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Cent. Eur. J. Chem. • 10(6) • 2012 • 1850-1858
DOI: 10.2478/s11532-012-0109-z

Central European Journal of **Chemistry**

The radioactivity and the chemical nature of additives as factors determining the photocatalytic activity of TiO_2

Research Article

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Received 29 April 2012; Accepted 26 July 2012

Abstract: Microcomposites consisting of TiO_2 and ThF_4 or UO_3 (0.5-2% of the TiO_2 mass) are produced by sol-gel synthesis of TiO_2 in presence of the respective additives. X-ray diffraction study reveals small effect of the latter on TiO_2 phase composition and cell parameters and significant influence on the crystallite size and UV/Vis reflectance spectra. The photocatalytic tests in presence of TiO_2-ThF_4 microcomposites under UV and solar irradiation show a non-monotonic increase of the Malachite Green degradation rate constant with the increase of ThF_4-content. No changes in the photocatalytic activity are observed in the presence of UO_3 but the latter composites exhibit activity in darkness. The results are compared with previously reported data on the performance of TiO_2-ThO_2 photocatalyst with the same radioactivity and suggest that both radioactivity and the chemical nature of the dopants are responsible for the photocatalytic performance of TiO_2-based composites containing radioactive substances.

Keywords: *Actinoids • Photocatalysis • Radioactivity • Sol–gel synthesis • TiO_2*

1. Introduction

Doping of TiO_2 with different elements is a common method to increase its photocatalytic activity and shift that activity to longer wavelengths. While the effect (positive or negative) of a significant number of the d- and 4f-elements – as well as some alkalis and number of non-metals – on the photocatalytic activity of TiO_2 is widely studied, the data on the effect of 5f-elements are very limited.

In a few patents, attempts are made to utilize the effect of natural radioactive components as TiO_2 dopants [1-3]. Devi *et al*. [4,5] modified sol-gel produced TiO_2 (anatase) with $Th(NO_3)_4$ (0.02 – 0.1%). Doping decreases the photocatalytic activity under UV irradiation but increases it under solar illumination. The catalyst with 0.06% Th^{4+} exhibits the highest activity under the both types of illumination which is ascribed to the peculiarities of the doped samples: higher surface area, the increased adsorption ability to water and hydroxyl groups, shift in the absorption band to visible region (important at solar irradiation), more efficient separation of charged carriers. The latter is due to the defect levels created by Th^{4+} ions in the TiO_2 lattice (which can capture and release the photogenerated electrons or holes). While the papers [4,5] are concentrated mainly on the role of Th^{4+}-ions as dopants modifying the physicochemical (and thence – the photocatalytic) properties of TiO_2, Yu *et al*. [6] pay attention to the activating function of the Th radiation originated from natural mineral monazite (rare earth/thorium phosphate) in synergism with cerium. The final material is effective against phenol and Methylene Blue degradation even in darkness. The interpretation of the effects is based on the role of cerium as a mediator in the processes taking place. The Ce-ions are excited by photons with energy above 5-6 eV and the following intensive luminescence in the interval 2.8-4.5 eV due to 5d→4f transitions is sufficient to excite TiO_2.

Our previous work [7] shows that radioactivity is one of the main reasons for increased photocatalytic activity

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of TiO_2-ThO_2 composites and the presence of Ce^{4+} ions is not an requirement for the realization of the ThO_2 effect. The photocatalytic tests under UV irradiation in the presence of microcomposites consisting of sol-gel synthesized TiO_2 and ThO_2 (0.5-2% of the TiO_2 mass) reveal an increase of the Malachite Green degradation rate constant depending non-monotonously on the ThO_2 content. The composite exhibits activity in darkness, also. The experimental results show that (despite the significant differences in the Ti^{4+} and Th^{4+} ionic radii and the composite nature of the prepared catalyst) a small amount of the added ThO_2 gets into the structure of the sol-gel prepared TiO_2. Thus the Th^{4+} could influence the TiO_2 photocatalytic performance *via* two ways – as a chemical dopant present in its crystal cell and as an ionization ray source.

The present work expands this investigation studying the performance of the catalysts under solar irradiation but its main aim is to compare and distinguish the role of the above mentioned two factors (radioactivity and the chemical nature of the additive) on the photocatalytic activity of TiO_2. Pursuing this aim, experiments were performed substituting ThO_2 with ThF_4 or UO_3. Synthesis and photocatalytic tests were carried out at the same conditions as those applied in [7]. The Th-content (and, respectively, the radioactivity) in the systems TiO_2-ThF_4 were the same as in the TiO_2-ThO_2 microcomposites. In the other studied system, the mass ratio TiO_2/UO_3 was the same as TiO_2/ThO_2 ratio used in the previous study [7].

