NEW MATERIALS FOR PHOTOCATALYTIC PURIFICATION OF AIR – A REVIEW

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Abstract: *Photocatalytic processes became to be used for water and air depollution. Titanium dioxide (TiO_2) as photocatalyst is activated by electromagnetic waves from UV-VIS range of spectrum and is used for degradation of some volatile organic compounds (VOCs) and nasty smells removal. The quality of air, equally indoor and/or outdoor is a serious environmental problem. Different methods are used for improving the air quality and photocatalysis as an advanced oxidizing process, could be a promising solution. Using different techniques, new materials were developed by scientists from many countries, proving a real interest for these new environmental friendly technologies. This study presents last developments regarding new photocatalytic materials which have to work not only in UV (like pure titanium dioxide) but also in Visible range of electromagnetic spectrum. Also these new photocatalysts have to be able to oxidize different types of organic and/or inorganic molecules and diminishing the non-desiderated co-products from occurring reactions. To achieve new materials with superior photocatalytic properties there are used different procedures in order to combine and control the precursory components. The objective of the study was the understanding of the TiO2-photocatalysis phenomena including gaseous and adsorbed phase mechanisms. This review presents some achievements in domain.*

Keywords: *photocatalysis, air depollution, VOCs removal, nitrogen oxides degradation*

1. Introduction

The quality of air, equally indoor and/or outdoor is a serious environmental problem. Different methods are used for improving the air quality and photocatalysis as an advanced oxidizing process, could be a promising solution.
Initially photocatalysis processes were developed in direction of applications for water treatment, to degrade some specific pollutants or dyes. During the last decade, appear new directions, as far as concern air depollution, because photocatalytic processes were able to oxidize most of common VOCs (volatile organic compounds).
This study presents last developments regarding new photocatalytic materials which have to work not only in UV (like pure titanium dioxide) but also in Visible range of electromagnetic spectrum. Also these new photocatalysts have to be able to oxidize different types of organic and/or

inorganic molecules and diminishing the non-desiderated co-products from occurring reactions. To achieve new materials with superior photocatalytic properties there are used different procedures in order to combine and control the precursory components.

2. Theoretical approach

Photocatalytical reactions occur at the interface between catalyst and reaction medium in condition of irradiation with waves with electromagnetic field from UV and VISIBLE range of the spectrum. Photocatalysts are semiconductors with a band gap between 1.4 and 3.6 eV. Incident photons having energy more than the band gap energy are absorbed and as a fact, electrons jump from Valence Band in Conduction Band, and subsequently appear pairs of electron-hole particles. This pairs of particles exhibit oxidative and reductive properties, promoting REDOX reactions.
The process follows few steps as described below:
1. semiconductors' photo-excitation with EM energy equal or higher then gap energy;

2. generation of the electron-hole pairs;

3. separation of electrons and holes, the rate of the process necessarily to be higher than the rate of the inverse process, although the photocatalyst is deactivated;
4. adsorption of the pollutants on the catalyst surface;

5. redox reactions on the photocatalyst surface occurring between electrons, gaps and molecules; the processes of this stage are determinants for final products formation;

6. desorption of the products from the catalyst surface.

The efficiency of photocatalysis is closed by the rate of use of EM energy and by reduction of the percent of recombination processes. The type, the structure and the morphology of the photocatalyst are very important properties determining the degradation of organic pollutants, destruction of bacteria and viruses, decomposition of dyes or synthesis of some compounds.
Titanium dioxide is the most used photocatalyst due to the fact it has some specific properties like a great capability for producing hydroxyl radicals, could be activated by solar irradiation, it is stable (even for extreme values of pH), it has low cost and could be prepared in laboratory as powder or thin films. Also, it has an acceptable economic cost and it is environmental friendly.
The processes occurring at TiO_2 surface could be briefly described by following equations:
- Generation of electron-hole pairs

$$2TiO_2 + h\nu \Leftrightarrow TiO_2 (e^-) + TiO_2 (h^+) \quad (1)$$

- Recombination of electron-hole pairs:

$$TiO_2 (e^-) + TiO_2 (h^+) \Leftrightarrow 2TiO_2 + (\text{heat, light}) \quad (2)$$

