

# Ph.D. Thesis Summary and theses



# Synthesis, morpho-structural characterization and environmental application of titania photocatalysts obtained by rapid crystallization

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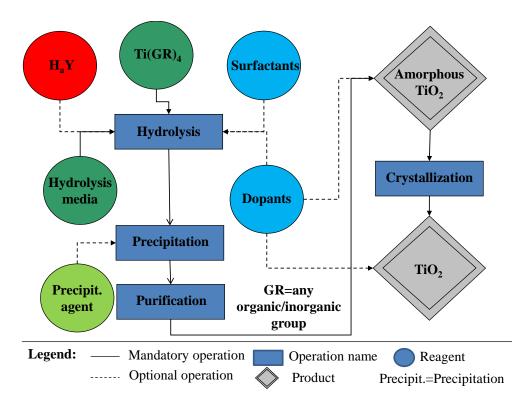
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#### Introduction

In the past decades the numbers of publications regarding photocatalysis have increased significantly. Several semiconductor materials were experimented with, as potential photocatalysts. Among the most studied materials were: titanium dioxide ( $TiO_2$ ) [1], zinc oxide ( $TiO_2$ ) [2], tungsten trioxide ( $TiO_3$ ) [3], etc.

It seems that the most promising material could be TiO<sub>2</sub> due to its high activity, non-toxicity and costs. This semiconductor was first time investigated in a photoelectrochemical process by *Fujishima and Honda* [1]. Their paper determined an exponential growth of the publications regarding this nanomaterial. Several synthesis ways were developed for this material, including the flexible sol-gel synthesis, flame hydrolysis or ball milling. From the listed methods, most likely the sol-gel route will be applied for mass production, due to high flexibility, high product yield and diversity. That is why the most of the publications, concerning titania photocatalysts, report a sol-gel based synthesis.

The sol-gel synthesis method contains several important steps, until nanocrystalline titania is obtained. These steps are visualized in *Figure 1*.



**Figure 1** – Schematic representation of the sol-gel synthesis of titania photocatalysts

From the previous figure it is clear that the sol-gel method itself is rather complex (from this complexity results the flexibility and diversity). From the listed operations the most common one is considered the crystallization (mostly a simple heat treatment/calcination is applied to crystallize the amorphous material).

The heat treatment itself is a simple procedure with four major (instrumental) parameters:

- i.) Treatment temperature
- ii.) The duration of the heat treatment
- iii.) The applied calcination atmosphere
- iv.) The applied heating rate

Usually the above mentioned system parameters are varied during the calcination of amorphous titanias. However, in nearly each case, in the published materials one, or in some cases even two parameters are not specified. Contrary to photocatalysis in other fields the calcination is considered one of the most important procedures in the synthesis of a specific type of material, thus separate studies can be found in the literature about the influence of the calcination parameters. Fortunately a small number of papers appeared also in the case of titania photocatalysts.

The most important is the work published by *Joung et al.* [4-5]. They managed to study the influence of the calcination time on the final properties of nitrogen doped titania. The mentioned paper presents two important study directions, namely:

- i.) short calcination times in the frame of the photocatalytic activity
- ii.) mechanistic aspects regarding the possible reactions, crystallization pathways during the calcination.

So based upon the previously mentioned facts we investigated in-detail the effect of the rapid calcination on the activity of sol-gel made titania and nitrogen doped titania photocatalysts.

#### The main objectives of the present PhD thesis

As it can be seen from the literature overview presented, the calcination step was considered to be a trivial one. Thus, in the majority of the research papers, related to the present topic (sol-gel made titanias), no attention was given to the calcination parameters, such as the calcination time, atmosphere, furnace type and heating rates.

