Structure and photocatalytic activity of flame-synthesized titanium dioxide catalysts

Ph.D. thesis booklet

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I. Introduction

Branches of industry and science dealing with TiO_2-assisted photocatalysis exhibited a massive progress over the last few decades. TiO_2-based heterogeneous photocatalytic reactions are capable of transforming both organic and inorganic materials in liquid as well as in gas phase. One of the main purposes of such applications is the decomposition/neutralization of substances harmful to the environment and health. Accordingly, TiO_2 is now routinely used as self-cleaning coatings on different surfaces (metal and glass parts of buildings, street tiles, surgery flooring, *etc*.) and it became an essential part of air-cleaning devices. Prospectively, its role may get more emphasized in future water treatment technologies, complementing or displacing oxidation techniques currently employed. It is also worth highlighting the germicidal activity of photocatalysis that acts through the oxidative destruction of cell walls.

Flame synthesis, that we used as well, is a modern manufacturing method of TiO_2. The essence of it is that when a titanium-containing liquid (precursor) is injected or evaporated into a sufficiently high temperature flame, the oxide formation and subsequent crystallization processes occur instantaneously. This technique offers several advantages over sol-gel technology that is also capable of industrial-scale production. It is fast, inexpensive, easy to regulate, and the crystallinity of the resulting TiO_2 is appropriately high so it does not require any post-synthetic heat treatment.

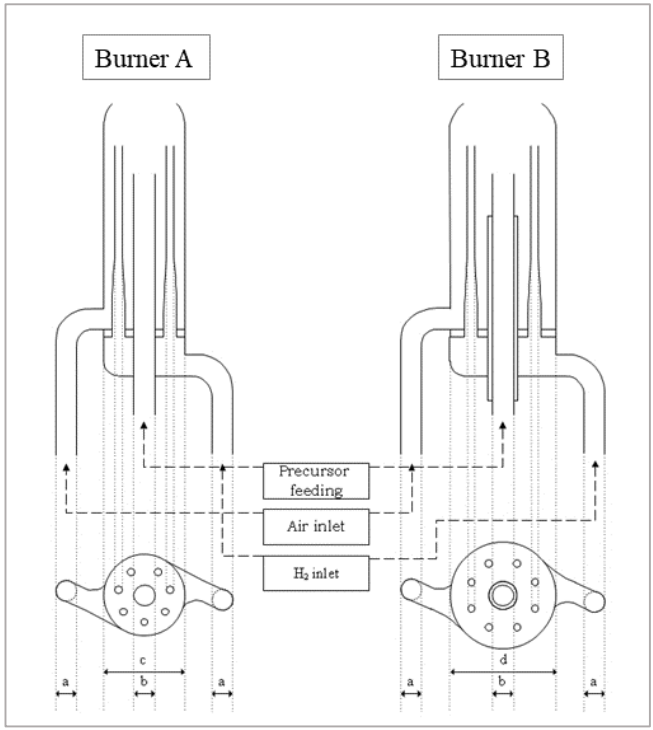
II. Objectives

A fundamental aim of the present work was the development of a flame synthesis method with which efficient TiO_2 catalysts could be manufactured. It included the design of reactors and all their supporting peripheral elements. As the following step of our studies, different sample series were prepared by systematically varying the available synthesis parameters. Structural characteristics of these catalysts have thoroughly been investigated in order to ascertain how they depend on manufacturing

circumstances. Photocatalytic activities were determined through liquid and gas phase model reactions. The comparison of these data provided valuable information on the media- and substrate-dependent behavior of the samples. We also deemed essential to get a deeper insight into the working mechanism of our catalysts. For this, we analyzed the primary product distribution of aqueous phenol degradation. Furthermore, oxygen depletion rate and total organic carbon content measurements were conducted in the same reaction system. Finally, with all the above results, we have attempted to find correlation between catalysts' structural/chemical properties and their activities, thereby contributing to a better understanding of TiO_2-related catalytic processes.

III. Experimental methods

Two burners with slightly different geometries were used for the **syntheses** (Figure). The flame was fed by a mixture of H_2 and air at each burner. The vapor of the liquid precursor ($TiCl_4$) was obtained by air bubbling. The resulting strongly acidic suspensions were dialyzed against distilled water. This experimental setup rendered the adjustment of basically three parameters possible: flame temperature, the mass flow and residence time of the precursor.



Cross-sectional views and some geometrical data of burners used for syntheses:
a = 5 mm; b= 3 mm; c = 27 mm; d = 35 mm

X-ray diffractometry (**XRD**) was employed in order to characterize the average particle size and phase composition of catalysts, while their specific surface area (SSA) was determined by **N_2-adsorption**.

