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Crystal structure, morphology and photocatalytic activity of modified TiO_2 and of spray-deposited TiO_2 films

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ABSTRACT

A short review is presented on the authors· investigations on the influence of the crystal structure and the morphology on the sorption ability and photocatalytic activity under UV-irradiation of thin TiO_2 films produced by spray-deposition process. Commercially available TiO_2 (Degussa P25 and Tronox), titania modified by mechanoactivation as well as TiO_2 doped with gold and, mainly, with lanthanides (produced by sol–gel process or from mixed-metal citric complexes) are used as starting materials. Organic dyes, phenol, oxalic acid and pesticides were used as model pollutant. Conclusions are drawn for the effect on the photocatalytic activity of films morphology, anatase content, substrate chemical nature, deposition conditions (temperatures of deposition and post-deposition annealing, suspension medium nature, additives presented and its ultrasonic treatment), type of titania used and its modification by mechanochemical treatment and by doping with gold or lanthanides (lanthanum, gadolinium and neodymium).

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1. Introduction

The TiO_2 is the most widely used heterogeneous photocatalyst, attracting researchers with its high oxidative power under UV-light and resistance to photo corrosion. Its main disadvantage is the low efficiency under visible light irradiation. General overview of the issue and some more particular problems could be found in number of reviews, for example [1–3].

In the present paper a short review of recent investigations of the authors is presented focused on the following issues:

(i) The relation "deposition conditions – phase composition/crystal structure/morphology – photocatalytic activity" of TiO_2 films.
(ii) The effect of the modification of the photocatalyst by:
  - mechanoactivation,
  - modification with gold,
  - doping with lanthanides (lanthanum, gadolinium and neodymium).

1.1. Spray-pyrolysis films deposition

A lot of methods have been proposed for photocatalytically active TiO_2 coatings preparation using commercially available TiO_2, titania, especially tailored for the purpose or prepared *in situ* in the course of the film deposition, combined with a variety of deposition modes (dip- or spin-coating, spray-pyrolysis, washing, doctors blade method), vapor phase deposition, pulsed laser deposition, magnetron sputtering, electrochemical methods, atomic layer deposition, oxidation of titanium substrate. Despite its limitations, the spray-pyrolysis has the advantage to be not expensive, of high productivity, permitting uniform coating of substrates with different size and shape. Grounded on the results of systematic comparison of prospects and limitations of different deposition modes, the conclusion is made [4] that the spray-pyrolysis technique provides the best perspective for the preparation of TiO_2 photocatalyst to be used for remediation of organic contaminated waters.

A brief review of the results obtained applying this method is done in [5]. The main attention is paid on the influence of (i) the nature of the initial material (Degussa P25 and other commercial products, as well as specially designed oxides), (ii) the deposition conditions (deposition and post-deposition annealing temperature) (iii) the presence of additives (polyethylene glycol, acetylaceton), (iv) the sonication of the initial materials, (v) the nature of substrates (glass, silica, silicon, stainless steel, titanium), etc, on the phase composition, crystallites size, morphology, adhe-

