Comparison of photocatalytic behaviour under UV-light of PdO-CeO$_2$/Al$_2$O$_3$ and PdO-CeO$_2$/ZSM5 for degradation of organic dyes

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Dedicated to Acad. Ivan Juchnovski on the occasion of his 80th birthday

PdO-CeO$_2$/Al$_2$O$_3$ and PdO-CeO$_2$/ZSM5 powder samples were prepared by impregnation and applied for photodegradation of aqueous solution of Malachite Green (MG) and Methyl Orange (MO) dyes under UV light. Physicochemical characterization of the samples was done by the following methods – AAA, BET, XRD, SEM and XPS. The palladium and cerium content in both investigated photocatalysts is found to be around 4.3 and 3 wt. %, the specific surface area for PdO-CeO$_2$/Al$_2$O$_3$ is 133 m^2/g while this one for PdO-CeO$_2$/ZSM5 samples is 188 m^2/g. The apparent rate constants of investigated dyes were in the following order: MO, PdO-CeO/Al$_2$O$_3$ (21.0 x10^{-3}min^{-1}) > MG, PdO-CeO/Al$_2$O$_3$ (13.9 x10^{-3}min^{-1}) > MO, PdO-CeO/ZSM5 (6.6 x10^{-3}min^{-1}) > MG, PdO-CeO/ZSM5 (5.8 x10^{-3}min^{-1}).

Key words: CeO$_2$, PdO, photocatalysis, dyes, waste waters.

INTRODUCTION

In textile industries, dyes are heavily used for coloring. Dye effluents discharged into waters may cause detremental effects of the environment and as consequence to the human health. Most desired way to reduce polution of waters is using clean technology such as photocatalytic treatment [1]. Heterogeneous photocatalysis has been considered as an inexpensive and efficient [2] way for the degradation of toxic organic compounds [3]. Recently there is an increase in the interest to semiconductor oxide photocatalysts due to their ability to convert photon energy into chemical energy [4].

It is urgent to create new catalysts, developing synergistic effect between the carrier and supported semiconductor oxides. It is aiming improvement of photocatalytic performance through optimization of processes of charge carrier transfer on semiconductor surfaces [5].

Mesoporous γ-Al$_2$O$_3$ support is reported as an electron acceptor with high surface area and ultraviolet-light-response ability [6]. Great attention of researchers have attracted to the supported noble metal catalysts, which may increase catalytic activity by suppressing the recombination of photoinduced carriers [7, 8].

Cerium together with its oxide is the most intriguing rare earth element and can be photo excited by absorbing photo energy [9]. Band gap of CeO$_2$ is 3.2 eV. The combinations with other oxides will lower the band gap and increase its reactivity [2]. The use of rare earth oxides has been described as a good opportunity for stabilization of the support and the active phase on it. In that respect, CeO$_2$ is an excellent choice to stabilize PdO [10].

PdO/CeO$_2$-Al$_2$O$_3$ and Pd/CeO$_2$/Al$_2$O$_3$ catalysts were tested for methane combustion and Water-Gas-Shift Reaction [7, 11]. Yuliati et al. found that cerium oxide supported on SiO$_2$ or Al$_2$O$_3$, promote photocatalytic non-oxidative direct methane coupling [9]. Photocatalysts containing Al$_2$O$_3$ modified with rare earth and noble metal oxides have been studed for degradation of pesticides [12].

Cr/ZSM-5 and CeO$_2$/MCM-48 were investigated for the photocatalytic oxidation of propane and Acid Orange 7 accordingly [13, 14].

Photodegradation of oxalic acids and bisphenol A on Fe$_3$O$_4$/SiO$_2$/CeO$_2$ and Al$_2$O$_3$ – Fe$_3$O$_4$ catalysts have been investigated in [15, 16].

In the present work we compare the catalytic behaviour of mixed PdO-CeO$_2$ oxides supported on Al$_2$O$_3$ and ZSM5 carriers. The process of photo-degradation under UV-light in aqueous solutions of two different dyes (Malachite Green and Methyl Orange) were also investigated and discussed.

EXPERIMENTAL

Sample preparation procedure

Carrier materials of both catalysts – H-ZSM-5 and γ-Al₂O₃ (Rhône Poulenc) were dried overnight at 120 °C, dispersed in water and impregnated for 16 h in prepared aqueous solution containing 5% Ce(IV) obtained from source $(NH_4)_2Ce(NO_3)_6$ and 1% Pd(II) obtained from source $Pd(NH_3)_2Cl_2$. The mixture was left until decolorization occurred. Then the zeolite and silica were filtrated, dried and calcined at 600 °C for 6 h [17].

Sample characterization

The X-ray diffraction (XRD) analysis was carried out on a Bruker-AXS, D8 Advance using CuKα radiation within a 2θ angle of diffraction interval of 10 ÷ 80 degrees.

PYE UNICAM SP 1950 spectrometer was used for determination of palladium content, after extraction with HCl by AAA method. Titrimetrical method was applied for determination of cerium loading.

