

# **BULGARIAN CHEMICAL COMMUNICATIONS**

**2017** Volume 49 / Special Issue L

Selection of papers presented on the IX National Conference on  
Chemistry, 29 September – 1 October, 2016, Sofia, Bulgaria

*Journal of the Chemical Institutes  
of the Bulgarian Academy of Sciences  
and of the Union of Chemists in Bulgari*

## Effectiveness of TiO<sub>2</sub>-based photocatalysts in the ozone assisted oxidative degradation of model wastewater contaminant adipic acid under UV-light irradiation

V.F. Georgiev<sup>1\*</sup>, V. Iliev<sup>1</sup>, A.E. Elias<sup>1</sup>, T.T. Batakliiev<sup>1</sup>, M.P. Anachkov<sup>1</sup>, V.E. Serga<sup>2</sup>, P.A. Karakashkova<sup>1</sup>, S.K. Rakovsky<sup>1</sup>

<sup>1</sup> Institute of Catalysis, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria

<sup>2</sup> Institute of Inorganic Chemistry, Riga Technical University, Riga, Latvia

Submitted November 10, 2016; Accepted February 21, 2017

Palladium and gold modified TiO<sub>2</sub> (Degussa P25) under the effect of feeding oxygen and ozone containing mixture to the reactor under UV-A and UV-C irradiation were examined for their catalytic activity in the reaction of adipic acid oxidation. The samples were synthesized by extractive-pyrolytic method by loading 0.5% of the active metal having particles size varying from 7 to 12 nm. The XRD, TEM and BET methods were employed for their structural and chemical characterization. In the presence of oxygen under UV-A light the apparent first-order reaction rates constants of Pd- and Au-modified TiO<sub>2</sub> samples were respectively 1.7 and 2.3 times higher than that of the pure TiO<sub>2</sub> under the same conditions. These higher reaction rate constants are due to the more efficient separation of the electron-hole charge carriers generated during irradiation. Further, the effectiveness of the catalysts in regard to the photooxidation of adipic acid in the presence of ozone is greater both under UV-C and UV-A light with all the tested samples. The reaction rate constants under monochromatic 254 nm irradiation are about 3 times higher than those evaluated with polychromatic ( $\lambda_{\text{max}}=365$  nm) light. This is due to the additional generation of HO<sup>•</sup> radicals by the ozone on the conduction band of the TiO<sub>2</sub> photocatalysts as well as the result of O<sub>3</sub> photolysis by the UV-C light photons of high energy.

**Keywords:** Photocatalysis, TiO<sub>2</sub>, Ozone, Nanosized photocatalysts

### 1. INTRODUCTION

Adipic acid is used primarily in the manufacture of nylon-6, 6 polyamide, polyester polyols, plasticizers, and lubricant additives. Worldwide demand for adipic acid is about 2 billion tons annually growing up continuously at a steady rate. This could result in its discharging into the environment through various waste streams. Many processes have been proposed over the years and they are being currently used to remove organic toxins from wastewaters. Adipic acid is classified as a hazardous substance and its complete degradation by photocatalytic oxidation is considered to be suitable process. Photocatalysis employing various semiconductors has been the focus of intensive investigations by a number of researchers [1– 6]. A number of metal composite systems have been investigated in degradation of water contaminants by photocatalytic processes through induced redox reactions on the surface of the catalyst. By illumination of the semiconductor catalyst with appropriate light energy, corresponding to the band gap, these processes involve a generation of conduction band electrons and valence band holes and they have been studied sufficiently well. An ideal photocatalyst should be stable, inexpensive, non-toxic and of course highly photoactive. Several semiconductors such as TiO<sub>2</sub>, ZnO, Fe<sub>2</sub>O<sub>3</sub>, WO<sub>3</sub>,

SnO<sub>2</sub>, ZrO<sub>2</sub>, CdS, SrTiO<sub>3</sub>, ZnS have band gap energies sufficient for catalyzing a wide range of chemical reactions. Considerable efforts have been devoted to the design of photocatalytic systems exhibiting a high efficiency for converting light into chemical energy [7 – 9]. Titania, the most thoroughly investigated semiconductor in the literature, seems to be the most promising for photocatalytic destruction of organic pollutants. This semiconductor provides the best combination between catalytic performance and stability in aqueous media. From a practical point of view one of the difficulties in developing a photocatalytic setup including semiconductor dispersion is the separation of the product from the photocatalytic slurry. This implies that the photocatalyst should be fixed on carrier material. It has been reported that TiO<sub>2</sub> is the most suitable because of its good anchoring on the support material [10].