- Surface reactions:

$$TiO_2 (h^+) + Red_1 \Leftrightarrow Ox_1^+ + TiO_2 \quad (3)$$

$$TiO_2 (h^+) + H_2O \Leftrightarrow OH^* + H^+ + TiO_2 \quad (4)$$

$$TiO_2 (h^+) + HO^- \Leftrightarrow OH^* + TiO_2 \quad (5)$$

$$TiO_2 (e^-) + O_2 \Leftrightarrow O_2^{-*} + TiO_2 \quad (6)$$

$$O_2^{-*} + H^+ \Leftrightarrow HO_2^* \quad (7)$$

$$2HO_2^* \Leftrightarrow O_2 + H_2O_2 \quad (8)$$

$$TiO_2 (e^-) + Ox_2 \Leftrightarrow Red_2^- + TiO_2 \quad (9)$$

- Degradation of different adsorbed substances, like volatile organic compounds, nitrogen oxides, bacteria, dyes, etc.

The processes are illustrated in figure 1.

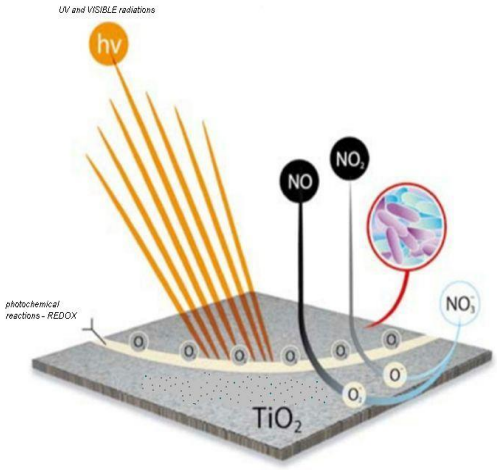

Figure 1. Processes occurring on the TiO_2 photocatalyst surface

3. Recent studies in air depollution and VOCs removal using photocatalysis promoted by titanium dioxide

We mention general studies about photocatalysis and applications in air depollution from publications covering last years.

B. Ohtani (Sapporo, Japan) pointed to what we know and what we don't know in present about photocatalysis [19]. It is a comprehensive study for documentation, a help for researchers.

J.-M. Herrmann (Lyon, France) realized a study about fundamentals and misconceptions regarding photocatalysis, a very useful material which points to some important theoretical and practical aspects of the processes[12].

M. Hunger and co. (Enschede, Holland) presented a comprehensive study about photocatalytic degradation of air pollutants [14]. NO was used for degradation rate measurements. Also it was described in brief an upcoming project in a Dutch city. This idea is applicable in next future and could help cities to be more comfortable.

Figure 2. An hypothetical ecological town with self-cleaning surfaces based on photocatalysis

The Program of „The 14th International Conference on TiO_2 Photocatalysis: Fundamentals and Applications (TiO2-14) The Conference Center Niagara Falls, New York, USA October 5-8, 2009" proved to be significant to point the newest achievements and tendencies in domain [29].

Useful for present stage documentation is the work presented by A. Selloni (Department of Chemistry, Princeton University, USA), at Workshop on Nanoscience for Solar Energy Conversion, 2008 and called „Materials-related aspects in TiO_2 - based photocatalysis: insights from first principles simulations" [21].

The study of different methods in TiO_2 photodegradation mechanism and gaseous and TiO_2-adsorbed phases was performed by P.-A. Deveau and co. (France) [7]. The development of photocatalysis processes offers a significant number of perspectives especially in gaseous phase depollution. It is proved that the photo-oxidizing properties of photocatalyst (TiO_2) activated by UV plays an important role in the degradation of volatile organic compounds (VOC). Heterogeneous photocatalysis is based on the absorption of UV radiations by TiO_2. This phenomenon leads to the degradation and the oxidation of the

compounds, according to a mechanism that associates the pollutant's adsorption on the photocatalyst and radical degradation reactions. The objective of the study was the understanding of the TiO_2-photocatalysis phenomena including gaseous and adsorbed phase mechanisms. Results obtained with three different apparatus were compared; gaseous phases are analyzed and mechanisms at the gaseous phase/photocatalyst interface are identified. Knowing the parameter is important for the design and construction of industrial size reactors that aim to purify the atmosphere.

