

Adsorption and Photocatalytic Degradation of Methylene Blue Dye Over Pd-CeO₂/TiO₂ and CuO-CeO₂/TiO₂ Catalysts

¹G.A. El-Shobaky, ²H.M.A. Hassan, ³K.S. Abdel Halim,
⁴S.A. El-Korashy and ²Shaimaa K. Mohamed

¹Department of Physical Chemistry, National Research Center, Dokki, Giza, Egypt

²Department of Chemistry, Faculty of Science, Suez Canal University, Suez, Egypt

³Central Metallurgical Research and Development Institute, Egypt

⁴Department of Chemistry, Faculty of Science, Suez Canal University, Ismaillia, Egypt

Abstract: Pd-CeO₂/TiO₂ catalysts, having different Pd content (0.5-3 wt %) and CuO-CeO₂/TiO₂ catalysts, having different CuO content (1-20 wt. %), were prepared by deposition- precipitation (DP) method followed by microwave irradiation for only two minutes. The catalysts were characterized by X-ray powder diffraction (XRD), N₂ adsorption-desorption, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) techniques. Adsorption and photocatalytic degradation of methylene blue (MB) dye under UV irradiation over the prepared catalysts were performed. The prepared catalysts have high specific surface areas and possessed mesoporous structures. The S_{BET} values of Pd-CeO₂/TiO₂ catalysts were decreased by increasing the Pd content. The S_{BET} values of CuO-CeO₂/TiO₂ catalysts were increased by increasing CuO loading up to 5 wt% then it decreased with further increase of CuO content. The adsorption of MB dye was greatly enhanced by doping with 3 wt. % Pd while the photocatalytic degradation of the dye decreased as the amount of Pd loadings increased. For CuO-CeO₂/TiO₂ system, adsorption of the dye was increased by increasing of CuO loadings in the range of 1 to 5 wt. % and the photocatalytic activity increased as the amount of CuO loadings increased from 1 to 10 wt. % then decreased with further CuO loading.

Key words: Microwave irradiation • Titania • Palladium • Copper • CuO-CeO₂/TiO₂ • Pd-CeO₂/TiO₂ • Methylene blue • Photocatalysis

INTRODUCTION

Wastewaters from various industries, factories and laboratories are serious problems to the environment. The discharged wastes containing dyes are toxic to microorganisms, aquatic life and human beings [1]. Advanced oxidation processes (AOPs) including heterogeneous photocatalysis, especially by TiO₂, have proved to be one of the most effective methods for water treatment [2]. Attempts to increase the TiO₂ efficiency have been made by doping and coating with transition metals [3-5], including noble metals [6,7], combining the effect of two semiconductors or covering the surface with dye microcrystallites to increase the optical absorption in the visible range [8]. The origin of the improved photo reactivity is clearly related to the efficiency of the doping centers in trapping charge carriers and interceding in the interfacial transfer. The

effect of doping on the activity depends on many factors, e.g. method of doping and type and concentration of dopant [9].

The present work is designated to investigate the adsorption and the photocatalytic degradation of MB dye over Pd-CeO₂/TiO₂, containing different Pd contents (Pd = 0.5, 1.5 and 3 wt %) and CuO-CeO₂/TiO₂, containing different CuO contents (CuO= 1, 3, 5, 10 and 20 wt %), nanocatalysts synthesized by deposition- precipitation method followed by microwave irradiation.

MATERIALS AND METHODS

Materials: Cerium nitrate hexahydrate Ce (NO₃)₃·6H₂O (99%), palladium (II) nitrate (99.9%), Copper nitrate (Cu (NO₃)₂·3H₂O) and NaOH were supplied by Sigma-Aldrich company. All chemicals are used without any further purification.

Catalysts Preparation: Both Pd-CeO₂/TiO₂ and CuO-CeO₂/TiO₂ catalysts contained 10 wt% CeO₂ with respect to TiO₂ support. The support was prepared by microwave assisted sol-gel method and was a mixture of rutile and anatase phases. A known amount of cerium and palladium or copper nitrates were added at room temperature to the suspension of TiO₂ support. 4M NaOH was added dropwise with continuous stirring until the pH of the resulting solution attained ~ 10. The resulting solution was then placed in a conventional microwave. The microwave power was set to 80% of 1000 W and operated in 30-s cycles (on for 10 s, off for 20 s) for 2 minutes. The resulting powder was carefully washed with distilled water and dried at 90°C.