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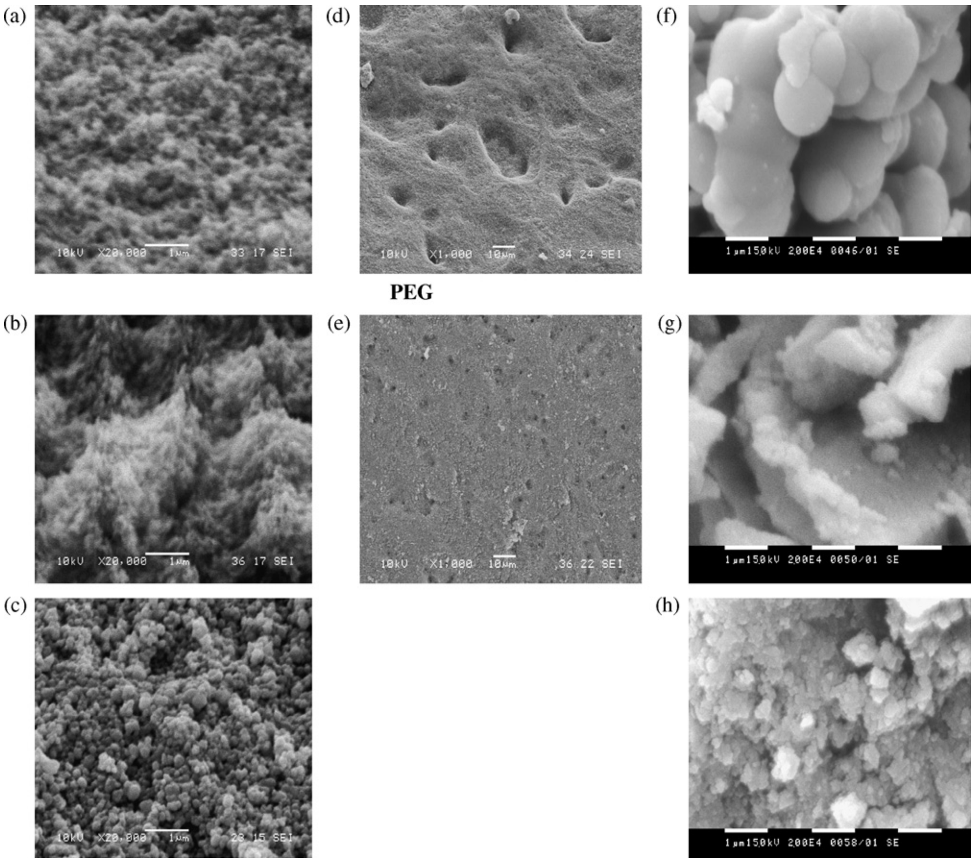

Fig. 1. (1) Films on glass (a, c) and steel (b, d, e) substrates produced from Degussa P25 (a, b, d, e) and Tronox (c) and in presence of PEG (d) and EG (e). For other deposition conditions see the text. (2) Sol–gel produced TiO_2 (f) and the same with 10% Nd, heated at 550 °C (g) and 700 °C (h).

sion, thickness and roughness of the films and their reflection on the photocatalytic activity.

1.2. Doping with lanthanides

The literature data on the effect of the lanthanides (Ln) on the TiO_2 photocatalytic efficiency are controversial but seems like the positive effect is dominating [6,7]. As it is seen in the literature overview made in [8,9], practically the effect of all of the naturally occurring rare earths (probably with the exception of Sc, Ho, Tm and Lu) is studied, applying different synthetic methods for the doping realization (mainly sol–gel, citric, auto-combustion, solvothermal and coprecipitation). The recommended optimal dopant concentrations vary in rather wide interval (for example from 0.9% to 10% for neodymium, 0.2% to 30% for lanthanum). The higher concentration is found necessary for catalyst effective under visible light irradiation [10]. Considering the physics and chemistry of the processes involved in photocatalyst, a lot of possible reasons for the rare earths effect are discussed: inhibition of the anatase to rutile transformation; formation of surface complexes with some pollutants (mainly aromatic carboxylic acids) leading to concentration of the organic pollutant at the semiconductor surface; increase the surface OH^-– concentration producing OH under UV-irradiation; reducing the band-gap energy because of the defect energy level induced by the 4f-atomic orbitals; half-filled electronic configuration of Gd^{3+}, promoting the charge transfer; larger specific areas obtained in the presence of lanthanides; decreased electron–hole recombination; increase in the interfacial electron transfer rate, formation of Ti^{3+}, etc.

1.3. Mechanoactivation

The reported results on the effect of the mechanoactivation are rather limited so far. Some works [11] show a decrease of the photocatalytic activity as a result of mechanical treatment. However the catalyst resulted in mechanochemical reaction between $TiOSO_4 \cdot xH_2O$ and Na_2CO_3 possess activity double increased than the expected one [12]. The high-energy ball milling is successfully used for nitrogen doping of Degussa P25 producing highly effective photocatalyst for the oxidative decomposition of nitrogen monoxide under visible light irradiation [13].

The present report summarizes the conclusion drawn from the study of the influence of the films preparation route and the modification of the TiO_2 by mechanical treatment and doping with gold and lanthanides on the phase composition, crystallites size, morphology, sorption and the activity of the photocatalysts (films or powders).

2. Materials and methods

The following types of TiO_2 were used as photocatalyst: (i) commercially available TiO_2 (Degussa P25 and Tronox) [5], (ii) pure or lanthanide-doped TiO_2 (Ln = La or Gd) prepared *in situ* by the so called polymerized complex method (with $Ti(OC_3H_7)_4$, $Ln(NO_3)_3$, citric acid and ethylene glycol as starting materials) [8], (iii) pure or lanthanide-doped TiO_2 (Ln = Nd) prepared by sol–gel technique from $Ti(OC_3H_7)_4$ [9], (iv) microcomposite TiO_2-photochemicaly produced gold nanoparticles, (v) TiO_2 mechanically activated in planetary ball mill Pulverisette 5 [14].