Transmission electron microscopic (**TEM**) measurements were performed to ascertain size distributions and morphology of particles. In order to ensure representative sampling of our statistics, images were taken from at least 8-10 different regions, applying mostly 92k-fold magnification. It meant the analysis of more than 800-1000 grains per each sample.

Out of the available imaging techniques, besides TEM, **scanning electron microscopy** (**SEM**) and **high-resolution transmission electron microscopy** (**HRTEM**) were also utilized. The advantage of the latter over

the other two methods is that it reveals lattice periodicities of the individual crystalline phases, thus enabling chemical identification of particles.

The hydrodynamic behavior of catalyst suspensions was studied by **dynamic light scattering** (**DLS**). This instrument offered the opportunity to simultaneously determine the given system's isoelectric point (pH_{IEP}) and hydrodynamic diameters of TiO_2 agglomerates (d_{DLS}).

The chemical quality of particle surfaces was investigated by **X-ray photoelectron spectroscopy** (**XPS**). The number, the position and the relative magnitude of peaks assigned to Ti 2p and O 1s binding energies were taken for ascertaining the oxidation state of TiO_2 and the density of hydroxyl (OH) groups.

Photocatalytic activities were tested in gas as well as in liquid phase. For the former, acetaldehyde and methanol, while in the latter case, phenol was applied as model compound. Changes of these substances' and their intermediates' equilibrium concentrations were monitored by chromatography. The efficiency of aqueous phenol breakdown was also characterized by the diminution rate of **dissolved oxygen** ($r_{0,O2}$) and of the **total organic carbon** (**TOC**) content.

IV. Results

IV.1. Results related to the synthesis method

- The diffusion flame reactors (Burner-A and -B) and their peripheral elements ensured stable and well-controllable operating conditions which eventually granted the desired level of reproducibility with respect to material characteristics and to photocatalytic activities of the products.
- It has indirectly been verified by experimental data that rutile particles do not exist at the very beginning of particle formation but they evolve from anatase clusters. In O_2-lean environment, rutile crystallites start to grow from smaller clusters due to oxygen vacancies appearing in the TiO_2 crystal lattice.
- Interactions of the individual gas streams passing through the reaction zone (H_2, air and precursor intake) were manifested themselves in distorting the results of sample characteristics that could theoretically be anticipated. This influence has shown large dependency on several factors, like burner geometry, absolute values of the individual flow rates and their ratios.
- Under certain conditions, the chemical transformation of $TiCl_4$ liberates such an extent of thermal energy that is comparable to the enthalpy content

of the flame. It may, thus, considerably influence the spatial temperature distribution of the reaction zone. Accordingly, controllability of the synthesis procedure can highly be improved by choosing an appropriate precursor gas phase concentration range.

- We revealed that the formation of polyhedral particles favors lower flame temperatures and shorter reaction zone residence times.

IV.2. Effect of particle morphology on photocatalytic activity

A-samples (produced by Burner-A) having more polyhedral grains usually display better performance in decomposing weakly adsorbing model substrates compared to catalysts, which consist rather of spherical crystallites. This interrelation led us to assume that polyhedral particles have higher efficiency in producing radicals. By contrast, no such correlation was found for oxidation processes occurring through direct charge transfer. These reaction rates appeared to be dominated by the measure of SSA.

IV.3. Chemical quality of TiO_2 surfaces

- The Ti^{3+} oxidation state could not be detected in any of the samples.
- While the aggregate atomic ratio of the two types of OH-groups (terminal and bridging) did not correlate to any TiO_2 property, the terminal ones (O_TH) were specific only to B-samples showing outstanding performances. The increased amount of O_TH-groups can be attributed to the enlarged exposure of {001} facets which, in turn, opens the way for a more efficient charge separation process induced by the synergism between these and {101}-oriented crystallographic surfaces.
- In accordance with literature findings, {001}/{101} surface area ratio – detected through the O_TH content – exhibited an optimum value with respect to photocatalytic activity.

IV.4. Hydrodynamic behavior of TiO_2 samples

- Investigated B-samples possess significantly lower pH_{IEP} values (2.2-4.0) than that of the reference catalyst P25-B (5.8). This may greatly contribute to their superior photocatalytic activities under the circumstances of aqueous phenol decomposition experiments.

- In line with pH_{IEP} and d_{DLS} data, most B-sample dispersions had remarkable stability even after 72 hours of storage at their natural pH-s (*ca.* 4.8 to 6.6).

