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Two component oxide compositions based on TiO_2 rutile: ultrasonic treatment, their physicochemical and photocatalytic properties

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The creation of oxide two-component systems based on TiO_2 rutile was studied. Influence of ultrasound treatment (UST) of these mixtures on their properties was established. The mixtures treatment less influences on the ratio of intensity of (110)/(101) reflexes of TiO_2 what testify any structural change of this oxide but in same time little increase of its particles size was observed. The little increase of the dimension particles for second oxide after UST for the studied mixtures excluding TiO_2/MgO and TiO_2/ZnO was observed. The partial transformation of MgO to $Mg(OH)_2$ as result of TiO_2/MgO composition treatment was shown which accompanied by decrease of MgO particles size. In the case of TiO_2/ZnO composition the partial destruction of ZnO was observed. The increase of the pores radius after UST with the change of surface element ratio determined by EDX method can testify that strong interaction between oxides takes place. This fact leads to an increase the band gap for the mixture in comparison with initial TiO_2 with its average value between characteristic for TiO_2 and other oxide in mixture. The study of photocatalytic properties of the samples in metronidazole (MN) oxidative decomposition in water shows that for all compositions, excluding TiO_2/ZnO where the activity is connected with more active ZnO in this reaction but not TiO_2, a decrease of initial rate constant K_d was observed. The reduction of rate constant was connected with a decrease of TiO_2 content in the mixtures and introduced value of rate constant determined to quantity of TiO_2 demonstrate its increase in comparison to individual TiO_2.This fact testify the strong interaction in complexes systems between two oxides. Obtained result permits to realize the MN photocatalytic degradation in water with an increase of the complexes catalyst content in reaction mixture what leads to an increase both rate constant and degree of antibiotic transformation. It was established that UST increased the stability of the samples in MN transformation and as result the conversion of MN has more value than in initial mixtures. An increase of degradation degree after UST of the samples correlates with the growth of medium pore radius in result of this treatment what can be connected with an increase of sample surface accessible to UV irradiation. It was shown that obtained composites demonstrate better properties in MN destruction in water in comparison with data known from the literature.

Keywords: complex oxide compositions, ultrasonic treatment, photocatalysis, metronidazole destruction

Introduction

Due to increase of the use of pharmaceuticals and drugs, the problem of effective wastewater purification is becoming more and more urgent. Their pollutions in water are the main problem that must be constantly solved. For the present time, several different types of emerging contaminants in water systems are known as new environmental hazards those need to be neutralized by appropriate methods [1-3]. One from such dangerous pollutants is metronidazole (2-methyl-5-nitroimidazole-1-ethanol, MN) which has been widely used to treat infections caused by anaerobic bacteria, bacteroides and protozoa. Since MN is non biodegradable and highly soluble in water, it can be accumulate in the aquatic environment [4]. Elimination of MN from water system is an important issue considering its toxicity, potential mutagenicity and carcinogenity [5, 6]. Decontamination of harmful substances in the water environment by the method of photocatalysis is the most promising means at present [7-10]. Successful use of this method is connected with availability and creation of highly efficient photocatalysts, which can be nanosized oxides of transition metals and systems based on them. From the point of view of practical application, the well-known best photocatalysts based on ZnO and TiO_2, last is one of the most widely studied semiconductors (n-type) due to its low cost, abundant resource, high photocatalytic activity, chemically and mechanically stable under ultraviolet (UV) irradiation, is not a toxic substance, and has industrial availability. Titanium dioxide can exist in eight crystalline polymorphs, of which only three, i.e. rutile (tetragonal), anatase (tetragonal) and brookite (orthorhombic), are naturally occurring [11]. In the most cases rutile phase as photocatalyst shows lower photocatalytic activity than anatase phase [12-14], but also it was shown, that TiO_2 rutile demonstrates high photoactivity in such processes as water splitting, destruction of dyes, various organic and pharmaceutical substances [13-16]. The preparation of this oxide by various methods and introduction of different additions permits to increase its catalytic performance.

Methods of synthesis of complexes catalysts on the TiO_2 base such as homogeneous co-precipitation, pyrolysis of salt solutions, compatible hydrolysis of salts, hydrothermal method, *etc*., do not always guarantee obtaining the final material with the necessary physicochemical and photocatalytic characteristics. So perspective to obtain the photocatalysts with improved characteristics is connected with alternative synthesis use [17, 18]. One of alternative method with influence on the properties of synthesized photocatalysts can be ultrasonic treatment or sonochemistry (UST) [19-24]. With minimal energy consumption, low emissions and intensification of the process, this synthesis method allows obtaining composite nanomaterials with high catalytic activity in various reactions [25-27].

In this study was examined the influence of UST on the physical-chemical and photocatalytic properties of semiconductor mixtures based on TiO_2 rutile with the addition of other oxide (ZnO, ZrO_2, MgO, SnO_2, Nb_2O_5). Photocatalytic properties of the samples were determined in the photodestruction of metronidazole.