Surface modification of TiO_2 with F^- has been investigated as an avenue to improve the photocatalytic performance of the TiO_2 (see for example [8,9] and the cited literature). Strong absorption of fluoride anions on the TiO_2 surface greatly affects its interfacial and surface properties [10]. Photocatalytic activity of F^--doped TiO_2 depends on the number of factors, including catalyst phase composition [9], nature of the pollutant (cationic or anionic dye [11]), doping conditions [8]. In most of the reported cases promotion of the TiO_2 photocatalytic activity resulting from the fluorination is found. However, the fluorination in the most of the studies is realized in a way (usually treating the TiO_2 with NaF solution), rather different from the one applied in the present work and the established mechanisms of the influence of the adsorbed F^--ions cannot be realized in the conditions of our work. So, a direct comparison of the results obtained in the present study for the system TiO_2-ThF_4 with the earlier results for the effect of F^--ions (when surface fluorinated TiO_2 is applied) is impossible. Further on in the text our speculations are limited within the frames of analogous systems produced by the same method in which the mechanism of additives' influence will be similar.

2. Experimental procedure

2.1. Catalysts synthesis and characterization

The composite TiO_2-ThF_4 and TiO_2–UO_3 were produced according to the same sol-gel procedure, applied for TiO_2-ThO_2 [7]. ThF_4 (Carlo Erba, ≥99%) or UO_3 (Chemapol) in the desired amount was suspended in 50 mL of absolute ethanol and 0.025 mol of $Ti[OCH(CH_3)_2]_4$ (99%, Aldrich) was added. After stirring diluted HNO_3 (volume ratio H_2O : 65% HNO_3 : absolute C_2H_5OH = 24 : 0.05 : 80) was added slowly to pH 3 and stirred again for 30 min. Finally, all products were dried at 120°C and calcinated for 3 h at 550°C. Samples, containing 0.5, 1.0 and 2.0% UO_3 by mass or such amounts of ThF_4 that ensure Th-content and radioactivity equivalent to 0.5, 1.0 and 2.0% of ThO_2, were produced.

The concentrations of the additives were predetermined by their amounts, introduced into the systems, and confirmed by energy-dispersive X-ray fluorescence analysis within the analysis error limits. A 0.25 g portion of the powdered sample was mixed with 1 g H_3BO_3 (spectroscopical grade), homogenized and pressed into a pellet of 25 mm diameter and 2 mm height. The samples were measured using a Si(Li) detector (Ortec) with energy resolution of 175 eV at 6.4 keV, thickness of the Be window 0.0254 mm and active area 28 mm^2. The detector was coupled to a spectroscopic amplifier (Ortec Model SLP-06175-P; CFG-PD), ADC (Canberra 8075) and MCA Canberra 35 Plus using ^{241}Am with activity of 3.7 GBq with ring geometry as the excitation source.

Gamma spectra of the final products were taken by a Canberra 35 4096-channel gamma spectrometer (HPGe detector, effectiveness 15%). The samples' activities were measured by the areas of 338.4 keV γ-peak of ^{228}Ac (for Th-containing samples) and of 185.7 keV peak of ^{235}U.

X-ray diffractograms of the specimens were recorded by Siemens D500 powder diffractometer at CuK_α irradiation (40 kV, 30 mA, 2θ step 0.02°/2 s) equipped with secondary monochromator to exclude K_β light. Quantitative analysis of the diffractograms was performed by the Rietveld method using the program BRASS [12]. Thus, the lattice parameters, the average crystallite size and the phase composition ratio of the obtained materials were calculated.

UV/Vis absorption and diffuse reflectance spectra of the powdered specimens were registered by means of

an Evolution 3000 UV/Vis spectrophotometer (Thermo Scientific) equipped with a Praying-Mantis accessory.

2.2. Photocatalytic tests

The photocatalytic tests were performed as described in [7] in slurry (1 g catalyst L^{-1}), using Malachite Green oxalate (MG, 10^{-5} M aqueous solution) as a model pollutant. After 30 min "dark" period (for establishing of equilibrium of the sorption process), the system was UV-illuminated by a Sylvania 18 W BLB T8 lamp (emission in the 345-400 nm region with a maximum at 365 nm), situated at 9.5 cm distance above the slurry under continuous magnetic stirring (400 min^{-1}) and bubbling with air (45 $dm^3 h^{-1}$). The dye concentration was followed spectrophotometrically by the band at 620 nm. Some of the experiments were performed under indirect sun light around 12-14.30 h during sunny days in May in Sofia (latitude 42.7°N, longitude 23.3°E, altitude 550 m above sea level). In the mentioned time period the sun intensity is comparatively constant (UV index 7.5-8.0 for one of the days, in which part of the experiments were done). "Solar" experiments were also done with TiO_2–1% ThO_2, prepared by the method, applied in [7] and showing best photocatalytic activity among ThO_2-containing specimens.