So, the present thesis investigates and elucidates the above mentioned parameters (focusing mostly on the treatment time) and has the following main objectives:

- **1.)** The calcination time as a critical parameter in the synthesis of titania photocatalysts at several heat treatment temperatures.
  - a.) The effect of the heat treatment time on the structure of TiO<sub>2</sub>
  - **b.**) The photocatalytic activity in the frame of the calcination time
- 2.) The synthesis of the nitrogen doped titanias and the fast heat treatment's impact on their visible light driven photocatalysis
  - a.) The effect of the heat treatment on the structure of N-TiO<sub>2</sub>
  - **b.**) The fast heat treatment's impact on the nitrogen incorporation

#### The synthesis of the fast heat treated titanias

TiO<sub>2</sub> samples were synthesized by a sol-gel method. 20.0 mL (to ensure the necessary quantity of base material) of TiCl<sub>4</sub> was added dropwise under vigorous stirring into 40.0 mL of concentrated hydrochloric acid solution. To avoid the overheating of the mixture from exothermic processes, the reaction vessel was cooled on an ice bath with the temperature maintained between 0 - 5 °C. This mixture was added dropwise under intense stirring into 600.0 mL of Milli-Q water. The final pH was below 1.0 and subsequently 10.4 mL of glacial acetic acid was also added dropwise. The pH was adjusted with an aqueous solution of ammonia (25 %) until a pH of 8 was obtained. The mixture was left for 2 days at room temperature to complete the hydrolysis. The precipitate was dried at 80 °C for 24 hours and the resultant white powder was milled.

This amorphous powder (30 g) was calcinated by heating in a quartz boat placed within a quartz tube in a tubular furnace under still air. A special heat treatment procedure was developed in which the temperature of the amorphous material was raised to the desired calcination temperature in a short time applying high heating rate in three steps (60, 20 and 10 °C/min). The heating rate was decreased as the temperature reached the threshold to prevent the overheating of the furnace. The studied calcination temperatures were: 400, 500, 550, 600 and 700 °C with calcination times of 5, 7.5, 10, 12, 15, 20, 30, 60, 90, 120 and 180 minutes at the given temperature. The gaseous thermal decomposition by-products were purged from the system by air in the last minute of the calcination procedure. The samples were kept for the pre-determined time at the given temperature, then removed from the furnace and left to cool down to room temperature.

The obtained samples were washed and centrifuged in Milli-Q water or in ethanol-water mixture (50:50 v/v%, 0.8 g product/50 mL) three times in order to remove any soluble impurities. The powder was finally redispersed in Milli-Q water and irradiated in a Petri dish with UV irradiation ( $\lambda = 365$  nm) to remove any organic traces from the TiO<sub>2</sub> samples.

#### The synthesis of the fast heat treated nitrogen doped titanias

N-doped TiO<sub>2</sub> samples were synthesized by the following sol-gel method. Different amounts of glacial acetic were added dropwise under vigorous stirring to HNO<sub>3</sub> (70%). The mixture was cooled down and kept at 5 °C in an ice bath. TiCl<sub>4</sub> (5 mL) was slowly added to the acidic media to avoid overheating. During the hydrolysis, NO<sub>2</sub> was released from the system and

the color of the dispersion turned brownish-orange (the measured pH was below 1.0 for all the dispersions).

The dispersion was stirred for 1 hour and subsequently added to 100 mL of double distilled water. Aqueous solution of  $NH_3$  (25 %) was used to precipitate the amorphous titania and the pH value was adjusted to ~8-9. To drive the hydrolysis to completion, the slurry was kept at room temperature overnight. A yellowish-white powder was obtained by drying the amorphous precipitate at 80 °C for 24 hours.

The amorphous sample was calcined in a muffle furnace (*Carbolite ELF 11/6 (201)*) to obtain crystalline  $TiO_2$ . The applied heating rate was 60 °C/min and the samples were calcined for 10 minutes at 400, 500 and 600 °C. Then, the samples were taken out and cooled to room temperature.

The samples were washed with double distilled water, and received 3 hours of UV (365 nm) treatment to remove all possible organic impurities. The obtained samples were dried at 80 °C. All the catalysts obtained were reproduced to gain higher accuracy for the conclusions

#### **Methods and instrumentation**

<u>X-ray diffraction (XRD)</u> patterns were recorded on a *Rigaku* and *Shimadzu 6000* diffractometer under the following conditions:  $\lambda_{\text{Cu K}\alpha} = 0.15406$  nm, 40 kV, and 30 mA, in the 20 – 40° (2Θ) region. The average diameters of the particles were estimated using the Scherrer equation [6]. The weight fraction of each crystal phase was calculated for each sample from the peak areas of the anatase, rutile and brookite peaks at 25.3° (2Θ) (101), 27.5° (2Θ) (110) and 30.8° (2Θ) (121), respectively. The calculations were performed according to *Zhang and Banfield* [7].

