2.5}O_4$ (МХТ-2часа) ($k=8.1 \times 10^{-3} \text{min}^{-1}$) с увеличаване на времето на мелене и намаляване на съдържанието на цинкови йони, включени в магнетитовата структура. Мьосбауерова спектроскопия беше извършена с цел изследване на промените в каталитичното поведение на използваните цинк феритен тип фотокатализатори при процеса на фоторазграждане на багрилото.