The data obtained were plotted in coordinates $\ln(C/C_0)/t$ (where C_0 is concentration after the "dark" period, and C is concentration after t min irradiation) and apparent rate constants of the degradation process were determined accepting first order kinetics. The sorption ability was calculated as a ratio $(C_{00} - C_0)/C_{00}$, where C_{00} is the starting solution concentration (before the "dark" period). The relative standard deviation of the results evaluated from three parallel experiments with composite containing 1% additive is 4%.

Table 1. Gamma doses of the prepared composites ($\mu Sv\ h^{-1}\ g^{-1}$).

Composite	At surface	At 20 cm from the surface
TiO_2 – 1% ThO_2/ThF_4	280.3	7.01×10^{-3}
TiO_2-1% UO_3	73.4	1.83×10^{-3}

3. Results and discussion

3.1. Radioactivity

The total radioactivity of the prepared samples is almost equal: 313.9 Bq g^{-1} (TiO_2-1% ThO_2/ThF_4) and 310.5 Bq g^{-1} (TiO_2-1% UO_3). The dose rate at composite surface and at 20 cm from the surface is shown on Table 1. It is seen that it is negligible compared to the natural gamma-background which reaches 0.4 μSv h^{-1}.

3.2. Crystal structure, crystallite size, phase composition

Fig. 1 represents the X-ray diffractograms of some of the studied composites. The diffractograms of TiO_2-ThF_4 composites are identical regardless of the additive content (within the studied concentration interval) (Figs. 1, 3-5). The same is also true of the composite TiO_2-1% UO_3. Data for the lattice parameters, crystallite size and phase composition of the samples are shown in Table 2. For comparison, the results [7] for TiO_2-ThO_2 composites are also included.

The influence of ThO_2 on the anatase crystal parameters and possible mechanisms for its incorporation in the host cell are discussed in [7]. No significant difference in the effect of the ThF_4 is observed – as in the case of the ThO_2 presence, the

Table 2. Lattice parameters (a, b, c, Å) size of crystallites (SC, nm), cell volume ($V\times10^{-6}$, pm^3) and phase composition (PC, %) of the studied TiO_2 samples.

№	Additive		Anatase					Rutile					Brookite					
	Type	%	a, b	c	V	SC	PC	a, b	c	V	SC	PC	a	b	SC	V	SC	PC
JCPDS*	-	-	3.77600	9.48600	135.25			4.59370	2.95870	62.43			9.184	5.447	5.145	257.380		
1	-	-	3.784(1)	9.481(3)	135.73	9	91						9.184(0)	5.447(0)	5.145(0)	257.380	7	9
2	ThF_4	0.5	3.783(8)	9.496(2)	135.96	22	90	4.571(7)	2.957(9)	61.82	13	2.5	9.018(2)	5.466(0)	5.266(9)	259.621	8	7
3	UO_3		3.783(2)	9.504(0)	136.03	13	100											
4	ThO_2		3.7803(5)	9.501(1)	135.77	18	96	4.587(3)	2.954(3)	62.14	25	3						
5	ThF_4	1.0	3.783(7)	9.497(2)	135.97	13	89	4.570(9)	2.963(2)	61.91	14	2.4	9.136(9)	5.459(3)	5.176(7)	258.221	21	8
6	UO_3		3.783(6)	9.503(3)	136.05	11	100											
7	ThO_2		3.7819(7)	9.501(2)	135.88	17	98											
8	ThF_4	2.0	3.784(6)	9.494(9)	135.99	11	85	4.570(7)	2.955(1)	61.74	14	3.2	9.216(5)	5.413(6)	5.183(7)	258.636	6	12
9	UO_3		3.785(5)	9.499(2)	136.12	29	100											