The most important process in photocatalysis employing semiconducting materials is without any doubt the charge separation of electrons and holes. In order to reduce the high recombination rate of photoexcited electron-holes (excitons) and utilize more efficient sunlight, a variety of methods, such as metal and nonmetal doping of TiO<sub>2</sub> have been applied. It has been demonstrated convincingly that the doping with noble metal leads to promotion of its catalytic efficiency in photooxidation processes [11

\*) To whom all correspondence should be sent:

E-mail: vlado@ic.bas.bg

– 13]. Alongside with the employing of TiO<sub>2</sub> in photocatalytic oxidation of water pollutants, the involving of ozone in the process can improve the oxidation processes leading to higher conversion degrees at low cost [14]. The photocatalytic ozonation consists in the simultaneous application of ozone and photocatalysis [15 – 17]. The combination of ozone in photocatalytic systems brings forth a synergistic effect based on the high efficient electron trapping by ozone molecules. In addition to it higher amounts of hydroxyl radicals are being generated when comparing with photocatalysis in the presence of oxygen alone [18].

To investigate the effect of various TiO<sub>2</sub> doped catalysts in the reaction of complete adipic acid oxidation in water under UV light illumination and elucidate the role of ozone in the above reaction, in the present work we successfully synthesized by extractive pyrolytic method Pd/TiO<sub>2</sub> and Au/TiO<sub>2</sub> catalysts with 0.5 % noble metal loading.

## 2. MATERIALS AND METHODS

### 2.1. Chemicals, experimental setup and procedure

Hexanedioic acid (adipic acid 99% purity) was acquired from Merck and it was used in all experiments as received. Paladium powder (≥99.9 %; Aldrich), HCl (35 %) and HNO<sub>3</sub> (65%) (Lachema), *n*-tri-octylamine (C<sub>8</sub>H<sub>17</sub>)<sub>3</sub>N (≥95 %; Fluka) and toluene (analytical grade; Stanchem) were used to produce the precursors. TiO<sub>2</sub> (Degussa, P25) was used as a starting photocatalytic material.

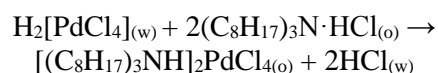
The studies on the photocatalytic oxidation of adipic acid have been performed in a specially designed cylindrical semi-batch reactor (100 mm internal diameter, 150 mm height) affording good absorbance of the incident UV light by the photocatalyst in the solution. In order to uniformly irradiate the entire volume of the solution, Philips (PL-S 2P or TUV PL-S) lamps for UV-A or UV-C irradiation were mounted radially relative to the axis of symmetry of the reactor inside a quartz tube. The photon flux in the UV light region at the external wall of the quartz tube was 10 mW cm<sup>-2</sup> (UV-A) and 14 mW cm<sup>-2</sup> (UV-C), determined by means of a Microprocessor-Controlled Radiometer (Cole Parmer 97503-00). The experiments were performed at a 12 dm<sup>3</sup>h<sup>-1</sup> gas flow rate of oxygen, or an oxygen–ozone mixture, at 293 K, pH 4 and atmospheric pressure. The aqueous suspension containing the respective catalyst sample at content of 1g/L was sonicated for 30 minutes before adding the adipic acid. Previously prepared solution of adipic acid was added to the aqueous slurry of the photocatalyst achieving an initial concentration of 8.3 x 10<sup>-3</sup> mol/L equivalent to 600 ppm TOC (Shimadzu VCSH).

Then the resulting mixture was transferred into the photoreactor and stirred magnetically for 30 min in order to reach the possible adsorption-desorption equilibria onto catalyst surface. The initial volume of the irradiated reaction mixture was 600 ml. During the direct ozonation and the photocatalytic process oxygen or oxygen-ozone mixture feed flow was bubbled continuously through a diffuser at the bottom of the reactor. The ozone concentrations at the reactor inlet and outlet were analyzed by means of an ozone analyzer, whereupon it was established that in the feed O<sub>2</sub>–O<sub>3</sub> gas mixture its concentration was 7.5 x 10<sup>-4</sup> mol/L providing a stoichiometric excess of ozone during the experimental runs. The concentration of the dissolved ozone has been evaluated to be 2.1 x 10<sup>-4</sup> mol/L on the basis of the reactor outlet concentrations by using values of Henry's constants at room temperature [19]. Samples were collected at every 30 min and filtered (Whatman, Grade 42) prior to be analyzed.

### 2.2. Photocatalyst synthesis

The extractive-pyrolytic method (EPM) was used for the catalyst samples preparation. Its simplicity and low cost, characterize the EPM as suitable for nanosized catalysts synthesis. As it can be seen below, this method allows depositing small amounts of noble metals (1–5 %) with particle size ranging from several nanometers to several tens of nanometers onto the surface of the support.