The films on glass, silica, ceramics, stainless steel, graphite, Ti and Ti-coated stainless steel were deposited. TiO_2 powder suspended in water or methanol (with ethylene glycol or polyethylene glycol 2000 or acetylacetone as additives), hydroxide sol or ethylene glycol solutions of the prepared mix-metallic citric complexes [15] were used as starting materials.

Earlier described spray-pyrolysis device and oxygen as carrier-gas were used at preliminary established optimal spraying conditions [16]. Post-deposition annealing of films was performed in furnace at defined temperatures. Sonication (20 min before spraying) was done by an ultrasonic disintegrator UD 20 (Technopan).

Some of the photocatalytic tests were performed in slurry (1 g TiO_2/dm^3) using powder catalysts prepared by sol–gel or citric [15] method.

Aqueous solutions of malachite green (MG, 10^{-5} M), methylene blue (MB, 2×10^{-6} M), phenol (10^{-4} M), oxalic acid (8.5 mM) and the Iodosulfuron herbicide (5×10^{-5} M) were used as model pollutants.

The decomposition of the dyes under UV-irradiation (Sylvania 18W BLB T8, distance from the treated suspension surface 9.5 cm, light intensity 5×10^{-5} W/cm^2) was determined spectrophotometrically, the concentration of the residual $H_2C_2O_4$ by TOC analyzer Shimadzu VCSH, the products of herbicide degradation were followed by HPLC-UV system and of the phenol by fluorescence method.

3. Results and discussion

3.1. Spray-drying production of TiO_2 films

The data reported below reveal some of the factors influencing the photocatalytic performance of the layers in the degradation of dyes and phenol. More details can be found in [5,17]. Typical degradation rate constants for some of the studied films are shown in Table 1.

3.1.1. Films thickness

Our experiments show that the effect on the photocatalytic activity of the film thickness increase from 0.35 mg/cm^2 to 1 mg/cm^2 is negligible (Table 1, exps. 1 and 2) and films of ~0.5 mg/cm^2 were used in the present study.

3.1.2. Films morphology

The SEM observation shows the coatings produced by the method used are porous with a strongly expressed agglomeration. The formation of wave-like surface (Fig. 1) leads to increased photocatalytic activity of the respective films. However such morphology is reached at different annealing temperatures for different substrates—300 °C for films on glass and 500 °C on steel (Fig. 1b).

- *Substrate nature and deposition/annealing temperature*. The influences of the substrate nature and the annealing temperature on one side and deposition temperature on other side are interconnected. These factors determine the morphological grains size which is also a rather important parameter. The grains size of the films on glass (deposited at 300 °C) are smaller than of ones produced on steel despite the lower deposition temperature (100 °C), applied in the later case. This causes a higher activity of the films on glass substrate.
- *Presence of additives*. The presence of additive (polyethylene glycol, PEG or ethylene glycol, EG) leads to the films with considerably different appearance compared with films produced without additives. The effects of PEG and EG on the morphology are rather different (Fig. 1d and e).

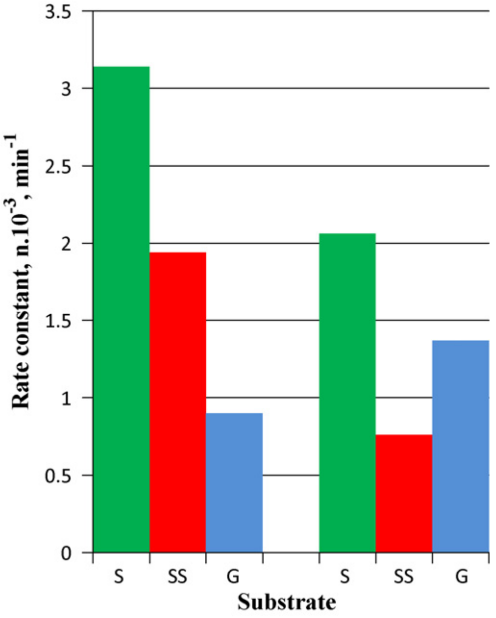

Fig. 2. Rate constant for TiO_2 films on silica (S), stainless steel (SS) and glass (G) annealed at 500 °C and 300 °C. All other deposition conditions are equal.