The specific surface area was established by the BET method using low temperature (77 K) nitrogen adsorption. JSM – 5510 JEOL scanning electron microscope was used for SEM investigations.

XPS investigations were carried out by means of a VG ESCALAB Mk II spectrometer using an Al Kα excitation source (1486.6 eV) with a total instrumental resolution of ~1 eV, under base pressure of 1×10^{-8} Pa. The C1s, O1s, Pd 3d, Ce3d, Al2p and Si2p photoelectron lines were recorded. The charging effects were corrected by using the C1s peak as reference at 285eV. The atomic concentrations of the constituent elements have been calculated using a peak area and Scofild's photoinization cross-sections.

The photocatalytic activity of PdO-CeO₂/Al₂O₃ and PdO-CeO₂/ZSM5 for the oxidative degradation of 5 ppm aqueous solution of Malachite Green or Methyl Orange dyes was evaluated. The 0.15g photocatalyst samples in 150 ml of dye solution were investigated in a semi-batch reactor under constant stirring, at room temperature. In order to obtain adsorption-desorption characteristics 30 minutes tests were carried out in the dark first, followed by 120 minutes period of UV illumination (power 18 W, $\lambda_{max} = 365$ nm). The separation of the powder from the suspension was carried out by centrifugation before the UV–Vis spectrophotometrical measurements (UV-1600PC

Spectrophotometer). The degree of dye degradation was calculated using the formula:

$$Degradation = \frac{(C_0 - C)}{C_0}100\%$$

where Co and C were initial concentration before turning on the illumination and residual concentration of the dye solution after illumination for selected time interval. The adsorption capacities of samples after 30 minutes dark period were determined by the equation:

$$Q = \frac{(C_0 - C)V}{m}$$

where C_0 and C are the initial and after half an hour in the dark concentrations of the dye, V is the volume of the solution and m is the weight of the photocatalyst.

RESULTS AND DISCUSSION

The palladium and cerium contents in both investigated samples were evaluated as about 4.3 wt. % and 3.0 wt. %, respectively. The specific surface area of PdO-CeO₂/Al₂O₃ sample is lower (133 m²/g) than this of PdO-CeO₂/ZSM5 sample (188 m²/g) [17]. The obtained XRD patterns of PdO-CeO₂/ZSM5 and PdO-CeO₂/Al₂O₃ photocatalysts are shown in Figure 1a and 1b respectively. In this Figure 1 it is seen that palladium exist mainly as PdO (PDF-75-584) and cerium as CeO₂ (PDF-34-0394). Simultaneously on the diffractograms are present some low temperature form of alumina: γ-Al₂O₃ (PDF-50-0741) and MFI structure [17].
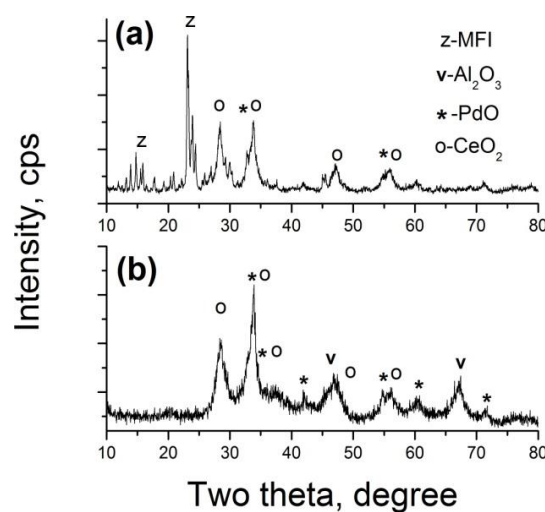

Fig. 1. XRD patterns of: (a) PdO-CeO₂/ZSM5, (b) PdO-CeO₂/Al₂O₃.

The morphology of both catalyst samples was studied by SEM. Figures 2 and 3 represent SEM images of PdO-CeO$_2$/ZSM5 and PdO-CeO$_2$/Al$_2$O$_3$ samples at magnification x 5,000 μm. The SEM image of PdO-CeO$_2$/ZSM5 shows porous structure. In the picture are visible round particles of irregular shape with different sizes around (0.3÷1.5 μm), some of them united in aggregates bigger than 5μm. The SEM image of PdO-CeO$_2$/Al$_2$O$_3$ shows big aggregates with cracks on them. Some particles and flakes in the range of 0.1÷2.5μm were alighted on the aggregates. From the SEM pictures of the both samples we can conclude that the sintering processes flow more intense in PdO-CeO$_2$/Al$_2$O$_3$ sample comparing with PdO-CeO$_2$/ZSM5 one.
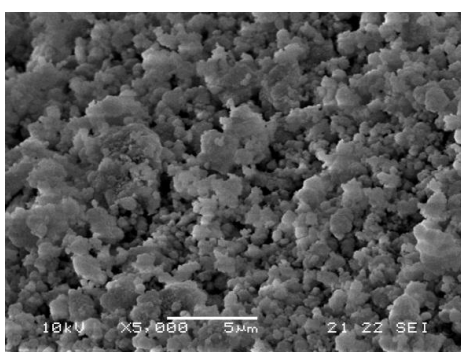