Experiment

Equimolar mixtures of TiO_2/ZnO, TiO_2/ZrO_2, TiO_2/MgO, TiO_2/SnO_2, TiO_2/Nb_2O_5 with a ratio of 1:1 were prepared from oxides TiO_2 (pfa), ZnO (p), ZrO_2 (p), MgO (pfa), SnO_2 (p), Nb_2O_5 (p). UST of oxide mixture composites was carried out on an ultrasonic generator “Titan ultrasonic” (Made in Ukraine) with a power of 80 W, a frequency of 20 kHz and a processed volume of 50 ml. For the synthesis, 5 g of the mixture and 40 ml of water were taken. Time of treatment was 1 h, only in case of TiO_2/ZnO mixture it was 0.5 h. After UST, the samples were dried in an air atmosphere at 120 °C, 1 h.

Physical-chemical properties of the initial and obtained samples were investigated by the following methods. Textural parameters, namely the specific surface area and sizes of pores were determined in the course of low-temperature adsorption-desorption of nitrogen by using a Quantachrome NOVA-2200e Gas Sorption Analyzer. Structural analysis was carried out by the method of powder X-ray (XRD) on a DRON-3M diffractometer using CuKα radiation with a wavelength of 1.5418 Å with scanning in the range of 2θ angles 15-90°. Calculation of the distances (d, nm) between the planes from the obtained X-ray patterns of the samples was carried out according to the Wolf-Bragg formula: $d = n\lambda/2\sin\theta$, the crystallite size (L, nm) was calculated using the X-ray line width method, which is based on the Debye-Scherrer formula: $L = k\lambda/\beta\cos\theta$. The obtained diffractograms were analyzed by using the JCPDS electronic database. The surface morphology of samples was investigated by scanning electron microscopy (SEM) on a Tescan Vega 3 LMU electron microscope with two detectors SE (“secondary electron” mode). Determination of the quantitative integral composition of the sample and distribution of elements on the surface was investigated using an Oxford Instruments Aztec energy dispersive X-ray microanalyzer with a ONE X-Max^{N}20 detector.

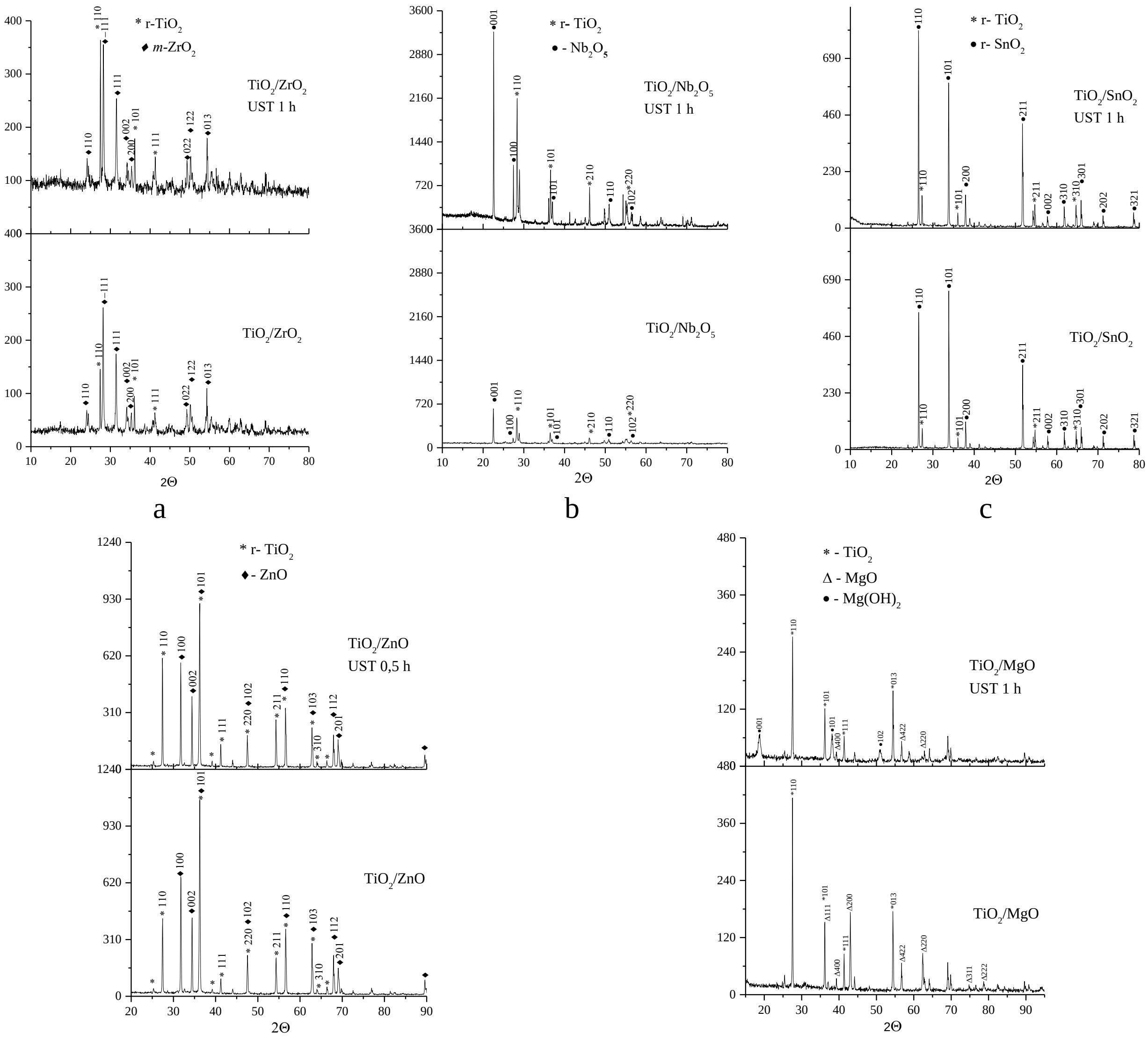
The photocatalytic properties of the samples were investigated in the destruction of metronidazole (AC "Lubnyfarm", NUA/6538/01/01, code ATX J01XD01) with its concentration in water equal to 0.015 g/l under ultraviolet irradiation (UV irradiation) using Optima high-pressure mercury lamp with a power of 125 W, which emits only in the UV part of the spectrum with $\lambda = 365$ nm. The study of photodegradation of the antibiotic was carried out under ambient conditions in a glass beaker with a working solution of 300 ml and a weight of catalyst 0.15 g (concentration of catalyst was equal 0.5 g/l). To achieve equilibrium, the MN adsorption the solution was stirred without UV irradiation during 1 h. The total duration of the photocatalytic destruction process was 5 h with constant stirring. To determine the photocatalytic activity of the synthesized composites, the optical density (D) of the solutions was measured over a certain time (each 1 h of the process) using a Shimadzu UV-2450 UV-Vis spectrometer in the wavelength range of 200-500 nm. From the obtained data the degradation rate constant (K_d) was calculated for each studied catalyst samples from the curves of dependence of $\ln(D/D_0)$ on time according to the formula: $K_d = \ln(D/D_0)/\Delta t$. The degree of photocatalytic efficiency (G) was determined according to the formula: $G = (C_0\text{-}C)/C_0 \times 100 = (D_0\text{-}D)/D_0 \times 100$, where C_0 is the initial concentration of MN in the solution, C is the concentration of MN in the solution at a certain time, D_0 is the initial absorbance of MN in the solution (when $t = 0$ min) and D is the absorbance after certain time of MN photodegradation at the corresponding λ_{max}. Band gap energy values were determined using the Kubelka-Munk phenomenological theory under the assumption of an indirect band gap. Using the method of electron spectroscopy (ES), the band gap energy (E_g) was determined, which was calculated from the absorption band using the formula: $E_g = hc/\lambda_0$, where h is Planck's constant ($4.135 \cdot 10^{-15}$ eVs); c is the speed of light ($3 \cdot 10^8$ m/s); λ_0 is the wavelength corresponding to the value of the absorption edge.