- *Sonication*. As can be expected the sonication decreases the presence of large grains.
- *Starting TiO_2 type*. The type of the starting TiO_2 has the strongest effect on the film morphology. Grainy structure with grains (approximately 50–200 nm in size), much bigger than the ones in Degussa P25 but much less agglomerated, is specific for Tronox type oxide (compare Fig. 1a and c).

3.1.3. Influence of the anatase content

Our observation is consistent with earlier observations [18,19] that a small amount of rutile in the anatase increases the catalyst activity. Films deposited at 100 °C from the product P25 of Degussa show higher (with 10–50%) value of the rate constant than films from the other commercial product used in the present study Tronox, containing 100% anatase (Table 1, exps. 3 and 4). However the rate constant for the films deposited at 300 °C from Tronox is with 40–50% greater than the one for films from Degussa P25 (Table 1, exps. 5 and 6). The effects are independent from the nature of the pollutant. It can be supposed that at higher processing temperatures the less agglomerated Tronox grains will ensure a larger specific surface area than the Degussa product. Obviously this will enhance the catalytic activity.

3.1.4. Influence of the substrate material

Among the four types of substrates (glass, steel, silica, graphite) applied at equal conditions, the films on silica demonstrate the highest photocatalytic activity both on phenol and on MB.

At post-deposition annealing temperature of 500 °C the rate constants of the films decrease in the order silica > steel > glass with differences of 2–3 times. Both observations are consistent with the data reported in [20]. However at lower annealing temperature (300 °C) the films on glass show a better performance than the one on stainless steel and the above discussed order is changed to silica > glass > graphite > steel (Fig. 2). Three possible reasons might be responsible for the effect observed: (i) the influence of the bonds formed between the TiO_2 and the substrate during the annealing especially at temperatures close to the glass melting interval [20]. (ii) At higher annealing temperature the penetration of substrate components into the film (as a result of diffusion) will be enhanced.

Table 1
Dependence of the rate constant ($n \times 10^{-3}$, $\text{min}^{-1}\,\text{cm}^{-2}$) for TiO_2 films on deposition conditions[a,b].

Sample no.	Deposition conditions							Pollutant	Rate constant
	TiO_2 type	Substrate	Medium	Additive	Sonication	Temperature, °C, of			
						Deposition	Annealing		
1[c]	D	G	W	AA	Yes	300	500	MB	0.51
2[d]	”	”	”	”	”	”	”	”	0.48
3	”	SS	”	PEG	”	100	”	Ph	2.72
4	T	”	”	”	”	”	”	”	1.81
5	D	G	”	”	”	300	”	MB	0.43
5a	”	”	”	”	”	”	”	Ph	1.62
6	T	”	”	”	”	”	”	MB	0.62
6a	”	”	”	”	”	”	”	Ph	2.42
7	D	SS	”	”	”	100	”	”	2.72
8	”	”	M	”	”	”	”	”	2.07
9	”	G	W	”	”	300	”	”	1.62
10	”	”	”	AA	”	”	”	”	1.45
11	”	SS	”	PEG	”	100	”	”	2.72
12	”	”	”	AA	”	”	”	”	1.06
13	”	G	M	No	”	25	”	”	1.20
14	”	”	”	”	No	”	”	”	0.90
15	”	”	”	”	Yes	”	400	MB	0.61
16	”	”	”	”	No	”	”	”	0.50
17	”	SS	”	PEG	”	”	500	Ph	1.94
18	”	”	”	”	”	100	”	”	1.49
19	T	”	W	”	Yes	”	”	MB	0.37
20	”	”	”	”	”	500	”	”	0.77
21	D	G	M	No	No	25	300	Ph	1.37
22	”	”	”	”	”	”	500	”	0.90
23	”	SS	”	”	”	”	300	”	0.76
24	”	”	”	”	”	”	500	”	1.94

[a] For more details see [5,17].
[b] D: Degussa P25, T: Tronox, G: glass, SS: stainless steel. W: water, M: methanol, AA: acetylacetone, PEG: polyethylene glycol, MB: methylene blue, Ph: phenol.
[c] Film thickness 0.34 mg/cm^2.
[d] Film thickness 1.01 mg/cm^2.

