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THE IMPACT OF TiO_2 MODIFICATIONS ON THE EFFECTIVENESS OF PHOTOCATALYTIC PROCESSES [REVIEW]

Abstract

This paper outlines the recent studies on the application of photocatalysis using semiconductors, with modified titanium dioxide (TiO_2) in the process of reducing chemical contamination of surface and ground waters. During the last forty years, an increasing interest in catalysts of this type is noticeable. Hence, a wide range of methods of TiO_2 modifications have been proposed so far by using its various polymorphs, composites with metals and non-metals and polymer-coatings or impregnating it with dyes that effectively absorb sunlight.

Key words

titanium dioxide, doping, metals, non-metals, dyes, photodegradation

Titanium dioxide

Inorganic semiconductors started to be used as photocatalysts in the 70s of the twentieth century. Among substances examined so far special emphasis should be placed on titanium dioxide, TiO_2 . This is an amphoteric solid, which is non-toxic and insoluble in water. It turned out that TiO_2 exhibits a high photocatalytic activity, and is also thermally resistant and relatively inexpensive. Therefore, it is considered to be one of the best examined semiconductors widely described in the literature. Titanium dioxide occurs in minerals and can be obtained from them after removal of other constituents (e.g. Fe, depending on the ore). This is an important raw material for the production of titanium metal. Due to its photochemical activity it may be used as a catalyst in photo-oxidation processes, e.g. in systems designed for removal of organic impurities from wastewater.

TiO_2 occurs in three minerals called rutile, brookite and anatase (Fig.1) [1-13].



Anatase



Rutile



Brookite

Fig.1. Polymorphic forms of TiO_2

Rutile (Latin "rutilus" which means red, from the color of some of its forms) is the most important and stable form of titanium dioxide. It is an accessory mineral of metamorphic and igneous rocks. Crystals of rutile exhibit birefringence. Its nanoparticles are transparent in visible light, but absorb UV light. Therefore, TiO_2 is used in the production of preparations which protect skin against harmful UV rays. Rutile may be obtained from anatase as a result of a polymorphic transformation in the temperature range 550-1000°C. Rutile is mainly used in the production of titanium white (known as pigment PW6), glass, titanium and its alloys [2,12-15].

Brookite (after H.J. Brooke, an English crystallographer and mineralogist) is the rarest form of TiO_2 . It is very difficult to obtain pure brookite, without a dope of anatase or rutile. Therefore, its properties were tested to a small extent. It occurs in the form of fragile, transparent crystals. It has a poorly developed specific surface area

and this is the main reason why it is used on a small scale (including production of titanium metal) [1,12,13,15,16].

Anatase (Greek “anataxis” which means extension) occurs as a transparent, fragile solid with a metallic luster. Like rutile, it is an accessory mineral of metamorphic igneous rocks. Anatase is the most thermodynamically stable when its crystalline size falls below 11 nm (11-35 nm for brookite and 35 nm for rutile) [17]. Only rutile and anatase have been considered for large-scale commercial use. Generally, TiO_2 is obtained after processing of natural sources (ilmenite, rutile and anatase minerals). An alternative way is the sol-gel route, involving hydrolysis of titanium alkoxides (typically Ti-propoxide and/or Ti-butoxide). The particular polymorphs are formed during calcination of the raw TiO_2 product, anatase at 400-500°C, rutile above 600°C and their blends between 500-800°C.

From the plethora of TiO_2 polymorphs, anatase is particularly recognized for its excellent photocatalytic properties, more than rutile and brookite ones [12-14,17,18]. Catalytic activity of anatase depends, among other things, on the size of grains as well as the surface structure and its morphology. Depending on the mean grain size, microanatase (200-500 nm) and nano-anatase (10-90 nm) have been distinguished. The specific surface area of these two types of anatase corresponds to 8 – 15 m^2/g and 50 – 100 m^2/g , respectively. Generally, nano-anatase is considered more active in photooxidation processes than its microcrystalline form [12-14,17,18].