The diffuse reflectance spectra (DRS) of all the samples were recorded to determine the sample's UV-VIS light absorption capacity, on a *Jasco-V650* diode array, computer controlled (with *SpectraManager* software) spectrophotometer equipped with an *ILV-724* integration sphere. The recorded spectral data were acquired in the 220-800 nm range, with 0.5 nm data pitch and 100 nm/min scan speed.

The specific surface area of the catalysts was determined by nitrogen adsorption at 77 K by a *Micromeritics* gas adsorption analyzer (*Gemini Type 2375*). All the samples received a preliminary heat treatment at 100 - 120 °C under  $10^{-2}$  Torr vacuum for 4 hours to eliminate the trace amount of water present in the samples. The specific surface area was calculated using the BET method.

<u>Thermoanalytical measurements (TG-DTA)</u> were carried out on a *Mettler-Toledo* instrument. The applied sample weight was 5 mg and the heating rate was 60 °C/min. The unusual heating rate was chosen because in the synthesis of the nanoparticles the calcination was carried out similarly.

<u>SEM-EDX analysis</u> was performed to evaluate the morphology of the amorphous starting material and the obtained well crystallized catalysts on a *Hitachi S-4700* Type II cold field emission scanning electron microscope equipped with a *Röntec QX2-EDS* spectrometer.

<u>Transmission electron microscopic (TEM)</u> studies were performed to characterize the particle size and size distribution and also to observe the morphology of the particles. The TEM micrographs were recorded on a *Philips CM 10* instrument operating at 100 kV using *Formvar* coated copper grids.

X-ray photoelectron spectra (XPS) of selected samples were taken with a SPECS instrument equipped with a PHOIBOS 150 MCD 9 hemispherical electron energy analyzer

operated in the FAT mode. The excitation source was the  $K_{\alpha}$  radiation of a magnesium anode ( $h \cdot v$  = 1253.6 eV). The X-ray gun was operated at 180 W (12 kV, 15 mA). The pass energy was set to 20 eV, the step size was 25 meV, and the collection time in one channel was 150 ms. Typically five scans were added to get a single spectrum.

Total organic carbon measurements (TOC) of the catalysts (10 mg) were performed with a *Euroglas 1200* TOC instrument. The TOC calibration curve was determined using aqueous solutions of glucose and each determination was reproduced three times. These measurements were executed to evaluate the quantity of the organic residues that are still present at the catalyst's surface, even after calcination.

Infrared spectra (IR) of the catalysts were recorded on two instruments. *Bio-Rad Digilab Division FTS-65A/896 FT-IR spectrometer* equipped with *Harrick's Meridian SplitPea single reflectance diamond ATR* accessory were used, in the range of 4000 - 400 cm<sup>-1</sup>, at 4 cm<sup>-1</sup> optical resolution. 256 interferrograms were accumulated providing high signal-to-noise ratio. *Bruker Equinox 55* spectrometer with an integrated *FRA 106 Raman* module using Nd-YAG laser (1064 nm) was also used in the determination of IR and RAMAN spectra. The measurements were recorded with a power incident of 300 mW and a spectral resolution of 1 cm<sup>-1</sup>. Samples were ground with KBr pressed into thin pellets (thickness ~ 0.3 mm) and IR spectra were recorded with a spectral resolution of 2 cm<sup>-1</sup>.

The concentration decrease of the chosen pollutant (phenol and monuron) was followed using an *Agilent 1100 series HPLC* (<u>High Performance Liquid Chromatography</u>) system. This consists of a binary pump; a micro vacuum degasser; a diode array detector ( $\lambda_d = 210$  nm); a thermostated column compartment and *ChemStation* data managing software. The chromatographic system was equipped with *Rheodyne Model 7725* injector with a 20  $\mu$ L loop and a *Licrospher RP-18* column. The eluent consisted of 5:9 methanol: water (v/v) mixture for phenol and a 1:1 acetonitrile: water (v/v) mixture for monuron; and the flow rate in all the cases was 0.8 mL/min.