Techniques: Phase identification and crystallite size of different phases present in the produced powders were performed at room temperature using X-ray diffraction (XRD, Bruker axis D8, Germany) with Cu-K α ($\lambda=1.5406 \text{ \AA}$) radiation and secondly monochromator in the range 2θ from 10° to 80°. Specific surface area (S_{BET}), total pore volume and pore size distribution of the samples were determined by BET surface area analyzer (Nova 2000 series, Quantachrome Instruments, UK). The (BJH) approach was used to calculate pore size distribution ($\Delta v/\Delta r$) of the samples. Prior to analysis, the samples were outgassed at 200°C and pressure of 10^{-5} Torr for 5 h. The size and morphology of the investigated catalysts were characterized using scanning electron microscope (SEM, JEOL-JSM-5410, Japan) and transmission electron microscopy (TEM), JEM-1230 (JOEL) operated at 120 kV. For the TEM imaging, the sample powder was dispersed in methanol by using ultrasonic radiation for 5 minutes and deposited onto the carbon-coated copper grids.

Photocatalytic Activity Measurements: The measurements were performed at room temperature as followed: 100 mg of the photocatalyst was added to a 250 ml beaker containing 100 ml of 4×10^{-5} mol/L MB solution. The solution was kept in dark under continuous stirring for 30 minutes in order to obtain adsorption equilibrium. A UV lamp (Handheld UV Lamp, LW/SW, 6W, UVGL-58, UVP, Inc.) positioned over the beaker was used as a light source to trigger the photocatalytic reaction. The MB solution was irradiated for 120 minutes using long wave UV (365 nm). 5 ml of the solution was withdrawn every 20 minutes and centrifuged. The concentration of MB solution was determined using an UV - visible spectrophotometer (A Shimadzu-1601PC UV-

Visible automatic recording spectrophotometer with 1 cm quartz cell was used for the absorbance and spectral measurements).

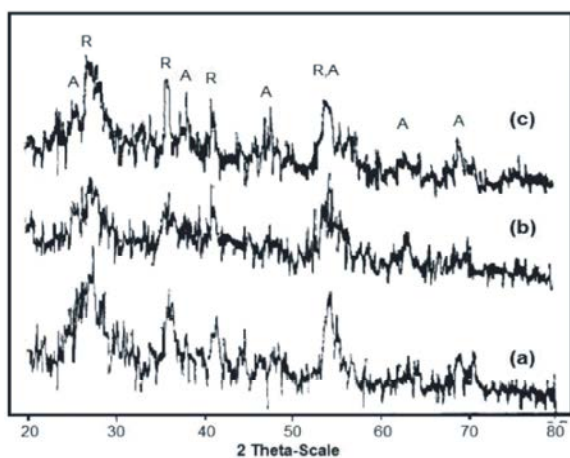
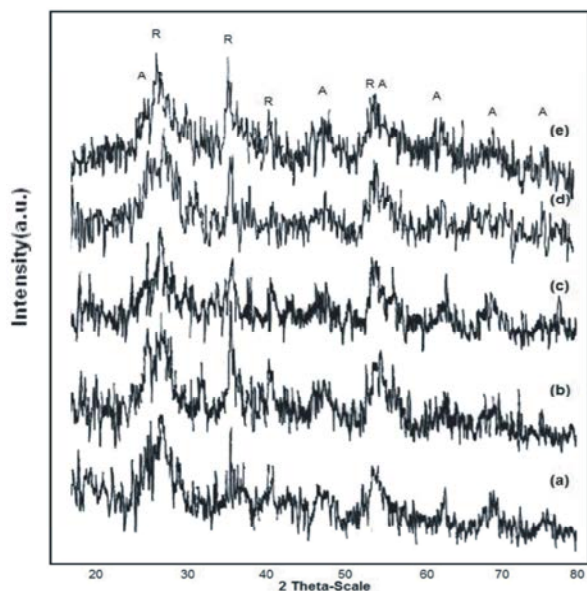
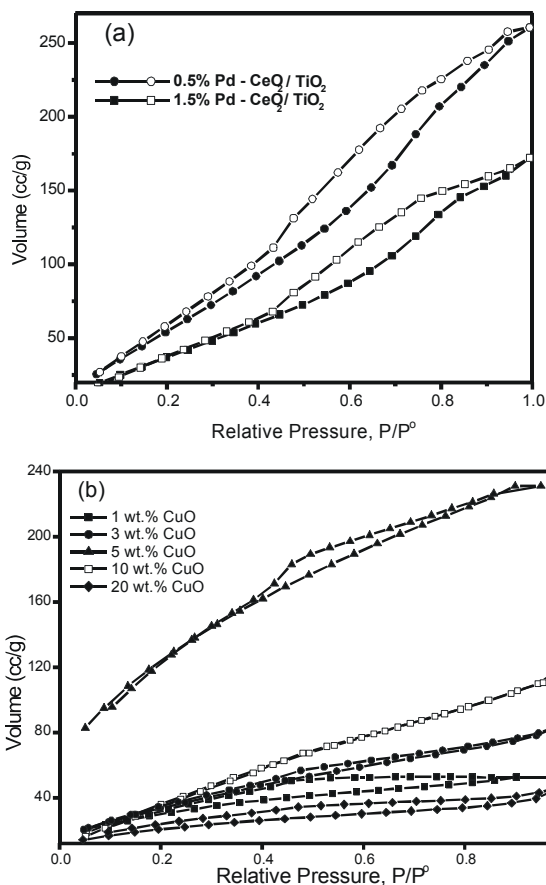
RESULTS AND DISCUSSION