For synthesis of palladium containing catalyst the method can be described as follows: at first a solution of dihydrogen tetrachloropalladate (H<sub>2</sub>[PdCl<sub>4</sub>]) was prepared. An amount of the palladium powder was dissolved in aqua regia and evaporated thereafter upon adding concentrated HCl to the wet salt, which was then diluted with 2M HCl to reach the necessary concentration (0.5 mol.L<sup>-1</sup>). The organic precursor (extract) was prepared by extracting the palladium from the HCl solution using (1 M) *n*-trioctylamine (C<sub>8</sub>H<sub>17</sub>)<sub>3</sub>N solution in toluene. The following chemical interaction is occurring during the extraction:



Where, the subscripts “w” and “o” denote the aqueous phase and organic phase, respectively. As a result, a solution of tri-*n*-octylammonium tetrachloropalladate in toluene was obtained. The results of the analysis of the aqueous solution after extraction using a HITACHI 180-50 atomic absorption spectrometer gave evidence that the palladium amount had been completely extracted into the organic phase. An appropriate volume of the

extract was used to impregnate the TiO<sub>2</sub> in order to produce photocatalyst sample having the required content of 0.5% palladium. After impregnation, the toluene was evaporated by drying at 90–110 °C. Finally, the sample was heated up to 300 °C at a temperature increase rate of 10 °C min<sup>-1</sup>. A similar procedure was employed for synthesis of a 0.5% gold containing catalyst.

### 2.3. Analytical methods

X-ray powder diffraction patterns were recorded on a Bruker D8 Advance powder diffractometer with Cu K $\alpha$  radiation source and SolX detector. The samples were scanned at 2 $\theta$  angles from 10° to 80° at a rate of 0.04° s<sup>-1</sup>. The X-ray power was operated with a current of 40 mA and a voltage of 45 kV.

The metal crystallite size and the metal phase distribution in Au/TiO<sub>2</sub> and Pd/TiO<sub>2</sub> composite samples were examined with a high-resolution transmission electron microscope (HRTEM JEOL 2100).

Ozone was continuously generated by electrical discharges in pure oxygen flow in a self-assembled apparatus having possibility of varying the operating voltage up to 20 kV. Its gas phase concentration was monitored with ozone analyzer BMT 964 based on the absorption of ozone at 254 nm.

The photon flux in the UV light region at the external wall of the quartz tube was 10 mW cm<sup>-2</sup> (UV-A) and 14 mW cm<sup>-2</sup> (UV-C), determined by means of a Microprocessor-Controlled Radiometer (Cole Parmer, 97503-00) fitted with 254 nm and 365 nm sensors.

The specific surface area of the samples was determined on a standard BET apparatus applying the volumetric technique, as the measurements of nitrogen adsorption and desorption were performed at liquid nitrogen boiling temperature of 77 K.

The mineralization degree was analyzed by means of (TOC) analyzer (Shimadzu VCSH).

## 3. RESULTS AND DISCUSSION

### 3.1. Catalysts characterization

The mechanisms of semiconductor photocatalysis are known to involve hydroxyl radicals, trapped electrons, and trapped holes on the particle surface. The processes of entrapping the holes or electrons, and hence a more efficient

generation of OH radicals can be improved further by synthesis of composite materials including noble metal clusters. Of great importance for the effectiveness of these processes is not only the amount of metal loaded onto photocatalyst but also the metal particle size as well. In order to avoid the excessive coverage of the photocatalyst surface, the metal loading must be within the range of 0.5-1 wt.% [20 – 22 ]. In view of above details mentioned we prepared catalysts with 0.5% loadings of gold and palladium onto TiO<sub>2</sub>.

The specific surface areas were determined by nitrogen adsorption to be the following values: TiO<sub>2</sub> – 49.9 m<sup>2</sup>/g; Pd /TiO<sub>2</sub> – 54.5 m<sup>2</sup>/g and TiO<sub>2</sub>/Au – 53.1 m<sup>2</sup>/g. The crystalline phase of the synthesized catalysts was analyzed by X-ray powder diffraction (XRD). Figure 1 represents the XRD spectra of the samples that revealed diffraction peaks corresponding to crystalline palladium and gold phases in separate. The main peaks correspond to a tetragonal TiO<sub>2</sub> – anatase, whose content dominates over that of the rutile, are also represented in the spectra. The crystallite sizes of the palladium and gold particles were calculated to be 10-15 nm. The addition of Au or Pd nanoparticles caused the appearance of small characteristic peaks associated with the dopants. The metal particles have not given rise to any extra strong peaks on the XRD spectra of the doped catalysts. A possible explanation could be that both Au and Pd loading contents of noble metals were too low (0.5% wt.) as well as the formation of small clusters of noble metals with undefined crystalline structure which remain unobserved in the XRD pattern [23].

The ability of the catalyst sample to absorb efficiently photoenergy, depends on the nature of the noble metal and on its content, and it must be sufficiently well dispersed in order to influence the TiO<sub>2</sub>. The morphology of the metal particles on the TiO<sub>2</sub> photocatalyst was studied by transmission electron microscopy (Fig 2). The particle sizes have been estimated by means of the ImageJ software. TEM images show that Pd (Fig. 2a) and Ag (Fig. 2b) nanoparticles are visible as small dark particles with size varying from 5 to 16 nm and a mean diameter of 5.9 and 7.1 nm respectively.