Although most literature data show that anatase is the most active TiO_2 polymorph, however, depending on the type and conditions of the realized catalytic process, the activity of anatase and rutile may be more or less similar.

Both anatase and rutile as well as their blends have been reported to prove effective photocatalysts in the degradation of a number of organic compounds, including phenols, organic acids and amines. Nevertheless, it was found that efficiency of these processes depends not only on the type of the catalyst used but also it is strongly related to the nature of the organic substrate. It has been proved, that in the case of some compounds anatase was more effective, while in others it was the rutile one. This issue clearly shows, that the photocatalytic activity of TiO_2 itself depends on a variety of physicochemical parameters which might have diversely affected its activity, including shape, size and specific surface area of TiO_2 grains as well as their pore structure and volume of pores. To understand the TiO_2 photocatalytic activity one must take into consideration the impact of such factors. It may be the case that a particular catalyst is effective in the degradation of a given chemical compound, but not necessarily for another one [2,3,19].

Mechanism of the photocatalytic reaction

Advanced processes of oxidation are determined by the formation of reactive oxygen species (ROS), including $\cdot\text{OH}$, $\text{HOO}\cdot$, $\cdot\text{O}^{2-}$ and singlet oxygen ($^1\Delta_g\text{O}_2$). From among them, the hydroxyl radical ($\cdot\text{OH}$) is considered the strongest and most reactive oxidant. For this reason, photooxidation processes may constitute an alternative to widely used methods of water treatment. Therefore, photocatalytic systems based upon the TiO_2 matrix seem to provide a very economic and prospective method of water purification. Extensive research is carried out worldwide towards the improvement of pro-ecological photocatalytic processes [5].

Photoactivity of titanium dioxide is related to the absorption of light at wavelengths less than 400 nm. Photons that correspond to this energy cause excitation of electrons in the semiconductor matrix from the valence band into the conduction band. As a result, electron-hole pairs responsible for the activity of the catalyst are generated. Oxygen and water molecules present in the system can be then converted into reactive oxygen species. Electrons on the surface of TiO_2 combine with oxygen, whereas the holes interact with the surrounding water phase to create reactive hydroxyl radicals. These are very strong oxidants, capable to degrade effectively a number of organic compounds [4,5,8,19,15,19-21]. Usually, complete mineralization of the original organic substrate and its conversion to CO_2 and H_2O is reported, along with the formation of other non-toxic inorganic compounds [2,3,19].

Modification of the TiO₂ matrix

To increase the rate and effectiveness of photodegradation processes, studies are performed on modification of the surface of TiO₂ grains by means of doping with metals and/or non-metals, dye impregnation and formation of mixtures containing specific amounts of the particular TiO₂ polymorphs.

Evonik P25

An example of the commercial mixture of TiO₂ polymorphs is Evonik P25, known as Degussa P25. It is widely used as a photocatalyst due to its high photochemical activity. Its composition varies, but normally it consists of anatase and rutile in quantity of about 70% and 20% respectively, and occasionally of the amorphous TiO₂ phase. Studies dedicated to the Evonik product revealed that particles of anatase and rutile form separate aggregates and the average size of their grains falls in the range of 25 to 85 nm. That is why this material has a relatively high specific surface area (49 m²g⁻¹) [22-24].

The photodegradation process of naphthalene with the use of anatase, rutile and Evonik P25 as catalysts was studied. It turned out that the process was much more effective when Evonik was used, and not anatase or rutile alone. In fact, it is very difficult to find a catalyst with a titanium dioxide matrix that shows higher activity than Evonik P25 and hence it is used as a basic TiO₂ catalyst [22-24].

Metal and non-metal doping

The most common methods of TiO₂ modifications are doping and impregnation with metal nanoparticles. This may be realized by introducing the dopant at the TiO₂ synthesis stage, as well as by adding it to a finished TiO₂ product. There are many methods of doping reported in the literature, dedicated to the particular TiO₂-dopant system, which depend on its assumed application [3,25].