Structural Characterization: Figure 1, depicts the X-ray diffractograms of Pd-CeO₂/TiO₂ solids with different Pd contents (0.5, 1.5 and 3 wt. %). The diffraction peaks of CeO₂ and PdO phases were not detected in the diffractograms of all Pd-CeO₂/TiO₂ solids. The absence of PdO phase might indicate that either PdO is present as a noncrystalline phase or the particle size is smaller than 3 nm and finely dispersed on the support. It is well known that ceria increases the dispersion of noble metals [10]. Thus, it is expected that during the co-precipitation of the mixed cerium and palladium salts, PdO is deposited in finely dispersed state. The diffraction peaks of CeO₂ and CuO phases were not detected in the X-ray diffractograms of all CuO-CeO₂/TiO₂ solids. The absence of the diffraction peaks of crystalline CuO could be discussed as follows: (i) highly dispersed copper species, (ii) small copper oxide clusters below the detection limit of X-ray diffractometer or (iii) existence of amorphous phase.

Surface and Textural Characterization: The N₂ adsorption-desorption isotherms of Pd-CeO₂/TiO₂ and CuO-CeO₂/TiO₂ catalysts are given in Figure 3. The obtained isotherms belong to type IV isotherms according to IUPAC classification and exhibited hysteresis loops of different shapes and areas. These hysteresis loops are characteristic of mesoporous solids. The catalysts showed type H2 loop according to IUPAC classification which indicate that the pore structure is complex and tend to be made up of interconnected networks of pores of different size and shape. The different surface characteristics of the investigated systems were computed and cited in Table 1. Examination of Table 1 showed the following: (i) Doping of Pd and ceria resulted in a progressive significant increase in the S_{BET} values. However, the increase was more pronounced in case of 0.5% Pd containing catalyst. This significant increase was followed by a progressive increase in the (V_p) values. (ii) The increase of Pd content within 0.5-3 wt. % brought about a progressive decrease in both S_{BET} and V_p values. (iii) The treatment of TiO₂ with both ceria and CuO resulted in a progressive increase in the S_{BET} and V_p values reaching a maximum limit at 5 wt. % CuO loading. However, the increase of CuO content above 5wt. %

Table 1: Surface characteristics of the prepared systems

Sample	S_{BET} (m^2/g)	V_p (cm^3/g)	Pore width (nm)
$\text{TiO}_2(\text{support})$	69	0.084	2.7
<i>Pd-CeO₂/TiO₂</i>			
0.5 wt.% Pd	279	0.402	3.2
1.5 wt.% Pd	177	0.266	2.9
3 wt.% Pd	159	0.117	2.6
<i>CuO-CeO₂/TiO₂</i>			
1wt.%CuO	111	0.082	1.8
3wt.%CuO	133	0.131	2.6
5wt.%CuO	466	0.357	2.6
10wt.%CuO	176	0.187	2.7
20wt.%CuO	75	0.073	1.7

Fig. 1: X-ray diffractograms observed for (a) 0.5, (b) 1.5 and (c) 3 wt. % Pd- $\text{CeO}_2/\text{TiO}_2$ solids. A: Anatase and R: RutileFig. 2: X-ray diffractograms observed for (a) 1, (b) 3, (c) 5, (d) 10 and (e) 20 wt. %CuO- $\text{CeO}_2/\text{TiO}_2$. A: Anatase and R: RutileFig. 3: Nitrogen adsorption-desorption isotherms of (a) Pd- $\text{CeO}_2/\text{TiO}_2$ catalysts with different Pd contents and (b) CuO- $\text{CeO}_2/\text{TiO}_2$ catalysts with different CuO contents

decreased the S_{BET} and V_p values. (iv) The pore width of the investigated samples is in the range of 1.7-3.2 nm which confirmed the nature of the prepared system as mesoporous solids.