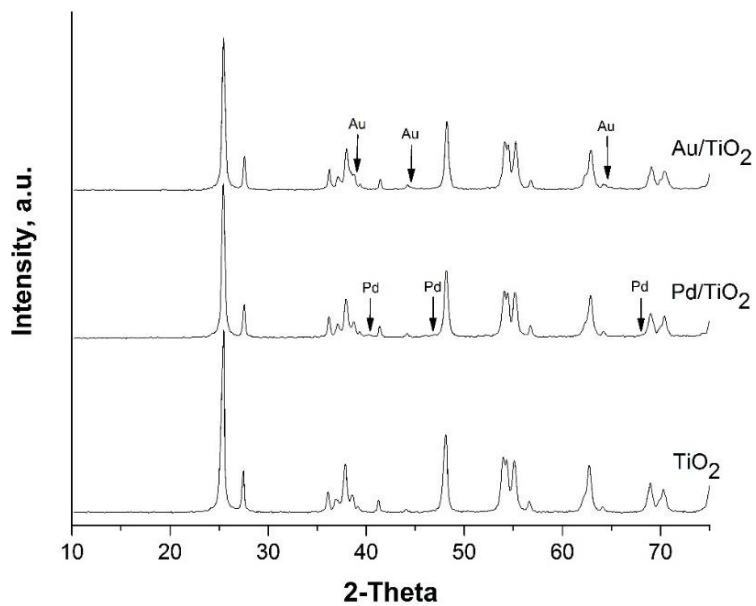


Figure 1. The XRD patterns of the photocatalysts.

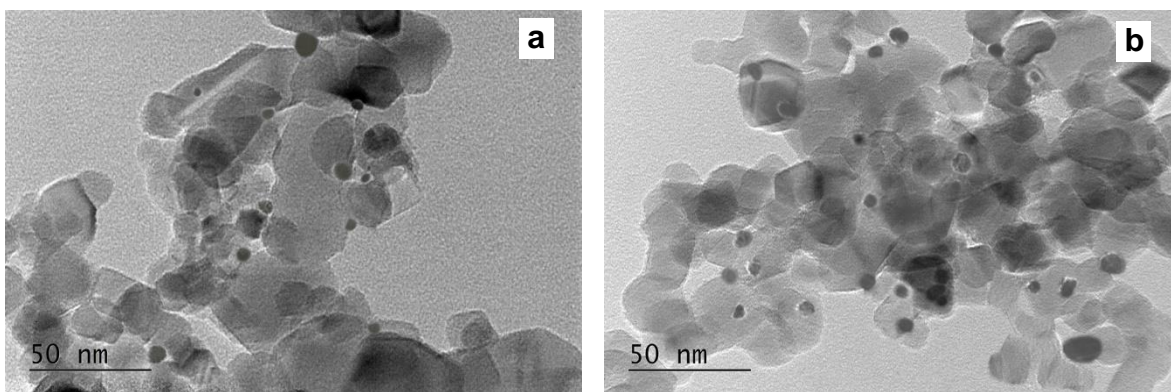


Figure 2. TEM micrographs of Pd/TiO<sub>2</sub> (a) and Au/TiO<sub>2</sub> (b) catalysts.

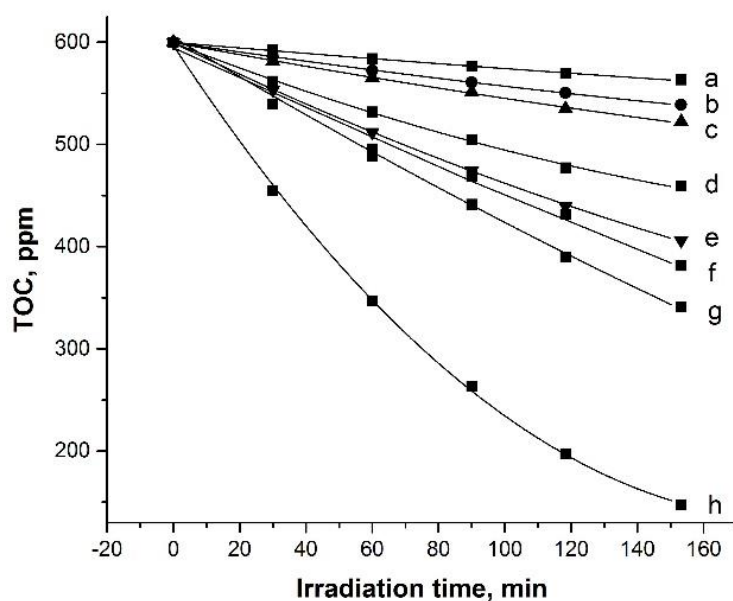


Figure 3. Total degree of mineralization of adipic acid catalyzed by: in the presence of O<sub>2</sub> ( $\lambda = 365$  nm) – (a) TiO<sub>2</sub>, (b) Pd/TiO<sub>2</sub>, (c) Au/TiO<sub>2</sub>; in the presence of O<sub>3</sub> ( $\lambda = 365$  nm) – (d) TiO<sub>2</sub>, (e) Pd/TiO<sub>2</sub>, (f) Au/TiO<sub>2</sub>; in the presence of O<sub>3</sub> ( $\lambda = 254$  nm) – (g) TiO<sub>2</sub>; (h) Au/TiO<sub>2</sub>.