Metal nanoparticles used for this purpose are mainly Pt, Au, Pd, Ru, Rh and Ag. It was proved that doping with gold has a positive influence on the mobility of electrons on the TiO₂/metal surface when exposed to UV radiation, which renders the photocatalytic process more effective. With respect to platinum, the quantity of oxygen adsorbed on the Pt/TiO₂ surface (which determines the activity of the photocatalyst), decreases when exposed to UV radiation, if the quantity of Pt increases, as compared to when UV was not used [3,6,7,19,26].

The major purpose of TiO₂ metal-doping is to prevent and/or delay the process of recombination of electrons and holes, and to effectively enhance the absorption of photons from the visible range. TiO₂ matrices may also be doped with ions of metals and non-metals. To determine the whole photo-oxidation process, it is important that ions are chosen appropriately [3,6,7,19,26].

Doping the TiO₂ matrix with transition metal ions (e.g. Fe(III), Ru(III), V(IV), Mo(V), Os(III), Re(V), Rh(III)) significantly improves the activity of the catalyst in photodegradation of CHCl₃ under UV radiation. In contrast, the presence of Co(III) and Al(III) ions decreases its effectiveness. Transition metals were studied much more thoroughly than noble metals. However, in a number of reports the effectiveness of doping with Ru(III), Rh(III), Pt(IV) and Ir(III) ions was emphasized, as well, e.g. in the process of 4-chlorophenol photooxidation [3,6,7,19,26].

Another approach assumed to improve the photocatalytic effectiveness of the TiO₂ matrix involved doping with non-metals, mainly N, C, S, B. However, in many cases, the results reported elsewhere were inconsistent and often controversial. For example, nitrogen-doped TiO₂ appeared effective in photodegradation of methylene blue, but was quite ineffective in the case of formic acid [3, 6,9,25,27].

Doping of TiO₂ matrices with two or more different elements was also studied. It turned out that doping of TiO₂ with two different metals (e.g. Sb/Cr or Pt/Cr), two different non-metals (e.g. N/F, N/S) as well as a metal and non-metal (e.g. Pt/N) did not produce any positive impact neither on the kinetics nor efficiency of the photodegradation of phenol, as compared to the reaction in which TiO₂ was doped with one metal or one non-metal only. However, this issue appears more complex and definitely must be related to the nature of the compound to be oxidized. For instance, photodegradation of 4-chlorophenol and acetaldehyde was found to proceed much more effectively in the presence of a double-doped matrix, such as the Pt/N-TiO₂ composite, than when the TiO₂ matrix was doped with either of these dopants alone [3, 6,9,26,27].

Function of inorganic anions

Inorganic anions adsorbed on the surface of a catalyst were found to affect the photo-oxidation process. Anions, such as fluorides, phosphides and sulfides, are not directly involved in photocatalytic reactions, but significantly influence the activity of a catalyst and hence the reaction mechanism. In this respect, the fluoride ion was the best examined one. It was proved that fluoride ions interchange with hydroxide ions on the surface of TiO_2 . Fluorination of the surface of TiO_2 has a major influence on its physicochemical and photocatalytic properties. It significantly changes its hydrophobic-hydrophilic character and speeds up the oxidation of organic and inorganic compounds. With the F-doped TiO_2 matrix it is possible to oxidize hydrogen cyanide, which is not possible when non-doped TiO_2 matrices have been used. However, fluorination of the TiO_2 surface is not always effective. For example, in the oxidation of platinum dichloroacetate, benzene or m-xylene, the use of TiO_2 doped with fluoride ions leads to a significant decrease in the reaction rate [3].

Dye impregnation

Catalytic properties of titanium dioxide can be improved by using a dye that strongly absorbs light in the UV-Vis range. In such a hybrid system the TiO_2 grains have been covered with a dye layer. Hence, the system modified in that way includes two cooperating photosystems: one located in the TiO_2 matrix and the other one in the chromophore system of the dye.