IV.5. Dissolved oxygen concentration measurements

The specific surface area- (SSA) and catalyst loading-normalized value of oxygen depletion rate ($r_{0,O2}/(SSA \times c_{TiO2})$) displayed a quasi-linear interrelation with the initial phenol breakdown rate ($r_{0,phenol}$). This justifies our hypothesis that at the early stages of the decomposition, the concentration of different intermediates may still be relatively low, therefore, phenol-radical interactions prevail.

IV.6. Mineralization efficiencies

Small SSA can be a considerable restraint on mineralization efficiencies since it determines the amount of typically well-adsorbing intermediates that transforms in a unit time. This is confirmed by the TOC results of our catalyst which has the highest activity but a relatively small SSA. Nevertheless, despite a presumably higher surface coverage, this sample preserved its higher phenol decomposition, thus, its higher radical production efficiency throughout photocatalytic runs.

V. Publications and conferences

V.1. Papers related to the thesis

1. **N. Balázs**, K. Mogyorósi, D.F. Srankó, A. Pallagi, T. Alapi, A. Oszkó, A. Dombi, P. Sipos
The effect of particle shape on the activity of nanocrystalline TiO_2 photocatalysts in phenol decomposition
Applied Catalysis B: Environmental 84, **2008**, *356-362.*
IF: 4.853 Cit.: 79

2. **N. Balázs**, D.F. Srankó, A. Dombi, P. Sipos, K. Mogyorósi
The effect of particle shape on the activity of nanocrystalline TiO_2 photocatalysts in phenol decomposition. Part 2: The key synthesis parameters influencing the particle shape and activity
Applied Catalysis B: Environmental 96, **2010**, *569-576.*
IF: 4.749 Cit.: 25

3. K. Mogyorósi, **N. Balázs**, D.F. Srankó, E. Tombácz, I. Dékány, A. Oszkó, P. Sipos, A. Dombi
The effect of particle shape on the activity of nanocrystalline TiO_2 photocatalysts in phenol decomposition. Part 3: The importance of surface quality
Applied Catalysis B: Environmental 96, **2010,** *577-585.*
IF: 4.749 Cit.: 39

4. **N. Balázs**, A. Gácsi, A. Pallagi, K. Mogyorósi, T. Alapi, P. Sipos, A. Dombi
Comparison of the liquid and gas phase photocatalytic activity of flame-synthesized TiO_2 catalysts: the role of surface quality
Reaction Kinetics, Mechanisms and Catalysis 102, **2011,** *283-294.*
IF: 0.829 Cit.: 8

V.2. Conference lectures (L) and posters (P) related to the thesis

1.P. **N. Balázs**, P. Sipos, A. Dombi
Synthesis and characterization of various TiO_2 samples made by flame hydrolysis
EC-DNAPL-1 ECOR-3, 2006.09.11-13, Göttingen, Germany

2.P. **N. Balázs**, A. Pallagi, K. Mogyorósi, T. Alapi, A. Dombi, P. Sipos

Comparison of the liquid and gas phase photocatalytic activity of flame-synthesized TiO_2 catalysts
13th International Conference on Chemistry, 2007.11.8-10, Cluj, Romania

V.3. Other papers

1. **N. Balázs**, P. Sipos
Limitations of pH-potentiometric titration for the determination of the degree of deacetylation of chitosan
Carbohydrate Research 342, **2007,** *124-130.*
IF: 1.720 Cit.: 60

2. Z. Ambrus, **N. Balázs**, T. Alapi, G. Wittmann, P. Sipos, A. Dombi, K. Mogyorósi
Synthesis, structure and photocatalytic properties of Fe(III)-doped TiO_2 prepared from $TiCl_3$ in phenol decomposition
Applied Catalysis B: Environmental 81, **2008**, *27-37.*
IF: 4.853 Cit.: 110

3. L. Óvári, A. Berkó, **N. Balázs**, Zs. Majzik, J. Kiss
Formation of Rh-Au core-shell nanoparticles on TiO_2(110) surface studied by STM and LEIS
Langmuir 26, **2010,** *2167-2175.*
IF: 4.286 Cit.: 19

4. Z. Pászti, O. Hakkel, T. Keszthelyi, A. Berkó, **N. Balázs**, I. Bakó, L. Guczi
Interaction of carbon monoxide with Au(111) modified by ion bombardment: a surface spectroscopy study under elevated pressure
Langmuir 26, **2010**, *16312-16324*.
IF: 4.286 Cit.: 26

5. É.G. Bajnóczi, **N. Balázs**, K. Mogyorósi, D.F. Srankó, Z. Pap, Z. Ambrus, S.E. Canton, K. Norén, E. Kuzmann, A. Vértes, Z. Homonnay, A. Oszkó, I. Pálinkó, P. 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.*
IF: 5.625 Cit.: 52