Thus the negative effect of Na^+ and the positive one of iron will be stronger expressed. (iii) Films SEM observations show significantly higher roughness of the film on glass which will ensure higher specific surface area.

3.1.5. *Influence of the suspension medium and presence of additives*

The difference in the rate constants received using the two media used (water and methanol) is not very large (20% when MB is applied as pollutant and 30% for phenol, Table 1, exps. 7 and 8). It can be speculated that the effect is connected with the boiling point of the suspension medium and, respectively, with the drying rate reflected on the film grain size and morphology.

There is not a significant difference in the rate constants when PEG or acetylacetone are used in the starting suspension deposited on glass at 300 °C (Table 1, exps. 9 and 10). However, when the film is deposited at 100 °C, the application of PEG instead of acetylacetone ensures significant increase of the rate constant (Table 1, exps. 11 and 12). The same tendency is observed using PEG instead of EG. It could be supposed that the effect is due to the difference in the decomposition temperature and rates of the additives. The relatively small differences will be more significantly exhibited at lower deposition temperature. Experimental prove is needed to accept such a supposition.

3.1.6. *Influence of sonication*

The ultra sound treatment ensures 20% (for MB) to 33% (for phenol) increase of the rate constant only if the deposition is done at low (ambient) temperature (Table 1, exps. 13–16). Most probably the positive effect of the de-agglomeration caused by the ultra sound treatment is enervated by the sintering, proceeding at elevated deposition temperature.

3.1.7. *Influence of the deposition and post-deposition annealing temperatures*

The optimal deposition temperature seems to depend on the grains size and the inclination to agglomeration of the starting TiO_2 used. Films from Degussa P25 deposited at 100 °C from methanol suspension show lower (with ~25%) rate constant compared with those prepared at room temperature (Table 1, exps. 17 and 18). However, a rather low deposition temperature cannot be recommended due to some decrease of the film adhesion. The Tronox grains, with a bigger size and less inclined to agglomeration, show two times higher activity when deposited at 500 °C instead of 100 °C (Table 1, exps. 19 and 20).

The rate constant of films from Degussa P25 decreases (with approximately 30%) when the deposition temperature is raised up to 500 °C. Some of the factors already mentioned may cause that decrease. Additionally, as can be seen from SEM—observations the film annealed at 500 °C is densified in comparison with the one heated at 300 °C and the decrease of the specific surface area can lead to the decreased activity, also. As for films from Degussa P25, this effect is more pronounced due to smaller morphological grains.

The influence of the increase of the post-deposition temperature on the rate constant is interrelated with the substrate nature as it was shown in Section 3.1.4 (Fig. 2, Table 1, exps. 21–24). The complete evaporation at higher temperature of undesired products, rested from the starting suspension, can also be one of the reasons affecting the activity [21].

3.2. Mechanical treatment as a tool for TiO_2 modification

3.2.1. Influence of the mechanoactivation on the crystal structure and phase composition of TiO_2

Surprisingly, it was established [14] that the stored energy during the milling in air in a stainless steel vessel is lower than in agate. The fact was explained by the effect of iron introduced in TiO_2 during the milling in steel triboreactor. The higher value of stored energy, a result of the milling in suspension than in air may be due to the change of the cell constant as well as to the suppressed Fe^{2+} diffusion as a result of lower temperature. The X-ray data show crystallite size reduction with 12–36% depending on the triboreactor material, milling medium and TiO_2 crystal modification; the effect reaches saturation for approximately 1 h. The particle average diameters decrease from 118 ± 40 nm to 88 ± 30 nm and 56 ± 12 nm after activation for 5 h in agate vessel in air and in suspension, respectively. The phase transformation of anatase to rutile is more pronounced when the activation is performed in air. The specific surface area reaches 58–69 $m^2 g^{-1}$ after 300 min milling in agate and steel. The EPR spectroscopy used proves the presence of Ti^{3+} in the sample, milled for 5 h in agate. IR and XRD investigations confirm the formation of traces of the polymorph TiO_2-II. However, it is hardly to believe that, when present in such a low amount, it could affect the photocatalytic activity.

3.2.2. Sorption ability of the mechanoactivated sample

The dye sorption (for both malachite green and methylene blue) on the activated sample is equal or greater than the one on the untreated product and depends on:

(i) The milling vessel material, the increase varying from 150–200% in agate to 500% in steel despite the opposite values of the stored energy. Most probably the greater effect obtained in steel is due to the shift down of the Fermi level as a result of Fe^{2+} incorporation. Indeed, 1.2 ± 0.2% of iron was found in the treated sample. The Fermi level drop promotes the adsorption of molecules with donor properties.