A dye may be incorporated into the TiO_2 matrix immediately during the synthesis (or just before calcination) of TiO_2 , however in such a regime the dye may often decompose or change its photoactivity due to chemical alterations. Another method consists in surface-decorating of TiO_2 crystals due to adsorption of the dye from a solution in an organic solvent. This technique seems more safe as far as the chemical stability of the dye is concerned [29,30]. Yet another methods involve mixing of the TiO_2 and dye powders followed by homogenization of the blend using a ball mill [29,30].

It turned out that phthalocyanines, synthetic analogues of the porphyrins, are well suited for this purpose. The phthalocyanine molecule, H_2Pc ($\text{Pc} = \text{C}_{32}\text{H}_{16}\text{N}_8$ is the phthalocyanine ligand) consists of four benzopyrrole units coupled by azomethine bridges into a characteristic macrocycle. Thus its core constitutes a very stable aromatic chromophore system. Impregnation of the TiO_2 surface with phthalocyanine derivatives or other dyes enhances the lifetime of the electron-hole pairs in the semiconductor matrix (TiO_2), which improves the effectiveness of a catalyst and speeds up the photodegradation process [21,25,27-32].

The effectiveness of such hybrid systems was proved in many studies i.a. photo-oxidation of 2-propanol in gas-solid and liquid-solid systems in the presence of catalysts such as $\text{TiO}_2@\text{LnPc}_2$ ($\text{Ln} = \text{Sm}, \text{Gd}, \text{Ho}$) [21,25,27-32], involving a microstructural anatase matrix, with grain size over 100 nm. Another example is photooxidation of 4-nitrophenol in the water phase, with the use of microanatase impregnated with lanthanide bisphthalocyanines, LnPc_2 ($\text{Ln} = \text{Nd}, \text{Sm}, \text{Gd}, \text{Ho}$) and/or metalloporphyrins (containing divalent ions of Mn, Fe, Ni and Cu). It was found that such catalysts may significantly increase the rate and efficiency of the process [21,25,27-32].

Summary

Hybrid systems involving the TiO_2 matrix represent a group of promising photocatalysts for application in photooxidation of organic and inorganic impurities occurring in the natural environment, including phenol derivatives, alcohols and sulfur compounds. It has been proved that doped or impregnated TiO_2 modifications demonstrate a significantly greater potential as catalysts when compared to bare TiO_2 . According to literature reports, such catalysts may improve the performance of the TiO_2 matrix and thus the reaction yield by at least several percent, and in some cases reaching almost complete mineralization (80-100%) of the organic substrate [29-32]. Moreover, TiO_2 based systems operating due to absorption of solar light are also possible, which is an additional advantage when regarding the ecological aspect [31,32]. Nevertheless, one must be aware that the applied photocatalyst must be adequately and individually tailored to the compounds to be oxidized and to the reaction conditions, otherwise it would not work effectively. Incidentally, the great number of literature data provided so far may sometimes be confusing, which makes it rather difficult to unequivocally compare the photo-oxidizing power of the proposed systems based on the reported features only. This is mainly because of different methods applied by the researchers when performing the tests as well as in evaluating of their results. And although it seems clear that doping may positively affect the photoactivity of the TiO_2 matrix, one

must take account of all external factors (e.g. temperature, pH, minor impurities, etc.) which may be crucial to achieve the maximum desirable catalytic effect.