### 3.2. Photocatalytic activity testing

Titanium dioxide doped with 0.5 wt% palladium and gold loading were prepared and tested in degradation of adipic acid in aqueous solution. Further, the ozone-oxygen gas mixture with ozone concentration of  $7.5 \times 10^{-4}$  mol/L was involved in the studied process. Figure 3 represents the kinetic curves of degradation of adipic acid in the presence of the tested samples under UV irradiation.

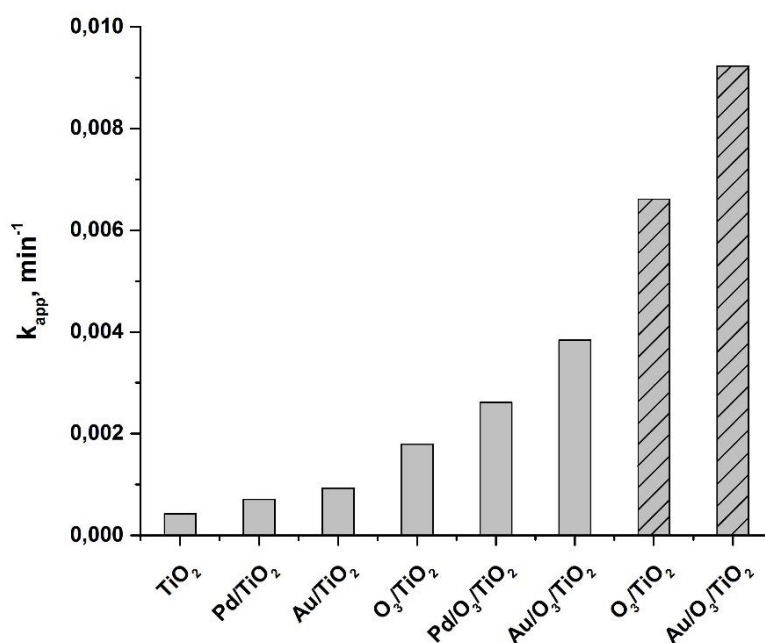
A number of investigators have reported that the rates of photodegradation of chemical compounds on semiconductor surfaces follow the classical Langmuir-Hinshelwood expression (Eq. (1)) and that the sorption of reactants to the semiconductor surfaces follows Langmuir sorption isotherms [24 – 26].

$$r = \frac{dC}{dt} = \frac{kKC}{1+KC} \quad (1)$$

Where,  $r$  is the oxidation rate of the reactant,  $C$  the concentration of the reactant,  $t$  the illumination time,  $k$  the reaction rate constant, and  $K$  is the adsorption-desorption equilibrium constant. If the initial concentration of the reactant  $C_0$  is of the order of millimoles, the above equation can be simplified to an apparent first-order reaction equation [27 – 29]:

$$\ln\left(\frac{C_0}{C}\right) = kKt = k_{app}t \quad \text{or} \quad C_t = C_0 e^{-k_{app}t} \quad (2)$$

In accordance with this, the rate constant of the adipic acid degradation (fig. 4.) was calculated based on equation (2).



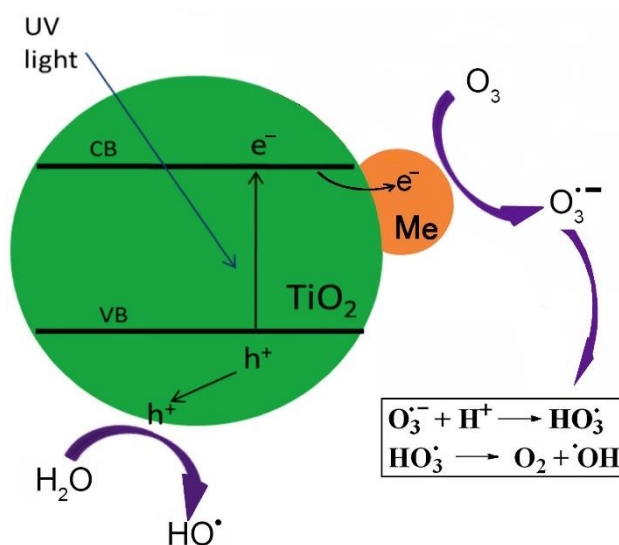
**Figure 4.** Apparent rate constants of adipic acid degradation under UV-light (■ 365 nm) and UV-light (▨ 254 nm).