Regarding VOCs (Volatile Organic Compounds) degradation, nasty smells removal, new materials with photacatalytic properties and new types of reactors, some recent studies are briefly pointed as follow.

M.M. Ballari and co. (Eindhoven, Holland) focused their work on NO and NO_2 degradation by photocatalytically active concrete[3]. The application of photocatalytic concrete containing TiO_2 in urban streets is a method to improve the air quality in highly polluted areas. By using this technology it is possible to degrade a wide range of air contaminants, like nitric oxide (NO) and nitrogen dioxide (NO_2), mainly emitted by automobiles. In their work paper, the photocatalytic degradation of NO and NO_2 was experimentally studied, and the atmospheric reactions involving nitrogen oxides and solar radiation were analyzed as well. In addition, the influence of different system parameters, such as inlet pollutant concentration, relative humidity, and irradiance was investigated in detail.

Peter C.K. Vesborg and co. (Lyngby, Denmark) studied gas-phase photocatalysis in μ-reactors [24]. They oxidized CO and methanol and demonstrate that the system exhibits great versatility as far as concern photocatalysts, illumination source and target reaction.

Photocatalytic reaction intensification using monolithic supports designed by stereolithography was studied by M. Furman and co. (Nancy, France) [10]. They designed an original photochemical reactor for polluted air treatment.

Photocatalysis of gas-phase toluene using TiO_2/SiO_2 composites was studied by C. Akly and co. (University of Florida, USA) [2]. The performances provided by this novel catalyst are suitable for large-scale applications.

A. Strini and L. Schiavi (Italy) studied toluene degradation in air using a cementitious material with photocatalytic properties, in low irradiance UV [22]. There was used a stirred flow reactor. Four pollutants were tested. They discovered a non-linear behavior of photoactivity at low irradiance.

C. Aguia and co. (Porto, Portugal) performed a study regarding the influence of photocatalytic paint components against the photooxidation of NO capability [1]. A high quality vinyl paint was used, modified with TiO_2 Degussa P25. It was concluded that the paint matrix plays an important role on the photocatalytic activity, because TiO_2 absorbs UV light in competition with other components; extenders, such as $CaCO_3$ impair photoactivity, more in the case water is involved in mixing the paint components; also organic components affect the performance of paint during a transient time of 100-250 h.

The study performed by J. Chen and C.-S. Poon from Hong Kong Polytechnic University pointed to photocatalytic activity of TiO_2 in modified concrete materials and the influence of glass cullets used as aggregates [5]. NO degradation was the measure of photoactivity. The glass cullets enhanced the photocatalytic activity of concrete, but a loss of 20% in photoactivity of surface layers was observed after 56 days curing. Another study of the same authors focused on fundamentals and applications of photocatalytic construction and building

materials [6].

H. Huang and D. Ye (Guangzhou, China) studied oxidation of gas-phase toluene in a combination process of photocatalysis downstream the non-thermal plasma reactor [13]. They investigated multiple synergies of O_3/UV/TiO_2 system. A good conversion rate for toluene was achieved.

D. Kibanova and co. (Mexico, USA) studied the synthesis and photocatalytic activity of small-sized TiO_2 supported on hectorite and kaolinite [16]. Photocatalytic performance of these new composites was evaluated with ATR-FTIR following the oxidation of adsorbed toluene and D-limonene, two air pollutants. In either case, the photocatalytic removal was a success.

H. Wang and co. (Jiangsu University, Zhenjiang, China) analyzed TiO_2 photocatalysis in a pulsed discharge system for phenol degradation [26]. The photocatalyst prepared with eight times dipping process proved a higher photocatalytic activity than other tested photocatalysts. Also H. Wang and co. followed enhanced generation of oxidative species for phenol degradation in a discharge plasma system coupled with TiO2 photocatalysis [27].