References:

- [1] M. Bellardita, A. Di Paola, B. Megna, L. Palmisano, Absolute crystallinity and photocatalytic activity of brookite TiO₂ samples, *ApplCatal B-Environ.* 201 (2017) 150-158.
- [2] H.S. Chen, C.Su, J.L. Chen, T.Y. Yang, N.M. Hsu, W.R. Li, Preparation and Characterization of Pure Rutile TiO₂ Nanoparticles for Photocatalytic Study And Thin Films for Dye-Sensitized Solar Cell, Hindawi Publishing Corporation Journal of Nanomaterials, 2011 (2011) 1-8.
- [3] H. Park, Y. Park, W. Kim, W. Choi, Surface modification of TiO₂ photocatalyst for environmental applications, *J PhotochPhotobio C: Photochemistry Reviews*, 15 (2013) 1-20.
- [4] A. Fujishima, T.N. Rao, D.A. Tryk, Titanium dioxide photocatalysis, *J PhotochPhotobio C: Photochemistry Reviews*, 1 (2000) 1-21.
- [5] D. Chen, A.K. Ray, Photocatalytic kinetics of phenol and its derivatives over UV irradiated TiO₂, *ApplCatal B-Environ.* 23 (1999) 143-157.
- [6] Y. Ohama, D. Van Gemert, Application of Titanium Dioxide Photocatalysis to Construction Materials, Springer 5 (2011).
- [7] O. Carp, C.L. Huisman, A. Reller, Photoinduced reactivity of titanium dioxide, *Prog Solid State Ch.* 32 (2004) 33-177.
- [8] R. Thiruvengkatachari, S. Vigneswaran, I.S. Moon, A review on UV/TiO₂ photocatalytic oxidation process, *Korean J. Chem. Eng.* 25 (2008) 64-72.
- [9] A. Fujishima, X. Zhang, D.A. Tryk, TiO₂ photocatalysis and related surface phenomena, *Surf Sci Rep.* 63 (2008) 515-582.
- [10] H.A. Foster, I.B. Ditta, S. Verghese, A. Steele, Photocatalytic disinfection using titanium dioxide: spectrum and mechanism of antimicrobial activity, *ApplMicrobiolBiotechnol.* 90 (2011) 1847-1868.
- [11] P. Verma, S.K. Samanta, Degradation kinetics of pollutants present in a simulated wastewater matrix using UV/TiO₂ photocatalysis and its microbiological toxicity assessment, *Res ChemIntermed.* 43 (2017) 6317-6341.
- [12] T. Kasza, Badanie właściwości fotokatalitycznych I charakterystyka fizykochemiczna nanokrystalicznych filmów TiO₂ na podłożu ceramicznym, Praca doktorska (2007).
- [13] E. Kusiak-Nejman, Preparatyka i badania fotokatalizatorów TiO₂/C do oczyszczania wody i ścieków, Praca doktorska (2012).
- [14] R.M. Kadam, B. Rajeswari, A. Sengupta, S.N. Achary, R.J. Kshirsagar, V. Natarajan, Structural characterization of titania by X-ray diffraction, photoacoustic, Raman spectroscopy and electron paramagnetic resonance spectroscopy, *SpectrochimicaActa Part A: Molecular and Biomolecular Spectroscopy*, 137 (2015) 363-370.
- [15] T. Ohno, K. Sarukawa, K. Tokieda, M. Matsumura, Morphology of a TiO₂ Photocatalyst (Degussa, P25) Consisting of Anatase and Rutile Crystalline Phases, *J Catal.* 203 (2001) 82-86.
- [16] J. H. Lee, Y. S. Yang, Synthesis of TiO₂ nanoparticles with pure brookite at low temperature by hydrolysis of TiCl₄ using HNO₃ solution, *J Mater Sci.* 41 (2006) 557-559.
- [17] X. Wei, G. Zhu, J. Fang, J. Chen, Synthesis, Characterization, and Photocatalysis of Well-Dispersible Phase-Pure Anatase TiO₂ Nanoparticles, Hindawi Publishing Corporation International Journal of Photoenergy, 2013 (2013) 1-6.
- [18] C. Liu, D. Zhang, Y. Sun, Synthesis of hollow anatase spheres with enhanced optical performance, *RSC*, 16 (2014) 8421-8428.
- [19] M. Răileanu, M. Crișan, I. Nitoi, A. Ianculescu, P. Oancea, D. Crișan, L. Todan, TiO₂-based Nanomaterials with Photocatalytic Properties for the Advanced Degradation of Xenobiotic Compounds from Water. A Literature Survey, *Water Air Soil Poll.* 1548 (2013) 1-45.
- [20] J.M. Herrmann, Titania-based true heterogeneous photocatalysis, *Environ SciPollut Res.* 19 (2012) 3655-3665.
- [21] R. Słota, G. Dyrda, M. Galbas, G. Mele, Fotokatalizatory hybrydowe z matrycą TiO₂ aktywowaną ftalocyjaninami lantanowców, *Chemik*, 68 (2014) 11-13.
- [22] B. Ohtani, O.O. Prieto-Mahaney, D. Li, R. Abe, What is Degussa (Evonik) P25? Crystalline composition analysis, reconstruction from isolated pure particles and photocatalytic activity test, *J PhotochPhotobio A.* 216 (2010) 179-182.