** Anatase: 73-1764, Rutile: 78-2485, Brookite: 96-900-9088*

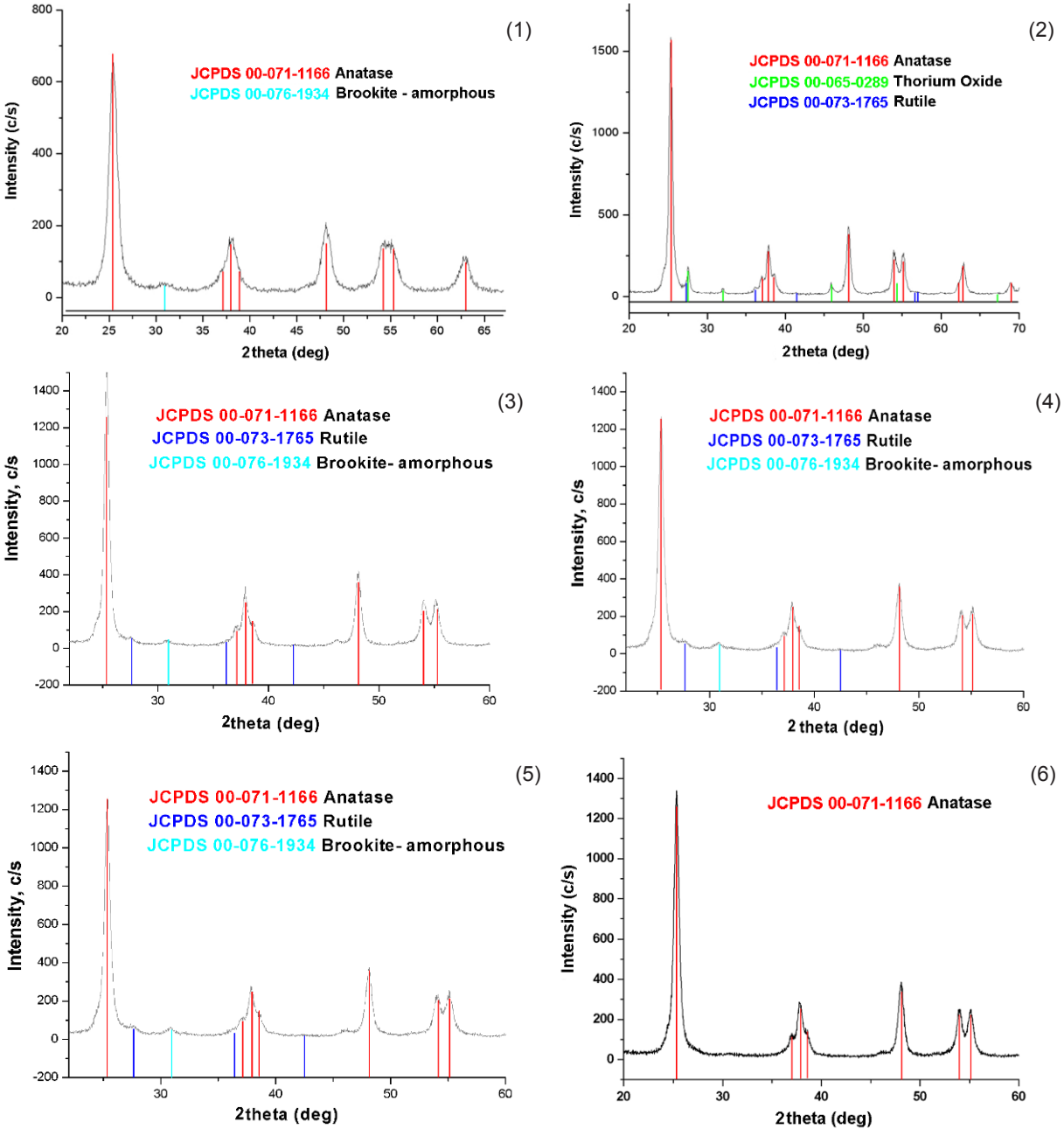

Figure 1. X-ray diffractograms of TiO_2 (1) and TiO_2 doped with 1% ThO_2 (2), ThF_4 0.5% (3), 1% (4), 2% (5) and UO_3 (6).

parameter *a* is practically not changed, the elongation of the parameter *c* is of the same order. The anatase cell volume increases monotonically with the additive concentration growth and at 2% additive content is 0.2% larger than that of the non doped TiO_2 prepared by the same way. The latter fact can be interpreted as an indication that small amount of the added compounds gets into the TiO_2 structure as is proven in [4,5], also. A slightly bigger enlargement of parameter *c* and of the cell volume (0.3% at 2% content) caused by UO_3 could be related to the smaller U^{6+} ionic radii (87 pm compared with 108 pm for Th^{4+} and 74.5 pm for Ti^{4+}) possibly leading to a slightly higher penetration of the additive in the TiO_2 structure.

In contrast with the system TiO_2-ThO_2 no reflexes of ThF_4 and UO_3 are observed in the respective composites' diffractograms. The same effect is observed in [5] and has been explained [13,14] with dispersion capacity of the metal oxides. Our experimental data show that the capacity of TiO_2 depends on the chemical nature of the added compound.