6. Z. Majzik, **N. Balázs**, A. Berkó

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Journal of Physical Chemistry C 115, **2011**, *9535-9544.*
IF: 4.805 Cit.: 9

7. Z. Majzik, **N. Balázs**, L. Robin, M. Petukhov, B. Domenichini, S. Bourgeois, A. Berkó
Tunneling induced decomposition of $Mo(CO)_6$ onto TiO_2(110) surface
Vacuum 86, **2012**, *623-626*.
IF: 1.503 Cit.: 2

8. Z. Majzik, **N. Balázs**, A. Berkó
Thermally activated reconstruction of TiO_2(110)-(1×1) surface in the presence of potassium: An STM study
Catalysis Today 181, **2012**, *89-94*.
IF: 2.980 Cit.: 3

9. P. Mutombo, **N. Balázs**, Z. Majzik, A. Berkó, V. Cháb
Theoretical study of the adsorption of rhodium on a TiO_2(110)-(1×1) surface
Applied Surface Science 258, **2012**, *4478-4482*.
IF: 2.112 Cit.: 3

10. A. Berkó, **N. Balázs**, G. Kassab, L. Óvári
Segregation of K and its effects on the growth, decoration, and adsorption properties of Rh nanoparticles on TiO_2(110)
Journal of Catalysis 289, **2012**, *179-189*.
IF: 5.787 Cit.: 7

V.4. Other conference lectures (L) and posters (P)

1.L. **N. Balázs**, P. Sipos
Különböző forrásokból származó kitozán minták analitikai kémiai jellemzése
XXVII. Kémiai Előadói Napok, 2004.10.25-27, Szeged

2.L. **N. Balázs**, P. Sipos
Analytical chemical characterization of chitosan samples of various origin
10^{th}. International Conference on Chemistry, 2004.11.12-14, Cluj, Romania

3.L. **N. Balázs**, P. Sipos

Comparison of ^{1}H-NMR, FT-IR spectroscopy and pH-potentiometry in the characterization of chitosan, a natural polysaccharide with wide ranging biomedical and environmental applications
7th Regional Conference on Environment and Health, 2005.06.17, Szeged, Hungary

4.L. **N. Balázs**, K. Demeestere, P. Sipos, A. Dombi, K. Hernádi
Szén nanocsövek felületére felvitt TiO_2 katalizátorok jellemzése
XXVIII. Kémiai Előadói Napok, 2005.10.24-26, Szeged, Magyarország

5.P. **N. Balázs**, K. Demeestere, K. Hernádi, B. Korbély, P. Sipos, A. Dombi
TiO_2-dal borított szén nanocsövek fotokatalitikus aktivitásának vizsgálata
II. Kárpát-medencei Környezettudományi Konferencia, 2006.06.01-03, Pécs, Magyarország

6.L. I. Ilisz, T. Alapi, K. Gajdáné Schrantz, Z. Ambrus, **N. Balázs**, P. Sipos, A. Dombi
Nagyhatékonyságú oxidációs eljárások a környezeti kémiában
II. Kárpát-medencei Környezettudományi Konferencia, 2006.06.01-03, Pécs, Magyarország

7.L. J. Kiss, L. Óvári, **N. Balázs**, Z. Majzik, A. Berkó
Characterization of Rh-Au core-shell nanoparticles on TiO_2(110)(1x2) surface: LEIS and STM study
26thEuropean Conference on Surface Science (ECOSS-26), 2009.08.30-09.04, Parma, Italy

8.P. Z. Majzik, **N. Balázs**, A. Berkó
Fabrication of Rh nanowire on TiO_2(110) surface by metal deposition at high temperatures
26thEuropean Conference on Surface Science (ECOSS-26), 2009.08.30-09.04, Parma, Italy

9.P. **N. Balázs**, L. Robin, Z. Majzik, M. Petukhov, S. Bourgeois, B. Domenichini, A. Berkó
Nanoscale decomposition of $Mo(CO)_6$ on TiO_2(110) surface induced and studied by STM
13th Joint Vacuum Conference (JVC-13), 2010.06.20-24, Štrbské Pleso, Slovakia

10.P. Z. Majzik**, N. Balázs**, A. Berkó

Atomically resolved STM detection of wagon-wheel-like TiO_x layer formed on Rh nanoparticles grown on TiO_2(110)
IVC-18, ICN&T-2010, ICSS-14, VASSCAA-5, 2010.08.23-27, Beijing, China

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Citations, total:	442	related to the thesis:	151