All the photocatalytic experiments were carried out in a <u>Heraeus photoreactor</u> equipped with *OSRAM Power Star HCl-TC 70 W/WDL* (in case of visible light driven degradation experiments) or TQ-150 high pressure mercury lamp (for UV photodegradation). Photocatalyst suspensions (400 mL) containing phenol or monuron ( $c_{0, phenol or monuron}$ = 0.1 mM for visible, 0.5 mM for UV light experiments,  $c_{TiO2}$  = 1.0 g/L) were used in all the experiments. In the case of

visible light experiments 1 M NaNO<sub>2</sub> was circulated in the cooling jacket of the lamp to cut off any remaining UV component ( $\lambda > 400$  nm) and to avoid the suspension's overheating (in the UV degradation experiments Milli-Q water was applied). The reactor was continuously purged by air (40 L/h) in order to keep a constant concentration of dissolved oxygen during the whole experimental run.

The initial photocatalytic degradation rate of the model compounds,  $(r_0)$  was considered to evaluate the efficiency of the photocatalyst. To determine  $r_0$ , an empirical function was fitted to the experimentally observed data points. Then,  $r_0$  was evaluated from the slope of the curve (at, t=0).

The heat treatment of the amorphous titania was executed in a tubular furnace (*Thermolyne 21100*, total length 38 cm, quartz tube length 64 cm, tube interior diameter 5.5 cm, quartz tube diameter 4 cm).

#### Results and discussions. Proposed theses

#### Highly active fast heat treated titanias under UV irradiation

T1. The structural parameters of the fast heat treated titanias are independent from the calcination time.

In the first step the influence of the calcination temperature and time was proposed. The calcination temperature's influence on the structural parameters showed the well-known particle size increase and anatase-rutile transformation at a given temperature. Surprisingly, at each calcination time value (at a given temperature) the same particle size and crystal phase composition was observed, as shown in *Table 1*.

**Table 1** – Crystal phase composition and primary particle size of the key samples treated at 400, 550 and  $600\,^{\circ}\text{C}$ 

Sample name	Anatase (wt %)	Rutile (wt %)	Brookite (wt %)	D <sub>A</sub> (nm)	D <sub>R</sub> (nm)	$S_{BET}$ $(m^2/g)$
RHSE-400-05	100	-	trace amounts	10.6	-	
RHSE-400-10	100	-		12.6	-	63.6
RHSE-400-15	100	-		12.4	-	
RHME-400-60	100	-		12.9	-	
RHLE-400-120	100	-		14.5	-	
RHSE-550-05	88.2	11.8	trace amounts	26.6	~85	
RHSE-550-10	86.5	13.5		22.4	~86	36.0
RHSE-550-15	84.2	15.8		30.2	~89	
RHME-550-60	85.3	14.7		29.8	~90	
RHLE-550-120	85.4	14.6		33.5	~86	
RHSE-600-05	77.8	22.2	-	38.8	~95	
RHSE-600-10	82.4	17.6		41.4	~95	16.1
RHSE-600-15	81.5	18.5		41.8	~95	
RHME-600-60	79.6	20.4		41.2	~99	
RHME-600-120	80.0	20.0		40.4	~100	
P25 B	89.0	11.0	-	26.0	~85	50.0
wSHLE-450-180	100	-	-	16.7	-	60.0

This observation is really important in the frame of the industrial production of photocatalysts, because a given crystal phase composition and crystallite size can be achieved

within a few minutes of calcination, thus saving a considerable amount of energy which would be required in the case of traditional (long) calcination.

T2. The activity of the fast heat treated titanias varied differently for each temperature series. At 600 °C 10 and 60 minutes; at 550 °C 5 minutes and at 400 °C 120 minutes were sufficient to obtain highly active catalysts.