Results and discussion

The structural characteristics of the synthesized composites were analyzed by X-ray diffraction. The diffractograms of initial mixtures (Fig. 1) show that the samples have a crystalline structure and their main reflections correspond to the phases of oxides that included in their composition (TiO_2 JCPDS 88-1175, ZrO_2 JCPDS 37- 1484, MgO JCPDS 45-946, SnO_2 JCPDS 41-1445, ZnO JCPDS 36-1451, Nb_2O_5 JCPDS 30-0873). On the diffractograms of all oxide mixtures, titanium dioxide has two main reflections from (110) and (101) planes at $2\theta = 27.4^o$ and 36.17^o, which correspond to the rutile phase [12, 16, 28]. It was established that UST of the initial mixtures leads to an increases their reflexes intensity practically for all compositions excluding TiO_2/MgO. In same time for all samples, the ratio intensity of reflexes of TiO_2 (110)/(101) planes less changed after UST and is equal to 2.0-2.1. The exception is the TiO_2/ZnO samples (Fig. 1 d) where the ratio intensity reflexes (110)/(101) for initial mixture is equal to 0.42 which is connected with superposition of two reflexes of (101) plane at $2\theta = 36.17$ (TiO_2) and 36.29^o (ZnO). In result of UST, this ratio increases up to 0.66 which can be connected with partial destruction of ZnO. Evidence in favor of ZnO destruction is two facts: i) the intensity of (110) TiO_2 reflection after UST increases in 1.2 times but the intensity of (100) ZnO ($2\theta = 31.82^o$) decreases in 1.3 times, ii) all other individual reflexes of TiO_2 increase their intensity but ZnO vise versa decreases. For the other compositions, UST leads to the intensity increase of the reflexes for both oxides, not only TiO_2 but other introduced oxide (Fig. 1 a, b, c).

The TiO_2/MgO composition in a manner stands alone. For TiO_2, therefore, as other cases, the intensity of its reflexes increases after UST and the ratio of intensity (110)/(101) planes rests without change (equal to 2.1). In same case the appearance of some new reflexes (Fig. 1 e) at 2θ = 18.81, 38.17 and 50.98° which correspond to (001), (101), (102) planes of $Mg(OH)_2$ [31] (JCPDS 84-2163) and a decrease of MgO reflexes intensity can be observed. So, as result of water presence in UST, the partial transformation of MgO to $Mg(OH)_2$ proceeds.