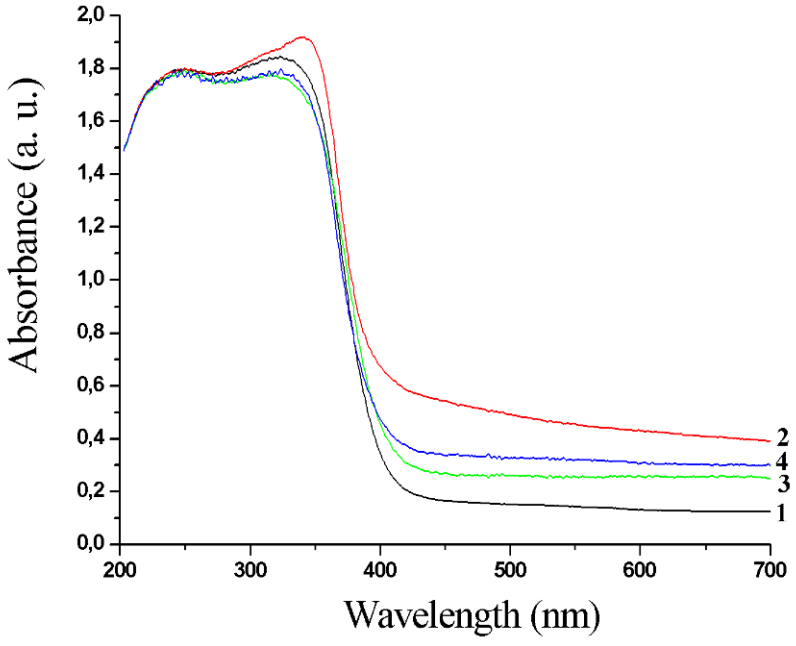

Figure 2. UV-Vis absorption spectra of TiO_2 (1) and composites TiO_2+1% UO_3 (2), TiO_2+1% ThO_2 (3), TiO_2+ThF_4 (equivalent by Th-content and radioactivity to 1% ThO_2) (4).

All studied additives cause a non-monotonic increase of the anatase crystallite size with the additive content increase (Table 2), reaching 22 nm (0.5% ThF_2) and 29 nm (2% UO_3) compared with 9 nm for the non-doped material. The effect of the ThF_2 on the brookite is statistically significant at higher (2%) additive content. Non-monotonic influence of the Th^{4+} content on the crystallites size is also reported in [4] in a rather different concentration interval.

It is known that the presence of 4f-ions stabilizes anatase modification (see, for example, [15]). The data in [4,7] suggest that ThO_2 has the same effect. Our results concerning UO_3-containing composites are also in agreement with the above results - only anatase is registered in this type of sample. The presence of ThF_4, however, has a different effect. The content of anatase in the TiO_2-2% ThF_4 sample decreases from 91% in the pure TiO_2 to 85% whereas rutile and brookite content increases from 0% to 3% and from 7% to 12 %, respectively. The reasons for the observed difference in the behavior of the studied thorium compounds are yet to be elucidated.

3.3. UV-Vis absorption and diffused reflectance spectra

Two partially overlapped bands with maxima around 246 and 323 nm are registered in the absorption spectra of the TiO_2 and TiO_2-Th composites, containing 1% additive (Fig. 2). In the analogous TiO_2-UO_3 specimen the latter band is shifted to 342 nm. Similar bands are observed in [5] in the intervals 200–215 and 340-350 nm. The variations in the ThF_4 content does not cause any changes in the UV spectral region suggesting that (as in case of TiO_2-ThO_2 system [7]) a rather limited amount (probably much below 0.5%) of Th-containing additive can be introduced into TiO_2 structure and, accordingly, a higher amount of the additive in the composite is meaningless from the point of view of its influence on the TiO_2 crystal and electronic structure.

The presence of Th-compounds does not lead to any changes in the reflectance spectra of the composites in the short-wave UV region (Fig. 3a) compared with the pure TiO_2. An increased absorption in the interval 385-400 nm is seen in the spectra of the Th-containing samples but not in UO_3-containing one. The visible light absorption by the composites containing 1% ThO_2 or ThF_4 is practically the same and much higher than that of non-doped TiO_2. The absorbance of the UO_3-containing composite is similar to that of the pure TiO_2.

The clearly expressed non-monotonic dependence of the reflectance on the ThF_4 content in the specimens is seen on Fig. 3b.

3.4. Sorption ability and photocatalytic activity

Fig. 4 shows the influence of the additive concentration on the sorption ability of the catalysts and on the rate constant of dye photocatalytic degradation. Fig. 5 compares the effects of different additives present in the composites in equal radioactivity/ concentration.