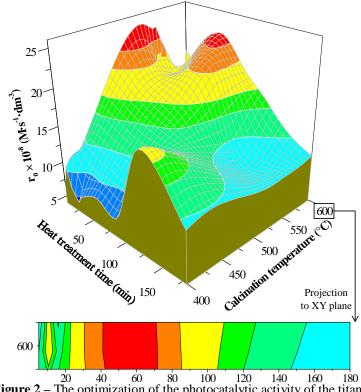


Figure 2 – The optimization of the photocatalytic activity of the titania samples as function of the heat treatment time and temperature. A separate projection was attached to reveal the maximum at 600°C and 10 minutes of calcination otherwise covered in the original surface plot

Surprisingly, we have observed that the activity of the fast heat treated titanias presented local maximuma at all the investigated temperatures. At 600 °C even two maxima were found. The T2 thesis point emphasizes the fact that the calcination is indeed a crucial procedure in the synthesis of sol-gel made titania photocatalysts. This unexpected result raised several questions related to these catalysts' functioning mechanism.

One of the raised problems is related to the appearance of activity maximuma at unusual calcination times. One, may think, that as the calcination time advances, so the catalysts 'surface

is getting more cleaner (carbon free), consequently a high activity could be obtained in the case of a long calcination process. However, the activity maximum at 5 minutes of calcination at 550 °C and 10 minutes of calcination at 600 °C partially negates the previously stated presumption. So, the answer lies elsewhere for these materials.

T3. By applying a fast calcination the catalysts' hydrophylicity is preserved. The surface OH groups are omnipresent in all the fast heat treated titanias.

In all the samples that presented high activity a considerable signal was found for the surface OH groups at 1635-1640 cm<sup>-1</sup>. Similarly to these materials, Evonik Aeroxide P25 also had a high surface OH concentration. From sample wSHLE-450-180, which was made following a classical calcination (long heat treatment time -3h and slow heating up 5°C/minute), this band was missing. For this material a low phenol decomposition rate was observed, emphasizing the importance of the studied fast calcination method.

T4. The sensitization of the surface by long chained hydrocarbons plays an important role in the activity of the fast heat treated titanias.

Besides the surface OH groups, long chained hydrocarbons were detected by infrared spectroscopy (bands at 2854, 2924, cm<sup>-1</sup> and in some cases at 2962 and 2978 cm<sup>-1</sup>) nearly on all the fast heat treated samples. Interestingly, the band was the most intense in the case of sample RHSE-600-10, which showed a significant UV activity towards phenol (~90% of Evonik Aeroxide P25's activity). In the DRS spectra of this material a slight red shift was observed, together with an absorption band centered at ~450 nm. This type of sensitization, which makes possible the absorption of lower energy photons, was also observed by *Lettman et al.* [8]. As the mentioned sensitizer's concentration on the surface diminishes (observable from the DRS spectra), so does the activity of the catalyst.

T5. The chemical state of oxygen at the catalyst surface is closely related with the calcination method.

Besides, the surface anchored groups, the surface quality itself could be important. By XPS the following oxygen forms were detected: surface OH-groups; adsorbed water; oxide oxygen at an unidentified oxygen form at low binding energies. The last one is detected only in

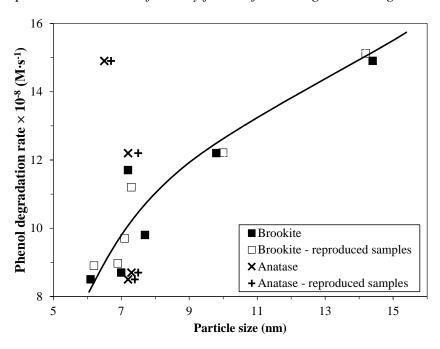
the samples that showed high activity and it was not detectable in Evonik Aeroxide P25 and in the traditionally calcined catalyst (wSHLE-450-180). This fact suggest that in these titanias some modifications could occur in the titania lattice, like the formation of oxygen vacancies/Ti<sup>3+</sup> centers.

#### T6. The presence of the unidentified oxygen forms is related with the presence of $Ti^{3+}$

Ti<sup>3+</sup> centers were identified by XPS in the sample RHSE-550-05. Interestingly in this sample was found the highest concentration of unidentified oxygen. If the low energy oxygen form's concentration is diminishing, than the Ti<sup>3+</sup> vanishes from the system. This could mean that these two species are closely related and they are present as active sites at the catalysts 'surface. As in the case of T5, Ti<sup>3+</sup> was found only in the fast heat treated samples.