The photonic efficiency of bare TiO<sub>2</sub> is low (<10%) as the photogenerated e<sup>-</sup>/h<sup>+</sup> pairs (~90%) recombine rapidly after excitation [30] which is evidenced by the results obtained by TOC analysis represented in Fig. 3 and 4. It was observed that the degradation of adipic acid over bare TiO<sub>2</sub> is taking place at a lowest rate constant compared to those achieved in presence of samples doped with noble metals. The principal approach to slow down the electron-hole recombination is based on the loading of electron accepting species on the TiO<sub>2</sub> surface. The sample from composite material containing 0.5% palladium exhibits 1.7 times higher effectiveness in mineralization of adipic acid than that manifested by the pure TiO<sub>2</sub> under irradiation with UV light 365 nm having rate constant of  $4.2 \times 10^{-4}$  min<sup>-1</sup>. The palladium particles having a higher work

function (5.2 – 5.6 eV) relative to those of TiO<sub>2</sub> (4.13 eV) [31] producing a high Schottky energy barrier at the inter-phase boundary facilitating the electron capture. In this case the photonic efficiency is increased by inhibition the electron-hole pair recombination as the photoelectron is transported to the outer system and transfer of holes to the reactants adsorbed on the TiO<sub>2</sub> surface is enhanced. The same tendency was observed in the presence of gold doped TiO<sub>2</sub> catalyst. It was found out that the rate constant of the reaction catalyzed by Au/TiO<sub>2</sub> was 2.3 times ( $9.25 \times 10^{-4}$  min<sup>-1</sup>) higher than that over pure TiO<sub>2</sub>. As it was mentioned above these small metal clusters (5-15 nm.) are regarded as photogenerated electrons scavengers preventing recombination and facilitate the subsequent redox reactions. As it is visible from Fig.3 and Fig.4 the presence of ozone leads to higher

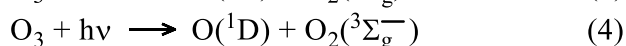
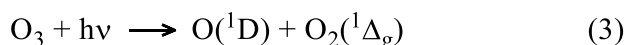
degrees of mineralization of adipic acid. Under irradiation with 365 nm UV light the values of the apparent rate constants of the samples were in order as follows: TiO<sub>2</sub><Pd/TiO<sub>2</sub><Au/TiO<sub>2</sub> which are about 4 times higher than those previously listed. It has been widely accepted that the holes cogenerated together with photoexcited electrons during absorption of UV light can interact with an organic molecule (at high concentration) or, in an aqueous solution, with water forming OH radicals [32] which are powerful oxidizing agents. This consideration indicates that the concentration of hydroxyl radicals

directly influences the rate of the reaction. Herein, by generating hydroxyl radicals appears to be the role of ozone and its impact on the effectiveness of the photocatalytic oxidation because the rate of the reaction of ozone with adipic acid is negligibly small, practically it does not interact with it [33]. Under our experimental conditions (UV-A light, pH=4), the adsorbed ozone is able to interact with deposited metal particle accepting the supplied by the metal photogenerated electrons to give ozonide radicals (O<sub>3</sub><sup>-</sup>) which subsequently form OH radicals (Fig. 5).

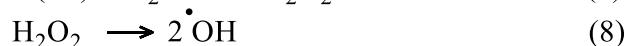
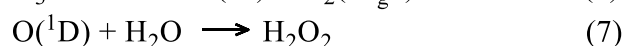
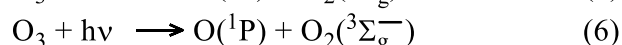
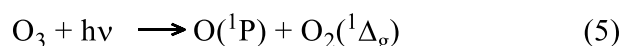


**Figure 5.** Schematic representation of the reduction of ozone on the metal surface.

The highest rate constant  $9.23 \times 10^{-3} \text{ min}^{-1}$  of the adipic acid removal was achieved employing the Au/TiO<sub>2</sub> catalyst in presence of ozone under 254 nm light, which is at about 2,5 times higher, compared to that over the irradiated with 365 nm light (Fig. 4). A possible hypothesis to explain this result could be the involvement the ozone photolysis under UV-C light. Upon photolysis, O<sub>3</sub> is decomposed into O<sub>2</sub> and oxygen atom O (<sup>1</sup>D) and O (<sup>3</sup>P) [34]. The major species formed under irradiation of ozone with UV-C light are excited oxygen atom O(<sup>1</sup>D) with quantum yield,  $\Phi = 0.9$  and singlet dioxygen, O<sub>2</sub>(<sup>1</sup>Δ<sub>g</sub>), as well as oxygen in its ground triplet state, O<sub>2</sub>(<sup>3</sup>Σ<sub>g</sub><sup>-</sup>) as follows:



The competitive reactions are of smaller importance that lead to formation of oxygen atom in its excited state O(<sup>1</sup>P), oxygen singlet O<sub>2</sub>(<sup>1</sup>Δ<sub>g</sub>) and O<sub>2</sub>(<sup>3</sup>Σ<sub>g</sub><sup>-</sup>) according reactions (5) and (6).