SEM images of 0.5 and 3 wt. % Pd- $\text{CeO}_2/\text{TiO}_2$ and 3wt. % CuO - $\text{CeO}_2/\text{TiO}_2$ are given in Figure 4. The SEM images show aggregation of spherical particles having diameters ranging from 0.7 to 1.6 μm and small irregular voids distributed among the particles. In case of Pd- treated catalysts, the aggregation of nanoparticles is more pronounced in case of 3 wt. % Pd- $\text{CeO}_2/\text{TiO}_2$. As a result, this influenced on a lower total pore volume, which is in good accordance with the results acquired from N_2 adsorption measurements.

TEM images of 0.5 and 3 wt. % Pd - $\text{CeO}_2/\text{TiO}_2$ and 3wt. % CuO - $\text{CeO}_2/\text{TiO}_2$ are given in Figure 5. The TEM images show closely aggregated nanoparticles having diameters in the range of 4 - 8 nm. A disordered wormhole-

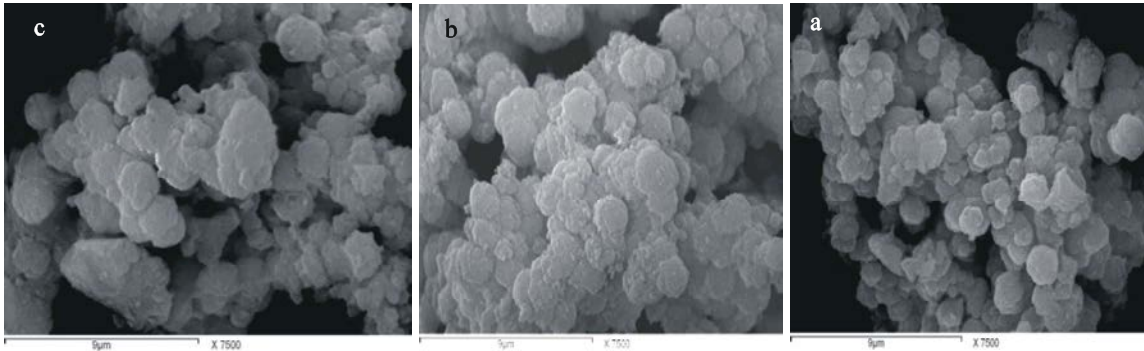


Fig. 4: SEM images of (a) 0.5, (b) 3 wt.% Pd-CeO₂/TiO₂ and (c) 3 wt.% CuO-CeO₂/TiO₂

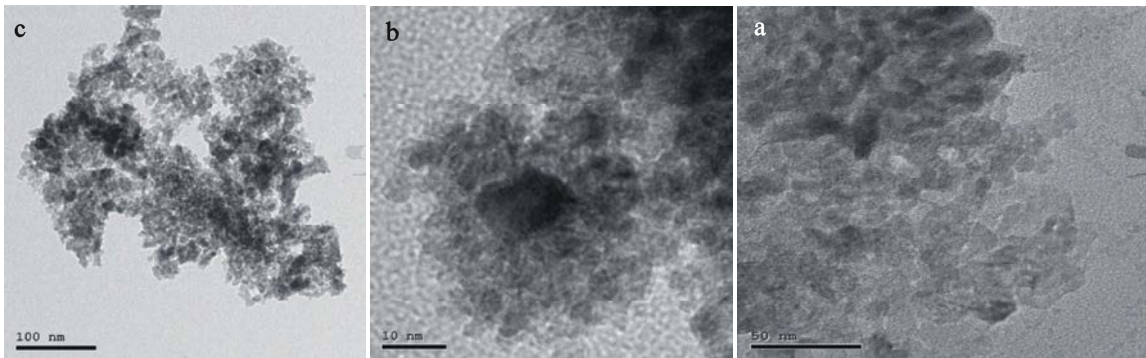


Fig. 5: TEM images of (a) 0.5, (b) 3 wt.% Pd-CeO₂/TiO₂ and (c) 3 wt.% CuO-CeO₂/TiO₂