The calculation of TiO_2 particles sizes shown in full correspondence with an intensity increase of its reflexes for all studied samples some increase of the particles dimension (Table 1) after UST. Also for the ZrO_2, Nb_2O_5 and SnO_2 can be observed a little increase of the particles dimensions after UST (Table 1). In the case of ZnO and MgO in accordance with analysis presented above, a decrease of particles size was observed.



a b c

d e

Fig. 1. Diffractograms of initial oxide mixtures and after UST

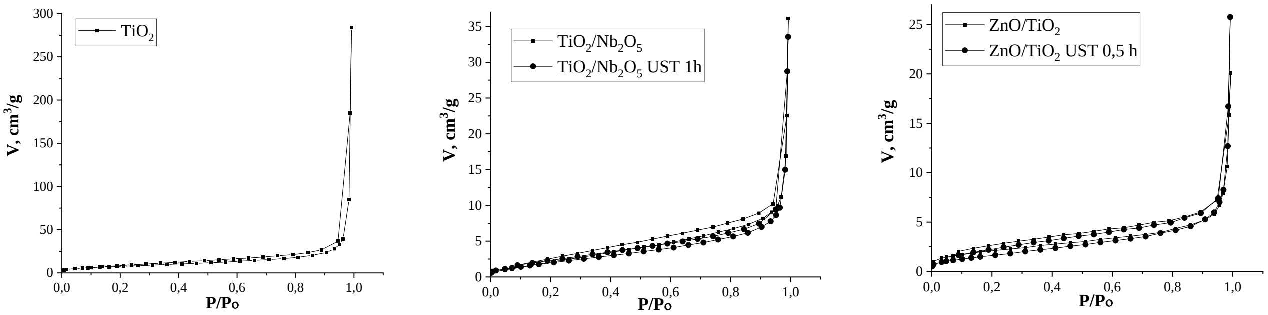
Analysis of nitrogen sorption-desorption isotherms shows that all composites are low porous, for example, two compositions and initial TiO_2 presented in Fig. 2 and UST less influence on the type of isotherms. According to Brunauer’s classification, adsorption isotherms belong to type III, when the energy released during the formation of a monolayer is little different from the energy of multilayer adsorption and the force of attraction between adsorbed molecules and the adsorbent surface is less than the force of interaction between adsorbed molecules. By the type of hysteresis loops, it can be assumed that the pores have a wedge-shaped shape with open ends.

Table 1. Some physical-chemical properties of the studied compositions

Sample	L*, nm		SSA, m^2/g	V_m, cm^3/g	R_m, nm
	TiO_2	MeO			
TiO_2 (initial)	55	-	12.0	0.20	31.3
TiO_2/ZrO_2 (initial)	52	33	7.0	0.05	13.8
TiO_2/ZrO_2-(UST)	56	34	7.5	0.09	23.4
TiO_2/ZnO (initial)	46	46	8.0	0.10	8.2
TiO_2/ZnO (UST)	49	41	6.0	0.06	12.3
TiO_2/SnO_2 (initial)	52	50	5.0	0.02	19.5
TiO_2/SnO_2 (UST)	58	55	6.0	0.04	21.2
TiO_2/Nb_2O_5 (initial)	48	50	10.5	0.15	13.8
TiO_2/Nb_2O_5 (UST)	53	55	15.0	0.28	19.7
TiO_2/MgO (initial)	50	39	9.0	0.12	28.2
TiO_2/MgO (UST)	56	21 (9)**	15.0	0.28	33.7

* L – the average size of crystallites calculated according to Debye-Scherrer's equation

** The average size of formed MgOH presented in parentheses



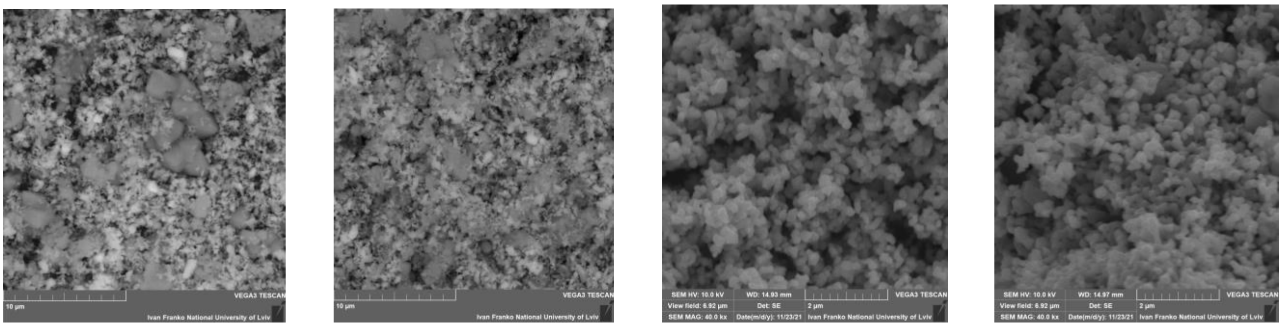
a b c

Fig. 2. Nitrogen adsorption-desorption isotherms obtained at 20 °C for TiO_2 and some oxides compositions

The data presented in Table 1 show that the specific surface area (SSA) of the initial mixture is less than in initial TiO_2 what is connected with low values SSA of other oxides introduced in mixtures. UST little influenced on SSA and its value is increased only in the case of TiO_2/Nb_2O_5 and TiO_2/MgO compositions. Analogous in the case of these compositions, the increase of total pores volume is observed that can be connected with partial agglomeration and formation of secondary porous systems [30-32].