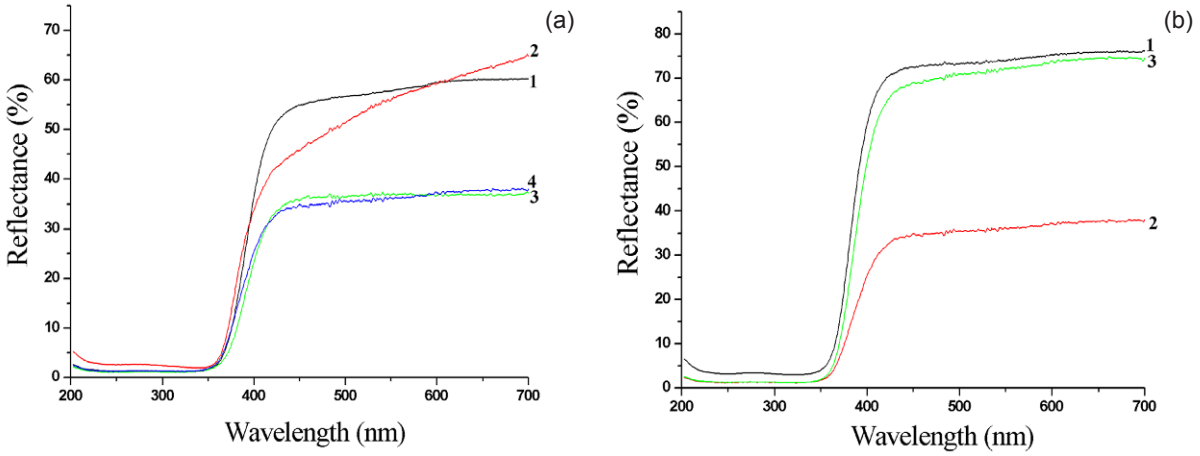

Figure 3. UV-Vis diffused reflectance spectra of: (a) TiO_2 (1) and composites TiO_2+1% UO_3 (2), TiO_2+1% ThO_2 (3), TiO_2+ThF_4 (equivalent by Th-content and radioactivity to 1% ThO_2) (4); (b) TiO_2+ThF_4, equivalent by radioactivity to 0.5% (1), 1% (2) and 2% (3) ThO_2.

Data on Fig. 5 show for the first time results on the performance of Th/U-doped TiO_2 under solar irradiation. It is seen that the degradation rate constants for all studied catalysts (including pure TiO_2) at these conditions are higher than at UV irradiation. The reason is in the very low-power UV irradiation source used in the present study (18 W) while much more powerful lamps are commonly used in similar photocatalytic tests (125 W Philips high-pressure mercury lamp [16], 150 W xenon lamp [17]), often immersed in the TiO_2-pollutant slurry [18]. At such conditions the degradation at UV illumination is much more effective than at sunlight treatment. For instance, the rate constant (min^{-1}) for the degradation of an herbicide decreases from 225 to 25 (using the commercial product Degussa P25 TiO_2) or from 36 to 9 (sol-gel produced TiO_2) when UV and solar irradiation are applied, respectively [18].

The experimental results obtained in the present work confirm the earlier results, reported and discussed in [7]: (i) As in the case of pure ThO_2, the pure ThF_4 (in amounts equal to the one contained in the composite TiO_2-1% ThF_4) show no measurable effect on the pollutant degradation under UV-irradiation and in darkness; *i.e.*, the results obtained with the studied composites have to be ascribed to a synergistic effect of the TiO_2/Th-compound. (ii) Independently of the compound nature and its relative amount (within concentration interval studied), the effect of Th^{4+} on the TiO_2 crystal structure and phase composition is rather weak (Fig. 1, Table 1) but influences significantly the size of crystallites (Table 1) and the composites' sorption ability and photocatalytic activity under UV-irradiation (Fig. 4). (iii) At certain Th-contents, an increase in composite photocatalytic activity compared with the non-doped TiO_2 is found (Fig. 4). As is seen from Fig. 3a, both Th-containing composites exhibit an increased absorption in the interval 385-400 nm compared to that of the pure TiO_2. As far as the applied UV source has an emission in the 345-400 nm region, this effect might have some contribution to the increased photocatalytic activity of the composites along with the effect from their radioactivity shown in [7]. (iv) The present experiments with ThF_4 confirm the non-monotonic character of the dependences of the sorption ability and photocatalytic activity at UV-irradiation on the Th-content in the composite (Fig. 4). The specific optical behaviour of the composite with 1% ThF_4 – compared with that of the samples with 0.5 and 2% additive (Fig. 3b) – confirms (under different experimental conditions) the non-monotonic changes of the band gap energy for TiO_2 in Th-doped TiO_2 samples reported in [5].

At the same time, the results in the present paper reveal a few peculiarities of the photocatalytic activity of the TiO_2-ThF_4 and TiO_2-UO_3 systems:

- *Weaker effect of ThF_4 compared with ThO_2 under UV irradiation* (Figs. 4,5). This difference cannot be due to a difference in the specific radioactivity of the samples, neither to the difference in their optical properties - the reflectance spectra of the two types of composites are identical in the UV spectral region (Fig. 3a). A possible reason for this effect could be the difference in the sorption ability of the two types of composites. Sorption of the pollutant on both studied catalysts varies in a relatively wide interval (Fig. 4; the variations are much more significantly expressed in TiO_2-ThF_4 system) without any clearly expressed dependence on the Th content. However, while the relations of the catalyst sorption ability and of the photocatalytic activity on the ThO_2 concentration in system TiO_2-ThO_2 are, in general, synchronous, the analogous relations for TiO_2-ThF_4 catalyst are mirror-images. The sorption is a compulsory stage in the overall photocatalytic process. However,