As the O(<sup>1</sup>D) is in highly energetic state it reacts very quickly with water molecule to give hydroxyl peroxide which further breaks down into hydroxyl radicals (reaction 7 and 8). It is supposed that H<sub>2</sub>O<sub>2</sub> is formed directly by the addition of O(<sup>1</sup>D) to H<sub>2</sub>O [35]. Upon photolysis of ozone, it is expected that the excited oxygen atom O(<sup>1</sup>P) should react with adipic acid. Hence cyclohexyl radicals and hydroxyl radicals are formed by H atom abstraction, which is promoting the destruction of the organic material by forming hydroxyl radicals through an additional route.

#### 4. CONCLUSIONS

The degradation rates of adipic acid in aqueous solution under irradiation with UV-A and UV-C light in the presence of doped with palladium and gold TiO<sub>2</sub> as well as the enhancement by ozone have

been determined. The characterization of metal-doped TiO<sub>2</sub> using XRD and TEM spectroscopy techniques revealed good degree of dispersion and nanometric size of noble metals clusters on the surface of TiO<sub>2</sub>. Due to the uniform distributions and small size (5-16 nm.) of the metal islands the blocking of fine pores of TiO<sub>2</sub> surface was prevented and the specific surface area of the doped and bare TiO<sub>2</sub> was similar. The photonic efficiency of Au/TiO<sub>2</sub> is almost comparable to that of Pd/TiO<sub>2</sub> but higher than that of Pd/TiO<sub>2</sub>. In general composite catalysts have better activity than pure TiO<sub>2</sub> as their rate constants are 1.7 (Pd/TiO<sub>2</sub>) and 2.3 (Au/TiO<sub>2</sub>) times higher. These results can be explained in terms of trapping of photogenerated electrons on the metal islands leading to better electron-hole charge carriers separation. The highest mineralization rates are achieved involving participation of ozone. Under irradiation with UV-A light in presence of ozone, it was determined that the rate constant of  $3.8 \times 10^{-3}$  employing the Au/TiO<sub>2</sub> and for the process carried under UV-C light the rate constant was about 2.5 times higher. These mineralization rates are due to the powerful capacity of ozone to generate radicals enabling the oxidation of organic pollutants.

**Acknowledgement.** *The authors gratefully acknowledge financial support by State Science Fund, Ministry of Education and Science of Bulgaria (Project DFNI T-02-16/12.12. 14.)*

#### REFERENCES

1. H. Yoneyama, M. Koizumi, H. Tamura, Bull. Chem. Soc. Jpn., **52**, 3449 (1979).
2. J. Kiwi, M. Graetzel, J. Am. Chem. Soc., **101**, 7214 (1979).
3. K. Domen, S. Naito, M. Soma, T. Onishi, K. Tamaru., Chem. Commun., **12**, 543- (1980).
4. L. Krasteva, K. Papazova, A. Bojinova, N. Kaneva, A. Apostolov, Bul. Chem. Comm., **45**, 625 (2013).
5. S. Siuleiman, D. Raichev, A. Bojinova, D. Dimitrov, K. Papazova, Bul. Chem. Comm., **45**, 649 (2013).
6. A. Masakazu, H. Nakaya, s. Kodata, Y. Kubokawa, K. Domen, T. Onishi, J. Phys. Chem., **90**, 1633 (1986).
7. S. Frank, A. Bard, J. Am. Chem. Soc., **99**, 303 (1977).
8. M. Halman, Nature, **275**, 115 (1978).
9. D. Dimitrov, M. Milanova, R. Kralshesvska, Bul. Chem. Comm., **43**, 489 (2011).
10. N. Serpone, E. Borgarello, R. Harris, P. Cahill, M. Borgarello, Solar Energy Materials, **14**, 121 (1986).
11. A. Milis, J. Peral, X. Domènech., Journal of Molecular Catalysis, **87**, 67 (1994).
12. M.I. Litter, J.A. Navío, J. Photochem. Photobiol. A: Chemistry, **98**, 171 (1996).
13. K. Wilke, H.D. Breuer, J. Photochem. Photobiol. A: Chemistry, **121**, 49 (1999).
14. S. Esplugas, J. Giménez, S. Contreras, E. Pascual, M. Rodríguez, Water Research, **36**, 1034 (2002).
15. W. H. Glaze, J. W. Kang, D.H. Chapin, Ozone Sci. Eng., **9**, 335 (1987).
16. G. R. Peyton, W.H. Glaze, Environ Sci. Technol., **22**, 761 (1988).
17. E. Gilbert, Ozone: Science & Engineering, **24**, 75 (2002).
18. S. Esplugas, J. Gimenez, S. Contreras, E. Pascual, M. Rodriguez, Water Research, **36**, 1034 (2002).
19. A. Sullivan, E. Roth, E. Danlel., Ind. Eng. Chem. Fundam, **20**, 137 (1981).
20. V. Kalarivalappil, C. M. Divya, W. Wunderlich, Suresh C. Pillai, Steven J. Hinder, Manoj Nageri, V. Kumar, Baiju K. Vijayan., Catalysis Letters, **146**, 474 (2016).
21. R. Najjar, M. Shokri, S. Farsadi, Desalination and Water Treatment, **54**, 2581, (2015).
22. A. Orlov, D. A. Jefferson, N. Macleod, R. M. Lambert, Cat. Lett., **92**, 4 (2004).
23. P. A. P. Nascente, S. S. Maluf, C. R. M. Afonso, R. Landers, A. N. Pinheiro, E. R. Leite, Appl. Surf. Sci., **315**, 490 (2014).
24. R. McEvoy, R. Matthews, R. Stephen, J. Photochem. Photobiol. A: Chem., **64**, 231 (1992).
25. V. Brezova, A. Stasko, Journal of Catalysis, **147**, 156 (1994).
26. E. Butler, A. Davis, J. Photochem. Photobiol. A: Chem, **70**, 273 (1993).
27. A. Houas, H. Lachheb, M. Ksibi, E. Elaloui, C. Guillard, Applied Catalysis B: Environmental, **31**, 145 (2001).
28. W. Z. Tang, H. An, Chemosphere, **31**, 4157 (1995).
29. I. Konstantinou, T. Albanis, Applied Catalysis B: Environmental, **42**, 319 (2003).
30. H. Zhang, G. Chen, D. Bahnemann., J. Mater. Chem., **19**, 5089 (2009).
31. A. Imanishi, E. Tsuji, Y. Nakato., J. Phys. Chem. C, **111**, 2128 (2007).
32. H. Ceriscber, A. Heller, The Journal of Physical Chemistry, **95**, 5261 (1991).
33. V. Georgiev, S. Rakovsky, K. Stanulov, A. Popov, Oxidation Communications, **31**, 151 (2008).
34. G. Hancock, P. Tyley, Phys. Chem. Chem. Phys., **4**, 4984 (2001).
35. H. Taube, Trans. Faraday Soc., **53**, 656 (1956).