(ii) The time of activation with a maximum at 1 h in air and decreases at further treatment due to agglomeration. As could be expected the latter effect is not observed during the treatment in suspension.

(iii) The time between the mechanoactivation and the photocatalytic test suggesting the role of crystal defects introduced in the course of milling and their relaxation in time.

(iv) The pollutant chemical nature—the treatment reverses adsorption ability of the titania on the MG and MB compared with non-activated sorbent. This effect shows a complicated nature of the interaction of the dye with the mechanically induced changes in the adsorbent.

It has to be concluded that the increased dispersity and specific surface area of the mechanically activated sorbent are not the only and, probably, not the main factors determining its adsorption capability.

3.2.3. Photochemical degradation by means of mechanoactivated sample

The degradation rate constant found for degradation of malachite green in slurry at conditions described in [14] is 14.0 min^{-1}. No difference is observed after activation of the TiO_2 in agate vessel for 60 min in air. The activation at the same conditions for 300 min leads to insignificant increase of the constant (15.5 min^{-1}). However, after milling in methanol suspension for 60 min the constant reaches 24.3 min^{-1} (1.7 times higher than for the non-treated sample). The effect of the steel-milling is opposite—after 300 min treatment in air and in methanol suspension the constants are 2.9 min^{-1} and 3.3 min^{-1}, respectively. The effect on MB degradation is similar—the degradation ability of films produced from 300 min steel-activated titania decreases with at least 20% [14].

At least two factors can be responsible for the degradation activity increase: (i) the increased dispersity of the photocatalyst, (ii) the point defects formed enhancing the separation of the photoinduced electron–hole pair.

In the same time few factors can inhibit the catalyst activity: (i) the mechanically induced partial transformation of anatase to rutile. (ii) The appearance of mechanically induced Ti^{3+} acting as charge-carrier recombination center. (iii) The dehydration of the air-milled substance (observed in other systems [22,21,12]) may have double effect due to decrease and increase (by different reactions) of the concentration of the OH which is the main oxidizing agent. The results obtained suggest that the negative effect is dominant. (iv) The adsorption of the pollutant on the photocatalyst surface is obligatory condition for degradation process realization. However, the heavily milled product possesses rather strong adsorption ability. (v) The formed crystal defects (hole traps, etc.). Most probably the latter two factors are the main impeding the degradation process.

3.3. Gold-modified TiO_2 [23]

Degussa P25 TiO_2 was supported by spray coating on the outer surface of quartz tubes (ϕ 20 mm, length 200 mm) and modified with nanosized gold particles (0.05–0.4%) by the photoreduction method [24,25]. The XPS study confirmed that the superficially attached gold is reduced to metal. The average size of the Au nanoparticles depends on the amount of metal, attached to the support and is typically 5–6 nm. The photocatalytic tests were performed in a flow reactor with the overall volume of the circulating solution of 1.2 dm^3 water solution of oxalic acid (8.5 $mmol/dm^3$). The irradiation was done with UV-C lamp (F4T5 TUV).

The presence of gold does not change significantly the specific surface area of the catalyst (50 m^2/g of the initial material, 47 m^2/g in the case of 0.4% Au). Despite this, the modification decreases its adsorption capacity in dark from 440 μmol $H_2C_2O_4/g$ for Au-free catalyst to 240 $\mu mol/g$ for catalyst loaded with 0.4% Au. This is due to the diminishing of the available adsorption centers.

A significant increase in photodegradation activity was observed for all modified samples. The maximum (51 $\mu mol/dm^3$ min) was registered at 0.16% Au loading of the TiO_2 and is approximately 2-fold higher than the non-doped titania (31 $\mu mol/dm^3$ min). It was assumed that the increased activity of the noble metal-modified catalyst is mainly due to (i) the increased separation of electrons and holes, (ii) higher rate of OH radicals formation, (iii) facilitated oxygen reduction. The decreased adsorption properties of the Au-loaded catalyst act in opposite directions and the efficiency of the photocatalytic process is a result of the interaction of the both groups of effects.