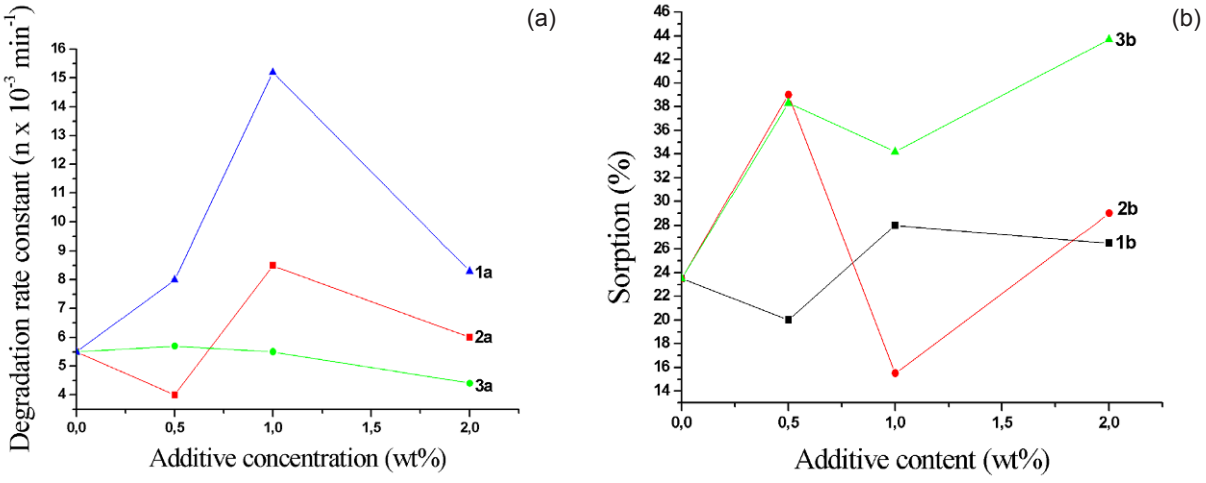

Figure 4. Relations of degradation rate constant under UV irradiation (a) and catalysts sorption ability (b) on additive concentration: ThO_2 (1), ThF_4 (2), UO_3 (3).

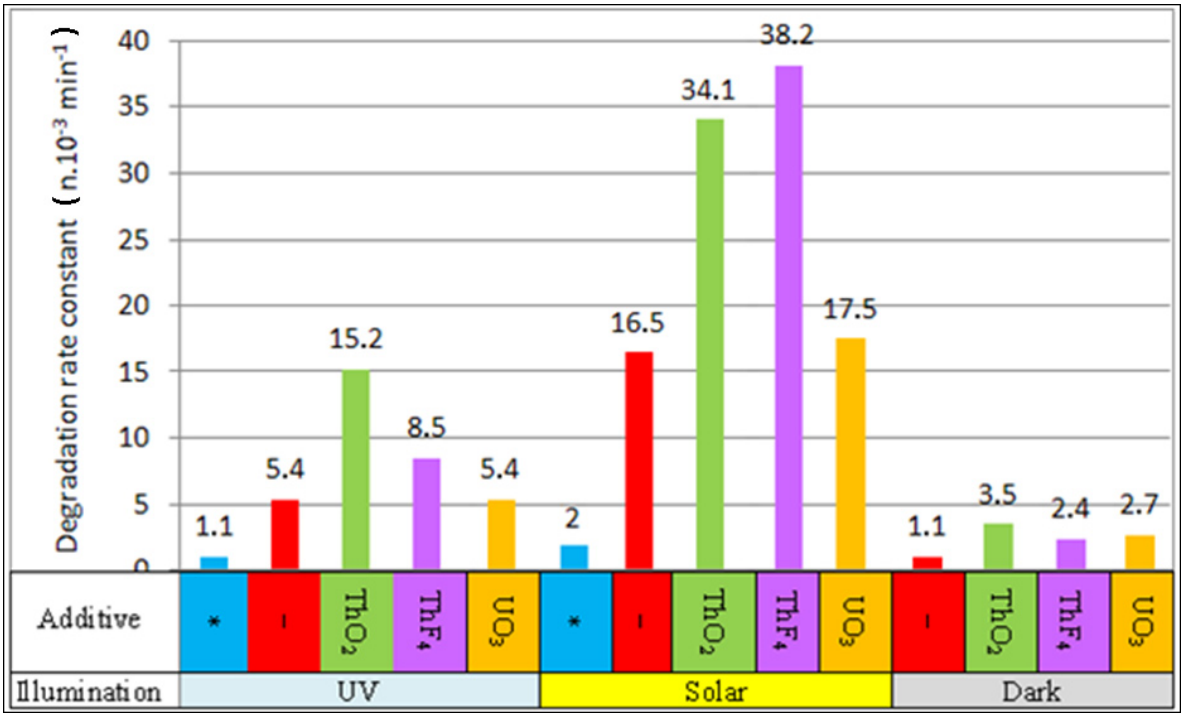

Figure 5. Degradation rate constant at 1% content of additives in the composites: * - photolysis, only; "-" pure TiO_2.

rather strong adsorption of the pollutant and, especially, of the degradation products can block the catalyst surface thus inhibiting its activity. The MG is a cationic dye and its strong adsorption on the F^--containing surface is to be expected. An increased adsorption of Rhodamine B is observed on the fluorinated TiO_2 surface [19]. We have no data on the MG degradation products. The observed bleaching of the solution can be due not to dye mineralization but to destruction of its chromophore part, only. The intermediate(s) may remain adsorbed on the surface decreasing the catalyst activity.