#### Highly active fast heat treated titanias under visible light irradiation

T7. The brookite particle size is one of the key factors for the high visible light activity



**Figure 3** – Correlation between the brookite primary particle size and phenol degradation rate; (the empty symbols represents results with the reproduced catalysts)

High visible light activities were observed for the rapid heat treated samples obtained from a sol-gel synthesis which included nitric acid. In these samples the anatase/brookite content

and anatase particle size were nearly identical. The brookite particle size was the only structure related factor changing throughout these samples. Catalysts with higher brookite particle size showed higher phenol decomposition rate.

T8. Bridged-nitro groups were present in all the fast heat treated samples. These species 'concentration increases concomitantly with the observed photocatalytic activity.

The nitrogen content was constant in all the samples which were calcined at the same temperature and no differences were observed in the nitrogen incorporation mode (interstitial). This fact points out that some nitrogen containing surface groups could be responsible for the high visible light driven phenol degradation rates. Bridged nitro species were detected in all these highly active materials. This group was totally missing (proved by infrared spectroscopy) from the samples calcined traditionally. If the base material (amorphous) was calcined at higher temperatures (500 °C and 600 °C) then the mentioned group was not detected at the catalysts surface.

#### **Conclusions**

The literature regarding sol-gel prepared titanias, treated the calcination as a standard procedure without seriously considering its complex influence on the photocatalytic properties on the obtained nanomaterials. It is well known how the temperature can modify the primary particle size and phase composition but no meticulous study was published regarding the influence of the calcination time.

We have successfully shown that in a temperature series, throughout the calcination times several surface parameters change continuously, like: the presence of NH<sub>2</sub>-group at lower temperatures, the influence of the long chained hydrocarbons, the dehydroxylation phenomena, the nitrogen incorporation, the evolution of the light absorption of the samples, etc. Several evidences were brought up to support the role of each surface parameter.

It was proven that very active catalysts can be made with just 5 (RHSE-550-05 sample) or 10 (RHSE-600-10 sample) minutes of calcination and experimental data were collected to explain their unusual properties. However, in some cases (RHME-600-60 and RHLE-400-120 samples) due to the longer calcination time a surface purification occurs and a photoactivity increase was observed. We demonstrated that at low calcination temperature, because of the surface coverage with organic residues/carbon deposits, only low UV activity can be obtained.

The samples treated at higher temperatures (above 500 °C) were more active than the solgel reference wSHLE-450-180 sample and only a few samples, such as RHSE-550-05 and RHME-600-60 exceeded the performance of the well-known P25 titanium dioxide (and obtained comparable reaction rates in the case of monuron degradation).

Two main synthesis aspects influencing the activity of the fast heat-treated nitrogen doped titania photocatalysts were studied in details. The importance of the hydrolysis media was proven by varying the concentration of acetic and nitric acid. The presence of the nitric acid was crucial for the formation of the brookite phase and there were no other correlations between the nitric acid concentration and the resulting catalyst properties. However, the acetic acid had a major impact on the structural parameters of the catalysts, particularly the brookite particle size and visible light absorbance. These two parameters are closely related to the visible light driven photocatalytic properties of the titania powders. It was shown that the size of brookite particle is very important even when there was low level of brookite content. The anatase particle size was independent of these experimental conditions.

These studies show that the catalyst's resulting morphology, structure and photocatalytic properties are dependent on the calcination time. Significant difference was observed in the photocatalytic activity of the two differently calcined materials, with the fast heat treated samples performing the best for phenol degradation under visible light irradiation. This result originates from the combined effects of higher concentration of incorporated nitrogen, the lack of dehydroxylation and the beneficial presence of the bridged nitro group. This photocatalyst was nearly twice as active as the traditionally calcined catalyst.