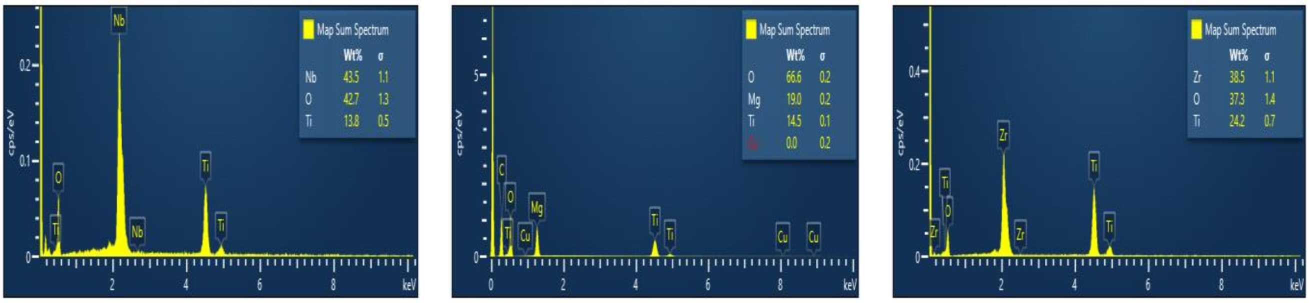
The study of the composites by SEM method in full accordance with XRD data show the less change in surface morphology of the samples and particles dimensions in result of UST (some characteristic results presented in Fig. 3). In contrary the results of EDX analysis demonstrate the UST influence on the elements ratio in surface layer of the samples (some results presented in Fig. 4 and full data in Table 2). From the data presented in Table 2 can be observed that for initial mixtures determined by EDX ratio of the elements less differs from calculated value at their preparation. Three variants of the UST influence on the elements ratio in surface layer of the samples were observed (Table 2 and Fig. 4): practically any influence of treatment on components ratio [TiO_2/SnO_2 and TiO_2/Nb_2O_5 (EDX spectrum for the last presented on Fig. 4 a)], a decreases of surface ratio as a result of treatment [TiO_2/ZnO and

TiO_2/MgO (EDX spectrum for the last presented on Fig. 4 b)], an increase of the surface ratio as treatment result (TiO_2/ZrO_2, EDX spectrum presented on Fig. 4 c).



a b c d

Fig. 3. SEM micrographs of the samples TiO_2/ZnO (a, b) and TiO_2/Nb_2O_5 (c, d). Initial mixtures (a, c), samples after UST (b, d)



a b c

Fig. 4. EDX analysis of the samples after UST: a – TiO_2/Nb_2O_5, b – TiO_2/MgO, c – TiO_2/ZrO_2

Table 2. Surface and photocatalytic properties of the studied compositions

Sample	EDX Ti/Me weight ratio*	E_g, eV	K_d 10^3, s^{-1}	$K_{d(TiO_2)}$** 10^3, s^{-1}	G***, %
TiO_2 (initial)	-	3.00	0.12	0.12	56.0
TiO_2/ZrO_2 (initial)	0.54 (0.53)	3.18	0.06	0.15	55.8
TiO_2/ZrO_2-(UST)	0.63	3.19	0.09	0.23	76.8
TiO_2/ZnO (initial)	0.69 (0.73)	3.20	0.23	0.46	98.0
TiO_2/ZnO (UST)	0.41	3.16	0.25	0.51	98.5
TiO_2/SnO_2 (initial)	0.40 (0.38)	3.20	0.05	0.14	77.1
TiO_2/SnO_2 (UST)	0.42	3.20	0.05	0.14	80.4
TiO_2/Nb_2O_5 (initial)	0.29 (0.25)	3.32	0.04	0.22	65.0
TiO_2/Nb_2O_5 (UST)	0.32	3.31	0.04	0.22	68.7
TiO_2/MgO (initial)	1.87 (1,98)	3.04	0.07	0.11	84.0
TiO_2/MgO (UST)	0.76	3.04	0.08	0.12	89.7

* ratio of the elements according preparation is in parentheses
** rate constant determined on quantity of TiO_2 in the sample
*** degradation degree of MN after 5 h photocatalytic reaction

Hence, the results obtained by EDX analysis show that UST of oxide mixtures in the most cases leads to migration of the elements from surface layer in the bulk of oxide without change their phase composition (the formation of new phases don't take place according XRD data). Analogous effect of the elements migration was observed early [18, 25, 33-34] at UST and mechanochemical treatment of the other oxides mixtures. It is necessary to note that the decrease of the titanium surface content as result of treatment was observed in cases of TiO_2/MgO and TiO_2/ZnO oxides mixtures use. This fact can be explained by partial dissolving of MgO with formation (see XRD data) of $Mg(OH)_2$ and for ZnO was proposed its partial solution with formation of $Zn(OH)_2$, also, for example the formation of zinc molybdates by UST and by hydrothermal method from ZnO/MoO_3 mixture [33, 35]. In our case, the formation of $Zn(OH)_2$ compound was not determined that permits to proposed its little quantity which cannot be detected by XRD method. These hydroxide compounds cover the surface of TiO_2 that accompanied by the decrease of Ti/Me surface ratio and in the case of XRD fixed $Mg(OH)_2$ this decline is more senses than for ZnO (Table 2). In other cases, UST leads to the mixing of the oxides with any effect on surface ratio of oxides or with little increase of TiO_2 surface content.