3.4. Lanthanides-doped TiO_2

3.4.1. Phase composition, crystal structure and morphology [8,9]

Thermal decomposition of Ti citrates and of sol–gel prepared hydroxide produces nanocrystalline TiO_2 with a high relative content of anatase (92%). It is known that the presence of lanthanides additionally impedes the transformation to rutile [26] and the process depends on the substrate nature (Table 2). In samples containing 10% Nd this polymorph was X-ray registered after ignition at 900 °C but not in specimens ignited at 700 °C. X-ray microanalysis shows a uniform distribution of the dopant.

Despite the larger ionic radius (La^{3+} 114 pm, Nd^{3+} 104 pm, Ti^{4+} 68 pm) the Ln doping reduces the interplanar spacing. The decrease

Table 2
Phase composition, crystallites size, sorption and photodegradation capability of lanthanide-doped TiO_2[a].

TiO_2 origin	Substrate	Anatase content, %	Crystallites size, nm		Morphological grains, μm	Sorbed pollutant, μmol/dm^2	Photodegradation rate constant, $n \times 10^{-2}$ min^{-1} dm^{-2}
			Anatase	Rutile			
Degussa P25	Glass	85	40	51		2.6	5.0
Ti^{4+}–citric complexes	”	92	20	20		1.4	2.5
Ti^{4+}–La^{3+}(5 mol%)–citric complexes	”	100	12			2.4	7.7
”	Ti	44	9	31		7.8	5.0
”	Ti on steel	65	7	11	1–1.2	3.8	23.0
Sol–gel Ti^{4+}–Nd^{3+}(10%)–hydroxide	–	100	23	30	~1		

[a] For more details see [6,9].

depends on the dopant content and (in the case of films) on the substrate nature. Even a small amount of Nd (0.05%) causes a shift of the anatase most intensive reflex with ~0.4%.

The films morphology (Fig. 1f–h) and grains size (Table 2) significantly depend on TiO_2 production mode and particularly on the heating temperature, the presence of lanthanide and on the substrate nature. The presence of Ln^{3+} (even at small amounts) decreases the crystallites size but make the sample more inclined to agglomeration with the synthesis temperature increase (Fig. 1f–h). In comparison with Degussa P25 product, the presence of 10% Nd in sol–gel produced oxide slightly increases BET surface area, practically does not change the total pores volume and average pore diameter but approximately ten times increases the volume of micropores. The main part of the pores volume for Degussa P25 is formed by the relatively wider pores (1.2–0.2 nm in diameter) and the main part of their surface—by the narrower ones (<0.06 nm). The introducing of 10% Nd shifts the distribution of the both parameters in opposite directions and they are grouped around pores diameter 0.24–0.1 nm.

3.4.2. *Influence of La and Gd on the catalyst sorption and photocatalytic activity [8]*

The experimental data reveal a complicated dependance of the films sorption properties and photocatalytic activity on the substrate type, the chemical nature of the dopant and the doping route. Contrary to the effect of La_2O_3 added to TiO_2 as a separate phase, the solid solution of the oxides (1–5 mol% La) produced by the thermal decomposition of the mixed Ti–La citric complexes [27] show an increased sorption and (in most cases) photocatalytic activity compared with that of pure TiO_2 produced by the same way (Table 2). The sorption ability (of specimen with 5 mol% La) decreases in the order Ti > Ti-coated steel ≥ graphite > silica > glass. The photocatalytic activity does not follow the changes of the sorption properties. The activity of the above mentioned specimens decreases in the order Ti-coated steel > glass > graphite = Ti > silica. The degradation rate constant for film on glass exceeds by ~45% the one of the commercially available referent material Degussa P25. The highest photodegradation rate constant was found for films deposited on stainless steel type 316, Ti-coated by direct current sputtering (Table 2). Differences in the photocatalytic activity were found also between the samples doped with La and Gd deposited under the same conditions. TiO_2 with 1 mol% Gd has a little bit lower activity than the analogous La-doped titania. However doping with 5 mol% Gd leads to 2.5 times higher rate constant than the doping with the same La-content. The effect can be related to the difference in the La and Gd ionic radii and the respective differences in the position of the Ln^{3+} in the TiO_2 crystal cell and their behavior. According to [28] the higher activity of Gd is ascribed to half-filled electronic configuration of Gd^{3+} promoting the charge transfer.