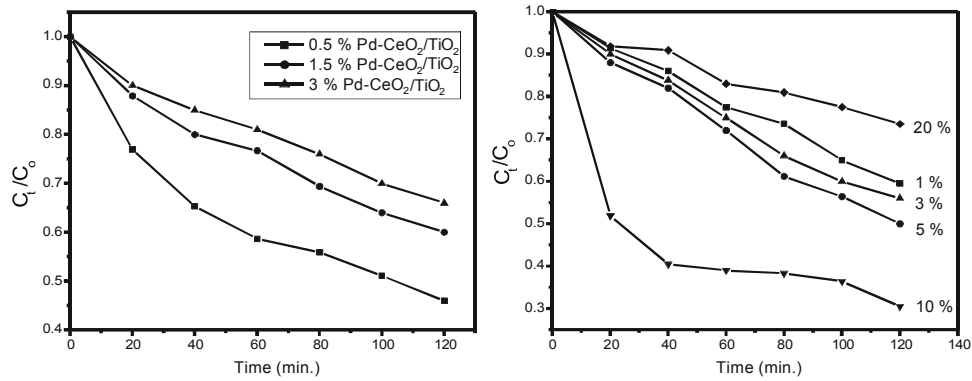


Fig. 6: Adsorption and photocatalytic performance of Pd-CeO₂/TiO₂ and CuO-CeO₂/TiO₂ systems

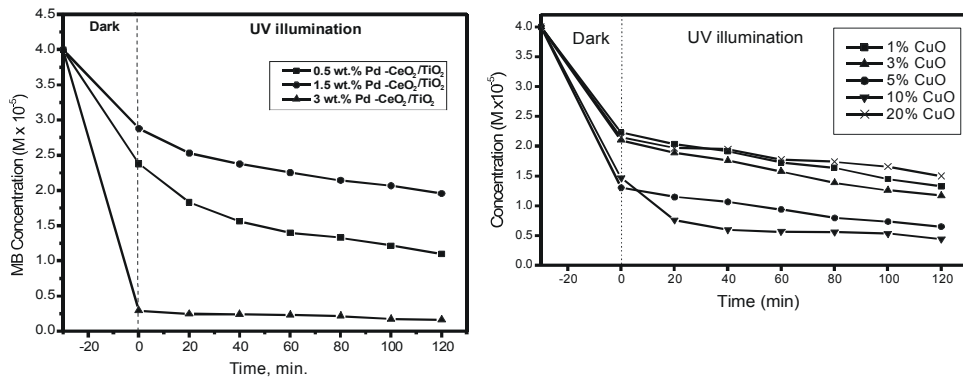


Fig. 7: Photocatalytic activity of Pd-CeO₂/TiO₂ and CuO-CeO₂/TiO₂ systems for the degradation of MB dye

like pore structures can be observed in all the prepared powders which are formed by the agglomeration of nanoparticles. The accessible pores are connected randomly, lacking discernible long-range order in the pore arrangement among the small particles. These observations may indicate that the mesoporosity is mainly due to the interparticle porosity rather than intraparticle porosity which is in a good agreement with the results obtained from N_2 adsorption-desorption isotherms.

Adsorption and Photocatalytic Degradation of MB Dye:

Before UV illumination of the MB solution, the solution was kept with the catalysts in dark in order to achieve adsorption/desorption equilibrium and to study the adsorption of MB on the prepared catalysts. Adsorption of MB dye in dark and photocatalytic degradation of MB dye under UVA illumination of the prepared catalysts as a function of time are shown in Figure 6. From this Figure, it can be seen that the adsorption of MB dye was greatly enhanced by doping with 3 wt. % Pd. However, no relation between the amount of Pd loadings and the specific surface area of the photocatalysts with the amount adsorbed of dye could be found. For CuO-CeO₂/TiO₂ system, it can be seen that the adsorption capacity towards MB dye was greatly enhanced by doping with 5 wt. % CuO. The adsorption of the dye was increased by increasing of CuO loadings in the range of 1 to 5 wt. %. However, increasing the loadings above this limit decreased the adsorption of MB dye. In this particular system, the adsorption of the dye seems to be correlated well with the measured specific surface areas of the catalysts which also increased in the range of 1 to 5 wt. % and decrease upon further loadings. The photocatalytic activity of the prepared systems for the degradation of MB dye under UVA illumination is shown in Fig. 7. From this Figure, it can be seen that the photocatalytic activity decreases within the Pd-CeO₂/TiO₂ system as the amount of Pd loadings increase from 0.5 to 3 wt.%. For CuO-CeO₂/TiO₂ system, it can be seen that the photocatalytic activity increases as the amount of CuO loadings increase from 1 to 10 wt. %. However, the photocatalytic activity decreases drastically upon further loadings.