It is well known that band gap energy (E_g) is an important parameter of semiconductor materials especially at their use as photocatalysts in different processes. The data presented in Table 2 demonstrate that only in the case of TiO_2/MgO composition, where TiO_2 was mixing with photo catalytically inert oxide (MgO) [36], the E_g value rests equal to rutile. In case of other mixtures, an increase of E_g was observed. For TiO_2/ZnO and TiO_2/Nb_2O_5 composites, Eg value is equal to second oxide but not TiO_2 (Table 2). For TiO_2/ZrO_2 and TiO_2/SnO_2 mixtures, E_g exhibits the intermediate value between TiO_2 and second oxide. The presented in Table 2 data demonstrate that UST less influences on E_g values. The last fact can be connected with minor changes in dimension particles after UST. At same time, the first step of the mixtures preparation connected with their mixing in agate mortar influences on the properties of obtained compositions as result of strong contact between different oxides particles creation [36].

The observed values of E_g predicts that the prepared samples will exhibit low photocatalytic activity in MN photodestruction under visible light irradiation and obtained data show that in reality photodestruction rate constant (K_d) in best case (TiO_2/ZnO) has value equal to $4\cdot10^{-6}$ s^{-1} and photodestruction degree (G) is 12 % after 5 h of reaction. As result, the photocatalytic activity of synthesized samples in MN decomposition in water was determined at UV-light irradiation and all obtained data are presented in Table 2. It can be seen that the rate constant and photo destruction degree at UV- light irradiation have larger values than at Vis-irradiation for all samples.

In the other hand, an increase of rate constant value in comparison to individual TiO_2 was observed in the case of the TiO_2/ZnO compositions use. This fact can be connected with higher activity of ZnO in MN photocatalytic degradation determined previously [37-39]. It was shown that this process in the equal conditions in the presence of ZnO different modifications proceeds with rate constant $K_d = 0.16\text{-}0.27\cdot10^{-3}$ s^{-1} and this value is in 1.6-3.4 times higher that obtained for TiO_2 [37, 38]. UST has less influence on the value of rate constant of MN photocatalytic degradation in the presence of the synthesized samples: it some increase observed in case of TiO_2/ZrO_2, TiO_2/ZnO and TiO_2/MgO compositions, this value is unchanged in case of TiO_2/SnO_2 and TiO_2/Nb_2O_5 composition.

In same time, it is necessary to note that preparation of the mixtures containing two oxides leads to decrease of the photocatalytic active TiO_2 content in the samples. This fact demonstrates the data EDX presented in Table 2. So, the quantity of active catalyst (TiO_2) at use the same content of composition (0.5 g/l) as catalyst in reaction mixture decreases. In this sense there is an exception, TiO_2/ZnO mixture where the more photoactive in this process oxide (ZnO) [37, 38] was introduced in composition. It is known [37, 38] that a decrease of TiO_2 quantity in reaction MN photocatalytic degradation accompanied by a decrease of the value rate constant in 1.6-2.0 times. The realized in this work investigation with decreases of TiO_2 content from 0.5 up to 0.25 g/l shows the decrease of rate constant from 0.12 up to $0.07\cdot10^{-3}$ s^{-1} also. From this point of view, it was interesting to determine what the dilution of photoactive oxide TiO_2 by introduction of second oxide (a decrease of TiO_2 quantity) influences on catalytic activity of the composition. The calculation of the value of rate constant refers to quantity of TiO_2 in the compositions ($K_{d(TiO2)}$) was realized and the obtained data presented in Table 2.

The presented in Table 2 results demonstrate that for the all compositions excluding TiO_2/MgO the values $K_{d(TiO2)}$ are more than for individual TiO_2. In case of the TiO_2/MgO composition, $K_{d(TiO2)}$ is equal the value obtained for TiO_2 what permits concludes that the photo catalytically inert oxide MgO [36] only dilute active titania without other influence on its properties. For the other compositions including TiO_2/ZnO, an increase of $K_{d(TiO2)}$ values in comparison to data of TiO_2 is observed that can testify the presence of strong interaction between two oxides. This conception confirmed by an increase of band gap width in these compositions (Table 2) in contrary to TiO_2/MgO. As result of the possibility of separation of electrons and holes expands [36] which accompanied by an increase of $K_{d(TiO2)}$. The system stands apart is TiO_2/ZnO where the growth of activity is connected with the presence of ZnO in composition (see above). It is necessary to note that value rate constant of photocatalytic degradation of MN on TiO_2/ZnO refers to quantity of ZnO in mixture is equal to presented data for $K_{d(TiO2)}$ (0.46 and $0.50 \cdot 10^{-3}$ s^{-1}, respectively, for initial and after UST mixtures). These data exceed the values of constant rate of MN degradation characteristic for individual ZnO (see above). So, it can by testify that in this composition the influence of one oxide on the other has place too.