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#### **Scientific activity**

#### Participation at conferences

#### PhD thesis related participations

#### 1.) Zsolt Pap, Virginia Danciu, András Dombi, Károly Mogyorósi

"Activity enhancement of titania based photocatalysts by special heat treatment and nonmetal doping"

Tudomány Hete a Dunaújvárosi Főiskolán, 9-14 November 2009, Dunaújváros, Hungary

#### 2.) Zsolt Pap, Zsuzsanna Cegléd, Virginia Danciu, András Dombi, Károly Mogyorósi

"Nitrogénnel modosított titán-dioxid előállítása, gyors kalcinálással"

IX. Környezetvédelmi Analitikai és Technológiai Konferencia, 7-9 October 2009, Sopron, Hungary

#### 3.) Zsolt Pap, Virginia Danciu, Zsuzsanna Cegléd, András Dombi, Károly Mogyorósi

"Activity enhancement of titania-based photocatalysts by special heat treatment"

16<sup>th</sup> Symposium on Analytical and Environmental Problems, 28 September 2009, Szeged, Hungary

#### 4.) Zsolt Pap, Zsuzsanna Cegléd, András Dombi, Pál Sipos, Károly Mogyorósi

"The effects of the fast heat treatment on the N-doped  $TiO_2$  photocatalysts activity and morphology"

5<sup>th</sup> European Meeting on Solar Chemistry and Photocatalysis: Environmental Applications, 4-8 October 2008, Palermo, Italy

#### 5.) Zsolt Pap, Zsuzsanna Cegléd, András Dombi, Sipos Pál, Károly Mogyorósi

"A gyors kalcinálás kedvező hatása a nitrogénnel dópolt titán-dioxid fotokatalizátorok aktivitására"

XIV Nemzetközi Vegyészkonferencia, 7-9 november, 2008, Cluj-Napoca, Romania

6.) Zsolt Pap, Ioana Ladiu, Károly Mogyorósi, András Dombi, Emil Indrea, Virginia Danciu

"Synthesis of nanosized N-doped TiO<sub>2</sub> in extreme pH conditions" Nanotech Insight '09, 29 March - 2 April 2009, Barcelona, Spain

#### 7.) Zsolt Pap, András Dombi, Károly Mogyorósi, Virginia Danciu, Lucian Baia

"The influence of the acetic acid and nitric acid concentration on the morpho-structural properties of N-doped titania"

SP3 - Third International Conference on Semiconductor Photochemistry, 12-16. April 2010, Glasgow, Scotland

#### 8.) Zsolt Pap, Virginia Danciu, András Dombi, Károly Mogyorósi

"The influence of rapid heat treatment on the photocatalytic activity of titania photocatalysts"

COST Workshop - Recent Achievements In Photocatalysis: Fundamentals, Applications And Standardized Test Methods, 18-19. January 2010, Grenoble, France

#### 9.) Zsolt Pap, Éva Karácsonyi, András Dombi, Károly Mogyorósi

"Gyors kalcinálású nitrogénnel dópolt titán-dioxid fotokatalizátorok előállítása és vizsgálata" DUF Tudomány Hete, 6-12 november 2010, Dunaújváros, Hungary

**10.**) **Zsolt Pap,** Éva Karácsonyi, Cegléd Zsuzsanna, András Dombi, Danciu Virginia, Ionel-Cătălin Popescu, Baia Lucian, Oszkó Albert, Károly Mogyorósi,

"Dynamic changes on the surface during the calcination of rapid heat treated TiO<sub>2</sub> photocatalysts"

Photocatalytic and Advanced Oxidation Technologies for Treatment of Water, Air, Soil and Surfaces, 4-8 July 2011, Gdansk, Poland

**11.**) **Zsolt Pap,** Éva Karácsonyi, Ceglédi Zsuzsanna, András Dombi, Virginia Danciu, Károly Mogyorósi

"Gyors kalcinálású titán-dioxid fotokatalizátorok fenolbontó-képessége és felületének vizsgálata"

X. Környezetvédelmi Analitikai és Technológiai Konferencia, 5-7 October 2011, Sümeg, Hungary

#### Other conference participations

1.) Virginia Danciu, Mihaela Popa, **Zsolt Pap**, Lucian Baia, Monica Baia, Veronica Coșoveanu, Florin Vasiliu, Lucian Diamandescu

"Iron doped and undoped TiO2 catalysts for advanced water treatment"

Environmental Applications of Advanced Oxidation Processes 7-9 September 2006, Chania, Greece

2.) Gábor Veréb, László Manczinger, Attila Gácsi, Zsolt Pap, Ákos Kmetykó, András Dombi, Károly Mogyorósi