CONCLUSIONS

The following are the main conclusions that may be withdrawn from the present work:

- Pd-CeO₂/TiO₂ catalysts, having different Pd content (0.5-3 wt. %) and CuO-CeO₂/TiO₂ catalysts, having different CuO content (1-20 wt. %), were prepared by deposition-precipitation method followed by microwave irradiation for only two minutes.
- The presence of smallest amount of Pd (0.5 wt.%) led to a considerable increase of its S_{BET} and V_p values which were found to decrease by increasing the Pd content above this limit.
- The specific surface area of CuO-CeO₂/TiO₂ catalysts was increased by increasing CuO loading up to 5 wt% then it decreased with further increase of CuO content.
- SEM images show aggregation of spherical particles having different diameters where the TEM results confirmed the nano-sized nature of the prepared solids.
- The adsorption of MB dye was greatly enhanced by doping with 3 wt. % Pd while the photocatalytic degradation of the dye decreased as the amount of Pd loadings increased.
- For CuO-CeO₂/TiO₂ system, adsorption of the dye was increased by increasing of CuO loadings in the range of 1 to 5 wt.% and the photocatalytic activity increased as the amount of CuO loadings increased from 1 to 10 wt.%.

REFERENCES

1. Akpan, U. and B. Hameed, 2009. Parameters affecting the photocatalytic degradation of dyes using TiO₂-based photocatalysts: A Review J. Hazard. Mater, 170: 520-529.
2. Mozia, S., M. Toyoda, M. Inagaki, B. Tryba and A. Morawski, 2007. Application of carbon-coated TiO₂ for decomposition of Methylene blue in a photocatalytic membrane reactor J. Hazard. Mater, 140: 369-375.
3. Xia, X.H., Y. Gao, Z. Wang and Z.J. Jia, 2008. J. Phys. Structure and photocatalytic properties of copper-doped rutile TiO₂ prepared by a low-temperature process Chem. Sol., 69: 2888-2893.
4. Xin, B., P. Wang, D. Ding, J. Liu, Z. Ren and H. Fu, 2008. Effect of surface species on Cu-TiO₂ photocatalytic activity Appl. Surf. Sci., 254: 2569-2574.
5. Xu, Y., D. Liang, M. Liu and D. Liu, 2008. Preparation and characterization of Cu₂O-TiO₂: Efficient photocatalytic degradation of methylene blue Mater. Res. Bull., 43: 3474-3482.

6. An, T., J. Liu, G. Li, S. Zhang, H. Zhao, X. Zeng, G. Sheng and J. Fu, 2008. Synthesis and photoactivity of Pd substituted nano-TiO₂ Appl. Catal. A, 350: 237-243.
7. Arbuj, S.S., R.R. Hawaldar, U.P. Mulik, B.N. Wani, D.P. Amalnerkar and S.B. Waghmode, 2010. Enhancement of photocatalytic activity by metal deposition: characterization and photonic efficiency of Pt, Au and Pd deposited on TiO₂ catalyst Mater. Sci. Eng. B, 168: 90-94.
8. Iliev, V., D. Tomova, R. Todorovska, D. Oliver, L. Petrov, D. Todorovsky, M. Uzunova-Bujnova, 2006. Photocatalytic properties of TiO₂ modified with gold nanoparticles in the degradation of oxalic acid in aqueous solution Appl. Catal. A, 313: 115-121.
9. Colón, G., M. Maicu, M.C. Hidalgo and J.A. Navío, 2006. Cu-doped TiO₂ systems with improved photocatalytic activity Appl. Catal. B, 67: 41-51.
10. Zhu, H.Q., Z.F. Qin, W.J. Shan, W.J. Shen and J.G. Wang, 2004. Pd/CeO₂-TiO₂ catalyst for CO oxidation at low temperature: a TPR study with H₂ and CO as reducing agents. J. Catal., 225: 267-277.