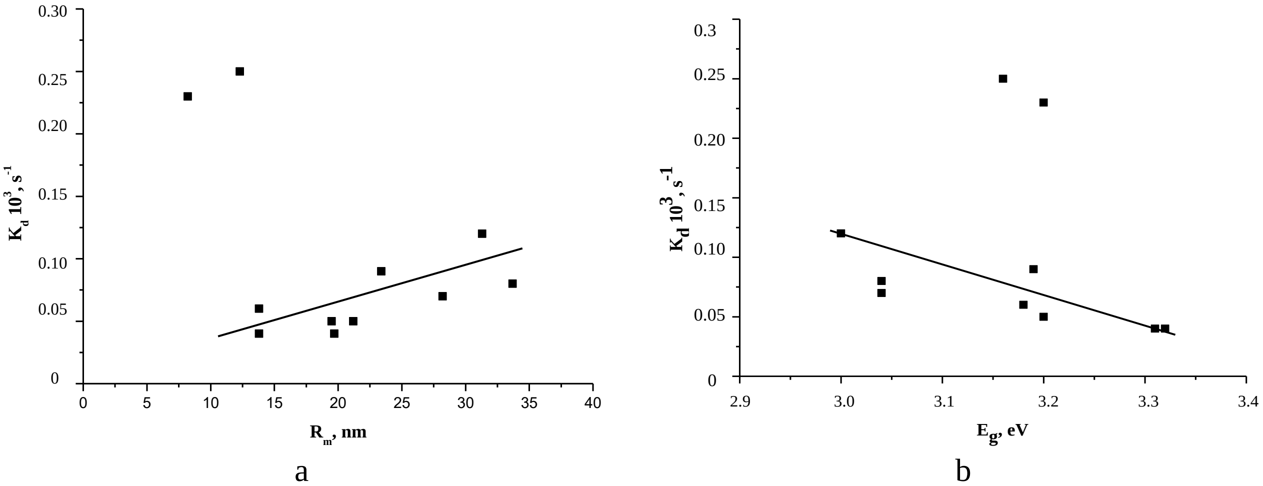
The data presented in Table 2 demonstrate that for practically all two components catalysts the degree of MN degradation has more value that for individual TiO_2. This data show advantages of the use these mixtures in the removal of MN from water as result of photocatalytic process. The best results were obtained at utilization of TiO_2/ZnO and TiO_2/MgO compositions.

The obtained results let to make an assumption connected with quantity of the catalyst in reaction mixture at MN photodegradation. Literature data [37, 38] show that an increase of the catalyst content up to 1 g/l accompanied by decrease of rate constant of MN photocatalytic degradation. In used mixtures the quantity of photoactive component in the most cases is near 50 % and it was interesting to study what an increase of the catalyst contain will be influence of rate constant. It was used two compositions after UST: TiO_2/ZrO_2 and TiO_2/ZnO. The obtained results show that in both cases the value of K_d increases: for the first composition up to $0.17 \cdot 10^{-3}$ s^{-1} and for second – up to $0.38 \cdot 10^{-3}$ s^{-1} but the $K_{d(TiO2)}$ rests practically without change – $0.22 \cdot 10^{-3}$ s^{-1} for first composition and decreases for second – $0.40 \cdot 10^{-3}$ s^{-1}. In same time the high degree of MN degradation (near 99 %) was obtained after shorter reaction time 3.5 and 2 h, respectively, for TiO_2/ZrO_2 and TiO_2/ZnO UST compositions. Thus, obtained result shows the perspective of the two components photocatalysts use and their UST.

The comparison of the photoactivity samples (K_d) in MN decomposition with their specific surface area and total pores volume data shows any connection between these parameters. In the other hand, the results presented on Fig. 5 a, demonstrate that rate constant of MN photodecomposition increases with increase of medium pores diameter. Separately located samples of TiO_2/ZnO compositions which activity was determined as connected with the presence of ZnO but not TiO_2, as for other oxide compositions. In same time it is necessary to note that for these TiO_2/ZnO samples an increase of K_d with growth of pores diameter observed, also. This correlation can be explained by an increase of sample surface area accessible to UV irradiation with growth of pores diameter analogously to presented in [36]. In same time these data shown positive effect of UST which leads to an increase of pores diameter (Table 1) and correspondingly to an increase of the samples photocatalytic activity (K_d) in MN oxidative decomposition.

On the other hand, the data presented on Fig. 5 b show~~s~~ that photocatalytic activity of the samples (K_d) in the process of MN destruction is decreased with an increase of band gap energy values of the compositions. Analogous relations are traditional in the case of photocatalytic processes. In this case, also, the sample of TiO_2/ZnO compositions located separately for same reason described below.

The data connected with the obtained degree MN decomposition attract attention because they demonstrate the positive effect of UST. In all cases this treatment permits to obtain the more value G (Table 2) than for initial oxides mixtures. It can demonstrate more stability of the compositions after treatment in the process of MN photodestruction and low influence of time reaction and change of MN concentration on their photocatalytic activity.



a b

Fig. 5. The dependence of rate constant of MN decomposition in its photocatalytic removal in water from average radius (R_m) of the oxides compositions (a) and determined band gap energy values for these samples (b)

Conclusions

The creation of oxide two-component systems based on rutile TiO_2 was studied. Influence of ultrasound treatment of these mixtures on their properties was established. It was shown that introduction of the second oxide accompanied by a decrease of the reflexes TiO_2 intensity as a result of its content decreases in the mixtures. The treatment of the mixtures less influence on the ratio of intensity of (110)/(101) reflexes of TiO_2 what testify any structural change of this oxide but in same time little increase of its particles size was observed. The partial increase of the dimension particles for second oxide after UST for the studied mixtures excluding TiO_2/MgO and TiO_2/ZnO was observed also. The partial transformation of MgO to $Mg(OH)_2$ as result of TiO_2/MgO composition treatment was shown which accompanied by decreases of MgO particles size. In case of TiO_2/ZnO composition according XRD data as result of UST the partial destruction of ZnO was observed.