"Water purification and disinfection on UV and visible light irradiated doped titanium dioxide photocatalysts immobilized on ceramic papers"

SP3 - Third International Conference on Semiconductor Photochemistry 12-16. April 2010, Glasgow, Scotland

**3.)** Károly Mogyorósi, Gábor Veréb, Zoltán Ambrus, **Zsolt Pap**, Ákos Kmetykó, András Dombi "Comparative study on different synthesis pathways for obtaining UV and visible light active bare and doped titanium dioxide photocatalysts"

SP3 - Third International Conference on Semiconductor Photochemistry, 12-16. April 2010, Glasgow, Scotland

4.) Attila Gácsi, Veréb Gábor, Zsolt Pap, András Dombi, Károly Mogyorósi

"Titán-dioxid alapú fotokatalizátorokkal kezelt kerámiapapír alkalmazása gázfázisú acetaldehid ártalmatlanítására"

DUF Tudomány Hete, 6-12 november 2010, Dunaújváros, Hungary

- **5.**) András Dombi, Ákos Kmetykó, Károly Mogyorósi, **Zsolt Pap**, Krisztina Vajda, Gábor Veréb "Titán-dioxid nanorészecskék fotokatalitikus alkalmazása vízkezelési eljárásokban"
- X. Környezetvédelmi Analitikai és Technológiai Konferencia, 5-7 October 2011, Sümeg, Hungary

**Papers** 

Papers related to the PhD thesis

1.) Zsolt Pap, Virginia Danciu, Zsuzsanna Cegléd, Ákos Kukovecz, Albert Oszkó, András

Dombi, Károly Mogyorósi,

"The influence of rapid heat treatment in still air on the photocatalytic activity of titania

photocatalysts for phenol and monuron degradation", Applied Catalysis B: Environmental

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I.F.: 4.749

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2.) Zsolt Pap, Lucian Baia, Károly Mogyorósi, András Dombi, Albert Oszkó, Virginia Danciu,

"Correlating the visible light photoactivity of N doped TiO<sub>2</sub> with brookite particle size and

bridged - nitro surface species"

Catalysis Communications Catalysis Communications 17 (2012) 1–7

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3.) Zsolt Pap, Éva Karácsonyi, Zsuzsanna Cegléd, András Dombi, Virginia Danciu, Ionel-

Cătălin Popescu, Lucian Baia, Albert Oszkó, Károly Mogyorósi,

"Dynamic changes on the surface during the calcination of rapid heat treated TiO<sub>2</sub>

photocatalysts"

Applied Catalysis B: Environmental; doi:10.1016/j.apcatb.2011.11.012

I.F.: 4.749

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#### Other papers

**1.**) Éva Bajnóczi, Nándor Balázs, Károly Mogyorósi, Dávid Srankó, **Zsolt Pap**, Zoltán Ambrus, Sophie Canton, Katarina Norén, Ernő Kuzmann, Attila Vértes, Zoltán Homonnay, Oszkó Albert, Pálinkó István, Pál Sipos,

"The influence of the local structure of Fe(III) on the photocatalytic activity of doped  $TiO_2$  photocatalysts—An EXAFS, XPS and Mössbauer spectroscopic study", **Applied Catalysis B:** 

**Environmental 103 (2011) 232-239** 

I.F.: 4.749

Cited: 2

#### **Accepted papers**

**1.)** Gábor Veréb, Zoltán Ambrus, **Zsolt Pap**, Ákos Kmetykó, András Dombi, Virginia Danciu, Andrew Cheesman, Károly Mogyorósi

"Comparative study on UV and visible light sensitive bare and doped titanium dioxide photocatalysts for the decomposition of environmental pollutants in water"

Submitted to Applied Catalysis A: General (Ms. No.: APCATA-D-11-00920,)

I.F.: 3.383

#### Papers under preparation

Chinese Journal of Catalysis: 1 (I.F. 0.566)

Reaction Kinetics, Mechanisms and Catalysis Letters: 1 (I.F.: 0.62)

Journal of Sol-Gel Science and Technology: 1 (I.F.: 1.393)

Journal of Materials Chemistry 1 (I.F. 5.1)

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<u>Journal of Materials Chemistry (I.F. 5.1)</u> – 9 paper peer-reviews