- *Slightly stronger effect of ThF_4 in comparison to ThO_2 under the solar irradiation.* Accounting for the experimental errors, the degradation rate constants for composites containing ThO_2 or ThF_4 are rather close (Fig. 5). This result is in agreement with practically equal reflectance spectra of the two types of catalysts in the visible spectral region (Fig. 3a). At the same time, the slight tendency for increase of the photocatalytic activity of TiO_2-ThF_4 composite could be related to the higher adsorption ability of the fluoride-containing composite. It will enhance the process of visible light photocatalytic

degradation initiated by a direct electron transfer from the photoexcited dye molecules to the TiO_2 conductive band reported for Rhodamine B [19].

- *Lack of effect of UO_3*. It was mentioned (chapter 3.1.) that the radioactivity of samples doped with UO_3 is almost the same as of Th-containing ones. Despite that, its addition has no effect on the TiO_2 photocatalytic activity under UV and solar irradiation (Figs. 4,5). However, the rate constants found for UO_3 and ThF_4 composites in darkness are practically equal, nevertheless that the gamma-dose of the UO_3-containing composite on the surface of the sample (where catalytic process takes place) is almost 4-times lower (Table 1). The catalyst performance in darkness is a direct consequence of its radioactivity (according to [6] the high energy of ^{238}U daughters and especially of ^{226}Ra is the main factor for the enhancing of the photocatalytic process evoked by the TiO_2/monazite catalyst) and from this point of view the activity in darkness is to be expected. Its independence on the gamma-dose confirm our earlier made supposition [7] that the ionization of the environment by the electrons and α-particles emitted from the radioactive component and electron-hole pairs produced by their interaction with the TiO_2 semiconductor are the main reasons for the effect of the radioactive component of the catalyst.

The different behavior of Th- and U- containing catalysts has to be ascribed to differences in their sorption ability (rather high for TiO_2-UO_3) and to the action of UO_3 as a chemical reagent. As was already mentioned, due to relative closeness of the ionic size of U^{6+} with that of Ti^{4+}, it can be more easily substituted into the TiO_2 lattice than can Th^{4+}. It can be observed from Table 1 that the unit cell parameter along *c*-axis and cell volume of the TiO_2 increase by 0.05-0.06% (up to 0.1% for the cell volume at 2% additive concentration) compared with the respective parameters for TiO_2-ThF_4 composite. In case of TiO_2 doping with U^{6+}, n-type behavior is expected, creating mid-band gap states just below the conduction band. These may serve as sites for recombination. U^{6+} is easily inclined to non-reversible reduction to the rather stable U^{4+} thus it may serve as a deep trap for photogenerated electrons. The trapping of electrons by U^{6+} is observed during high-energy mechanical treatment of UO_3 leading to its mechanochemical reduction [20]. The experimental results strongly suggest that (within the studied interval of UO_3 concentrations in the composite) the positive and negative effects are canceled out keeping TiO_2 photocatalytic activity constant.

4. Conclusion

Formation of TiO_2-ThO_2/ThF_4/UO_3 composites do not cause significant changes of sol-gel produced TiO_2 crystal cell parameters. ThO_2 and UO_3 inhibit phase transformation of anatase to rutile. In TiO_2-ThF_4 samples, however, TiO_2 presents in the three polymorphs with the domination of anatase. Independently of the chemical nature of the studied additives, they cause increase of the crystallite size of the formed anatase.

The photocatalytic activity of TiO_2-ThF_4 under UV irradiation depends on the additive content and at 1%, the MG degradation rate constant is 1.6 times higher than that of the pure TiO_2. At these conditions the enhanced action of the ThF_4 is significantly weaker than that of ThO_2 with the same radioactivity. However, at solar irradiation the activity of the TiO_2-ThF_4 composite (measured by the rate constant) is 2.3-fold higher compared to the pure one and comparable with that of TiO_2-ThO_2 composite. UO_3 addition (0.5 – 2%) does not change the TiO_2 activity.

The photocatalytic activity of all studied composites in darkness demonstrates the influence of the ionizing radiation emitted by Th and U and their daughter products on the TiO_2 activity, confirming the conclusion on this point made in [7].

The reported results (along those previously reported) on TiO_2-ThO_2/ThF_4/UO_3 show that the chemical form of the radioactive additives and type of illumination during the degradation process are also important factors determining the TiO_2 photocatalytic activity.

Acknowledgment

The work is performed under the financial support of the NATO Science for Peace Program (contract SfP 982835) and of Bulgarian Fund for Scientific Investigations (contract DO 02-252/08). The authors are indebted to Mr. M. Tsvetkov, MSc for the help with the X-ray diffractometry.

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