The changes in specific surface area and pores volume after preliminary processing in agate mortar and as result of UST with an increase of medium pores radius after ultrasound treatment with the change of surface element ratio determined by EDX method can testify that strong interaction between oxides takes place. This fact leads to an increase the band gap for the mixture in comparison with initial TiO_2 with its average value between characteristic for TiO_2 and other oxide in mixture.

The study of photocatalytic properties of the samples in MN oxidative decomposition in water shows that for all compositions, excluding TiO_2/ZnO where the activity is connected with more active ZnO in this reaction but not TiO_2, a decrease of initial rate constant K_d was observed. The rate constant of MN photodegradation was connected with a decrease of TiO_2 content in the mixtures and introduced value of rate constant determined to quantity of TiO_2 demonstrate its increase in comparison to individual TiO_2. This fact is a consequence of strong interaction in complexes systems between two oxides. Obtained results permit to predict and realized the MN photocatalytic degradation in water with an increase of the complexes catalyst content in reaction mixture what leads to an increase both rate constant and degree of MN transformation. It was established that UST increased the stability of the samples in MN transformation and as result the conversion of MN has more value than in initial mixtures.

An increase of MN degradation degree after UST correlates with the growth of medium pore radius in result of UST what can be connected with an increase of sample surface accessible to UV irradiation. It was shown that obtained samples demonstrate better properties in MN destruction in water in comparison with data known from the literature. So, the perspective of complex oxide compositions creation on the base of one known photocatalyst and use of UST were shown.

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Двокомпонентні оксидні композити на базі TiO_2 рутилу: ультразвукова обробка, їх фізико-хімічні та фото каталітичні властивості

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Вивчено створення оксидних двокомпонентних систем на основі рутилу TiO_2. Встановлено вплив ультразвукової обробки (УЗО) на властивості даних композитів. Показано, що дана обробка сумішей мало впливає на їхні структурні характеристики, а саме, на співвідношення інтенсивності (110)/(101) рефлексів TiO_2, але в той же час спостерігається незначне збільшення розміру його частинок. Для другого оксиду також відбувається невелике зростання розміру його частинок в результаті УЗО, виключенням є TiO_2/MgO та TiO_2/ZnO зразки. Показано, що в результаті обробки TiO_2/MgO суміші відбувається часткове перетворення MgO у $Mg(OH)_2$, яке супроводжується зменшенням розміру MgO частинок. У випадку TiO_2/ZnO суміші спостерігається часткове руйнування ZnO як результат УЗО.

Встановлено, що УЗО сприяє збільшенню середнього радіусу пор композицій одночасно зі зміною поверхневого співвідношення елементів, визначеного ЕДА методом, що може свідчити про сильну взаємодію між оксидами в суміші. Даний факт веде до зростання значення енергії ширини забороненої зони (Eg) оксидної системи у порівнянні з вихідним TiO_2. При цьому, у більшості випадків значення Eg має середню величину між показником характерним для діоксиду титану та іншого оксиду в зразку.

Дослідження фотокаталітичних властивостей зразків в процесі окислювальної деградації метронідазолу (МН) у воді показують, що для всіх композитів спостерігається зниження значень константи швидкості K_d. Виключенням є TiO_2/ZnO система, фотоактивність якої пов’язана з більш активним ZnO в даній реакції, але не з TiO_2. Падіння значень K_d можна пояснити зниженням вмісту TiO_2 у сумішах і даний показник визначається кількістю рутилу в них, а введене значення $K_{d(TiO2)}$, яке визначене для кількості TiO_2, демонструє її підвищення у порівнянні з індивідуальним TiO_2. Даний факт свідчить про сильну взаємодію в складних системах. Одержаний результат (підвищене значення $K_{d(TiO2)}$ для композитів, у порівнянні з TiO_2) дозволив реалізувати фотодеструкцію МН у водному середовищі із більшим вмістом складного каталізатора в реакційній суміші, що веде до зростання значень константи швидкості та ступеню деструкції антибіотику. Встановлено, що УЗО метод підвищив стабільність зразків у процесі перетворення МН і, як результат, конверсія антибіотика має більші значення, ніж для вихідних сумішей.

Підвищення значень ступеню деградації МН для УЗО зразків корелюється із зростанням середнього радіусу пор в них, що може бути пов’язано із збільшенням їхньої поверхні, яка доступна для УФ-опромінення. Показано, що одержані композити демонструють кращі властивості в деструкції МН у воді у порівнянні з відомими зразками в літературі.

Ключові слова: складні оксидні композити, ультразвукова обробка, фотокаталіз, деструкція метронідазолу