ЕФЕКТИВНОСТ НА ФОТОКАТАЛИЗАТОРИ НА ОСНОВАТА НА TiO<sub>2</sub> В  
ПОДПОМОГНАТО ОТ ОЗОН ОКИСЛИТЕЛНО РАЗГРАЖДАНЕ НА АДПИНОВА  
КИСЕЛИНА КАТО МОДЕЛЕН ЗАМЪРСИТЕЛ В ОТПАДНИ ВОДИ ПРИ ОБЛЪЧВАНЕ С  
УВ СВЕТЛИНА.

В.Ф. Георгиев<sup>1\*</sup>, В. Илиев<sup>1</sup>, А.Е. Елияс<sup>1</sup>, Т.Т. Батаклиев<sup>1</sup>, М.П. Аначков<sup>1</sup>, В.Е. Серга<sup>2</sup>,  
П.А. Каракашкова<sup>1</sup>, С.К. Раковски<sup>1</sup>

<sup>1</sup> *Институт по катализ, Българска академия на науките, София 1113, България*

<sup>2</sup> *Институт по неорганична химия, Технически университет в Рига, Рига, Латвия*

Постъпила на 10 ноември, 2016 г.; приета на 21 февруари, 2017 г.

(Резюме)

Катализатори на основата на паладий и злато модифициран TiO<sub>2</sub> (Degussa P25) бяха изследвани за каталитичната им активност при фоторазграждане на адипинова киселина в присъствието на кислород и озон, под действие на УВ светлина. Пробите бяха синтезирани чрез екстракционно-пиролитичен метод с 0.5% съдържание на активен метал и размер на частиците вариращи от 7 до 12 нм. За установяване на структурните и химични свойства са приложени методите XRD, TEM и BET. В присъствието на кислород и облъчване с UV-A светлината, скоростните константи на реакцията в присъствие на паладий и злато модифицирани TiO<sub>2</sub> материали бяха съответно 1.7 и 2.3 пъти по-високи от тези на чист TiO<sub>2</sub> при същите условия. Това се дължи на по-ефективното разделяне на зарядите (електрон-дупка), генерирани при облъчване. Освен това, ефективността на катализаторите в присъствието на озон е по-голяма, както при облъчване с UV-C така и с UV-A светлина за всички проби. Скоростните константи на реакциите проведени в присъствие на озон при облъчване с 254 нм светлина, са около 3 пъти по-високи, в сравнение с тези облъчени с 365 нанометра. Това се дължи на допълнителното генериране на HO• радикали под действие на озонения радикал O<sub>3</sub><sup>-</sup>, образуван върху зоната на проводимост на фотокатализатора TiO<sub>2</sub>, от една страна, и в резултат на фотолиза на озона при облъчване с UV-C светлина, от друга страна.