3.4.3. *Influence of Nd on the catalyst photocatalytic activity*

The photocatalytic tests with sol–gel produced Nd-doped TiO_2 for the degradation of MG reveal the following factors influencing the degradation process (apart from the strong effect of the illumination intensity):

(i) The heating temperature in the course of catalyst synthesis. Pure TiO_2 annealed at 550 °C shows higher activity than that heated at 700 °C due to higher rutile content and agglomeration in the latter (Table 3, exps. 1 and 1a). As was already mentioned, the presence of Ln impedes the anatase–rutile phase transformation and the doped “high-temperature” product may be more active. The effect is pronounced in degradation of the herbicide iodosulfuron under sun-light illumination (Table 3, exps. 4 and 4a) [29]. After 120 min treatment the decrease of the iodosulfuron concentration is ~25% with product obtained at 550 °C and ~85% with the one, prepared at 700 °C (Fig. 3).

Table 3
Apparent degradation constant ($K \times 10^{-3}$, min^{-1}) for sol–gel produced Nd-doped TiO_2.

Sample no.	Catalyst	Temperature of synthesis, °C	Irradiation	Pollutant[a]	K
1	TiO_2	550	UV	MG	5.9
1a	”	700	”	”	3.5
2	TiO_2–0.1% Nd	550	”	”	7.3
3	TiO_2–10% Nd	”	”	”	8.8
4	”	”	Sun	”	6.0
4a	”	700	”	”	10.8
5	”	550	”	I	2.5
5a	”	700	”	”	9.2
6[b]	”	”	UV	”	25.0
7[c]	”	”	UV	”	4.0

[a] MG: malachite green, I: iodosulfuron.
[b] Model pollutant solution is prepared in MiliQ device.
[c] Tap water. All other experiments are performed with distilled water.

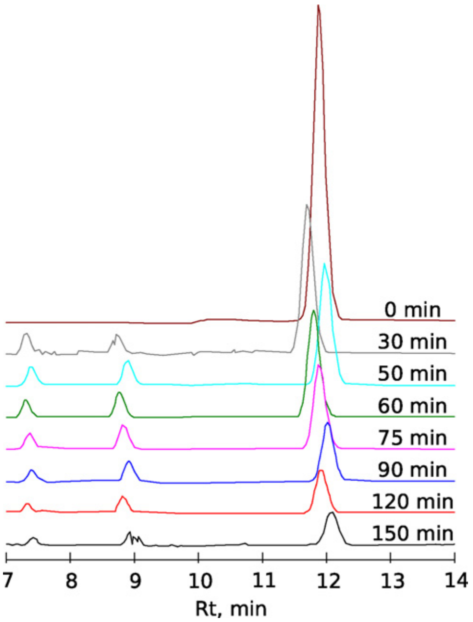

Fig. 3. HPLC chromatogram of iodosulfuron after different time intervals of photocatalytic treatment with TiO2–0.1% Nd (annealed at 700 °C).

(ii) The amount of Nd. The introduction of even small amount of Nd (0.1%) leads to an increase of the degradation rate constant with more than 20% (Table 3, exp. 2). The rather high dopant content (10% proposed in [10]) leads to an increase of the rate constant under UV-irradiation with almost 50% (Table 3, exp. 3) but its real advantage is seen under sun-light illumination (Table 3, exps. 4, 4a, 5 and 5a).

(iii) The pH of the suspension. The degradation proceeds ~4 times faster at pH 7 even when the decolourization due to partial transformation of the MG to its colourless leucoform is taken into consideration. The activity differences could be ascribed to the change in the amount of surface hydroxyl groups [30].

(iv) The bubbling of air during the photocatalytic treatment causes increase of the iodosulfuron degradation rate constant 2.5 times at UV-irradiation and has a weak effect at visible light illumination.

(v) The substitution of the high-purity water with tap one as dispersion medium of the pollutant decreases both adsorption and degradation rate constant. The decrease of the latter is 4–9-folds, strongly expressed independently of the catalyst type and illumination (Table 3, exps. 6 and 7). The same effect is observed applying neodymium–nitrogen-codoped catalyst (the respective data are not shown in the present paper).

3.5. *Conclusion*

The study performed helps for further elucidation of the factors influencing the photocatalytic performance of TiO_2 thin films as well as the effect of its modification by mechanical activation and doping with lanthanides. The main conclusion which can be drawn is that the factors responsible for the catalysts performance are interconnected. That is why complex studies are to be performed in order to find optimal conditions for their synthesis and coatings deposition.

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