M. Faure and co. (Nancy University, France) compared different types of reactors used for air treatment [9]. They studied decomposition of different VOCs (Volatile Organic Compounds) in diverse conditions (like gas transit time through reactor, relative humidity, temperature). The aim of the study was to systematize the necessaries data for proper design of photoreaction systems.

A novel photocatalytic monolith reactor for multiphase heterogeneous photocatalysis was designed and studied by P. Du and co. (Delft, Holland) [8]. This was so-called Internally Illuminated Monolith Reactor (IIMR). The results were discussed for different substances which were oxidized and a comparison with other types of reactors was made.

C_2H_2 oxidation by plasma/TiO_2 combination and influence of the porosity against photocatalytic mechanism and plasma exposure were studied by O. Guaitella and co. (Lyon, France) [11]. The synergy plasma/photocatalysis is well known and could be a convenient solution for oxidation of acetylene.

Benoit Boulinguiez and co. (France, Algeria) studied photocatalytic degradation of ammonia and butyric acid in a plug-flow reactor and they moderated degradation kinetic with contribution of mass transfer [4]. Those substances were chosen because they are air pollutants and odorous contaminants. They found that chemical degradation kinetics follows the Langmuir–Hinshelwood model.

Reduction of nasty smells through photocatalytic oxidation was studied by G. Vincent and O. Zahraa [25]. They successfully performed degradation of 2-butanone and methyl-ethyl-ketone (MEK), two VOCs which could cause olfactory discomfort. Acetaldehyde results as by-product in both cases.

H.-H. Ou and S.-L. Lo (Taiwan) studied phocatalysis of gaseous trichloroethylene (TCE) and the effect of oxygen and relative humidity on the generation of dichloroacetyl chloride and phosgene [20].

F. Thevenet and co. (Lyon, France) studied oxidation of acetylene by photocatalysis coupled with dielectric barrier discharge [23]. VOCs removal from air requires oxidative processes. A special reactor has been designed and interactions between photocatalysis and non-thermal plasma were investigated. Acetylene has been selected as model molecule in order to evaluate oxidation efficiency.

Removal of VOCs by photocatalysis process using adsorption enhanced TiO_2-SiO_2 catalyst was the interest of L. Zou and co. (Australia) [28]. VOCs exist in both the indoor and outdoor environment. Some of them are toxic and carcinogenic to human health. In the experiment toluene

was used like VOC indicator. The catalyst was synthesized using a sol-gel technique. Toluene was successfully removed from air but there were detected some suspected intermediates or aliphatic hydrocarbons and CO, too.

The preparation of porous nano-TiO_2 with high activity and the discussion of the cooperation photocatalysis mechanism were performed by Y. Jiang and co. (China) [15]. A new preparation method was used. The researchers proved relations between the crystalloid and the size of TiO_2 nanograins, depending also by the technical conditions in which the process occurred.

T. Morikawa and co. (Toyota, Japan) created a new photocatalyst using titanium dioxide doped with nitrogen ($TiO_{2-x}N_x$) which yields a high reactivity under visible light irradiation [18]. This material exhibits a photodecomposition rate for gaseous acetaldehyde 5 times higher than simple TiO_2, and also exhibits significant antibacterial properties. It works under visible light (below 520 nm) and it has production low costs.

M. Mohseni (Vancouver, Canada) studied gas phase trichloroethylene (TCE) photooxidation through TiO_2 photocatalysis [17]. Even TCE oxidation was successfully achieved; small quantities of phosgene and dichloroacetyle chloride (DCAC) were produced as by-products.

3. Conclusions

Photocatalysis offers new perspectives in many fields of technology and industry. It is a clean and environmental friendly process. There were developed procedures for purifying water and for dyes degradation. Now air depollution is the new trend of researches in the domain of applications of photocatalysis. Some pollutants, like nitrogen oxides and volatile organic compounds were successfully degraded by photochemical methods. The achievement results could promote new commercial applications.

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