- [23] T.S. Natarajan, H.C. Bajaj, R.J. Tayade, Enhanced direct sunlight photocatalytic oxidation of methanol using nanocrystalline TiO_2 calcined at different temperature, *J Nanopart Res.* 16 (2014) 1-16.
- [24] D. Kwon, S.H. Lee, J. Kim, T.H. Yoon, Dispersion, Tractionation and Characterization of Sub-100 nm P25 TiO_2 Nanoparticles in Aqueous Media, *ToxEHS* (2010) 78-85.
- [25] E. Grabowska, Otrzymywanie nowych fotokatalizatorów o podwyższonej aktywności w świetle UV oraz Vis, Praca doktorska (2011).
- [26] M. Tygielska, B. Tryba, Wpływ domieszkowania WO_3 do TiO_2 na poprawę jego zdolności fotokatalitycznych, *Oficyna Wydawnicza Politechniki Wrocławskiej*, 4 (2014) 922-931.
- [27] J. Carbajo, P. Garcia-Muñoz, A. Tolosana-Moranchel, M. Faraldos, A. Bahamonde, Effect of water composition on the photocatalytic removal of pesticides with different TiO_2 catalysts, *Environ Sci. Pollut Res.* 21 (2014) 12233-12240.
- [28] G. Marcì, E. García-López, G. Mele, L. Palmisano, G. Dyrda, R. Słota, Comparison of the photocatalytic degradation of 2-propanol in gas-solid and liquid-solid systems by using TiO_2 - LnPc_2 hybrid powders, *Catal Today*, 143 (2009) 203-210.
- [29] R. Słota, G. Dyrda, K. Szczegot, G. Mele, I. Pio, Photocatalytic activity of nano and microcrystalline TiO_2 hybrid systems involving phthalocyanine or porphyrin sensitizers, *Photoch. Photobio. Sci.* 10 (2011) 361-366.
- [30] E.G. Kogan, A.V. Ivanov, L.G. Tomilova, N.S. Zefirov, Synthesis of mono- and bisphthalocyanine complexes using microwave irradiation, *Mendeleev Commun.* 12(2) (2002) 54-55.
- [31] G. Mele, R. Del Sole, G. Vasapollo, E. García-López, L. Palmisano, J. Li, R. Słota, G. Dyrda, TiO_2 -based photocatalysts impregnated with metallo-porphyrins employed for degradation of 4-nitrophenol in aqueous solutions: Role of metal and macrocycle, *Res. Chem. Intermed.* 33 (2007) 433-448.
- [32] G. Mele, E. García-López, L. Palmisano, G. Dyrda, R. Słota, Photocatalytic degradation of 4-nitrophenol in aqueous suspension by using polycrystalline TiO_2 impregnated with lanthanide double-decker phthalocyanine complexes, *J. Phys. Chem. C* 111 (2007) 6581-6588.