Fig. 2. SEM picture of PdO-CeO$_2$/ZSM5 sample.
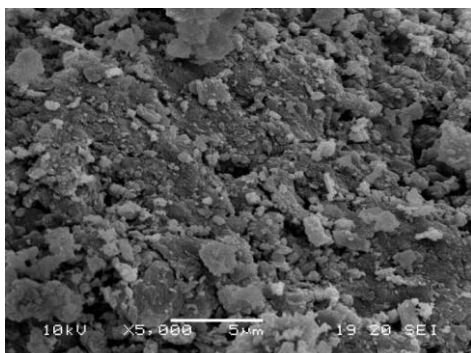

Fig. 3. SEM picture of PdO-CeO$_2$/Al$_2$O$_3$ sample.

The surface composition and the oxidation states of the constituent element in the studied photocatalysts were proved by XPS.

The concentrations of the elements on the surface of the both catalysts are shown in Table 1.

The O1s, Ce3d and Pd3d photoelectron spectra of PdO-CeO$_2$/Al$_2$O$_3$ and PdO-CeO$_2$/ZSM5 are presented in Fig. 4. In the O1s photoelectron spectrum of PdO-CeO$_2$/ZSM5 photocatalyst is distinguished, low binding energy wide shoulder with a maximum at around 529.4 eV, a main peak at 532.5 eV and additionally to the main and low binding energy peaks a peak at ~534 eV is observed.

Table 1. Concentrations of the elements (at.%) on the surface of the photocatalysts.

Sample	C	O	Ce	Si	Al	Pd
PdO-CeO/ZSM5	13.30	56.57	2.27	20.59	1.61	5.65
PdO-CeO/Al$_2$O$_3$	20.67	46.88	0.92	-	29.40	2.13

The first two mentioned peaks are associated to CeO$_2$ and SiO$_2$, respectivelly [18,19,20]. The higher binding energy peak is due to the absorbed water species on the catalyst surface. In region of O1s photoelectron line for the second studied catalyst PdO-CeO$_2$/Al$_2$O$_3$, we detect (only) one peak having binding energy around 531.4 eV, typical for the Al$_2$O$_3$. The Pd3d photoelectron spectra are characteristic of presence of PdO on the catalysts surfaces. The visible differences are observed for the recorded Ce3d spectra. It is well known that the Ce3d region has well separated spin-orbit components (Δ=18.6 eV). After deconvolution of the Ce3d complex structure ten peaks are distinguishable that are referenced to the 3d$_{3/2}$ and 3d$_{5/2}$ spin orbital splitting and are signed according the Burroughs et al. [21] to the existence of both Ce^{3+} and Ce^{4+} states. The amount of Ce(IV) in the studied catalysts samples could be evaluated as a percentage of the area of the u^{III} peak at 916.8 eV to the total Ce3d area. Thus, the percentage of the u^{III} peak with respect to the total Ce3d peak area varies from 0 to 14%, when the Ce(IV) percentage to total amount of Ce varies from 0 to 100%. The calculated area ratio are 11.57% for PdO-CeO$_2$/ZSM5 and 5.53% for PdO-CeO$_2$/Al$_2$O$_3$, respectively.
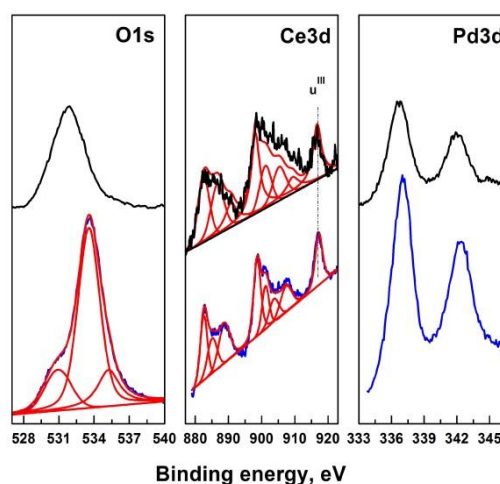

Fig. 4. O1s, Ce3d and Pd3d spectra of PdO-CeO$_2$/ZSM5 (blue line) and PdO-CeO$_2$/Al$_2$O$_3$ (black line) samples.

The photocatalytic performances of PdO-CeO₂/Al₂O₃ and PdO-CeO₂/ZSM5 samples tested for degradation of two dyes-Malachite Green and Methyl Orange is presented in Fig. 5. The degree of dye degradation of investigated dyes on the two studied photocatalytic systems decrease in the following order: MO, PdO-CeO/Al₂O₃ (97%) > MG, PdO-CeO/Al₂O₃ (90%) > MO, PdO-CeO/ZSM5 (73%) > MG, PdO-CeO/ZSM5 (68%).
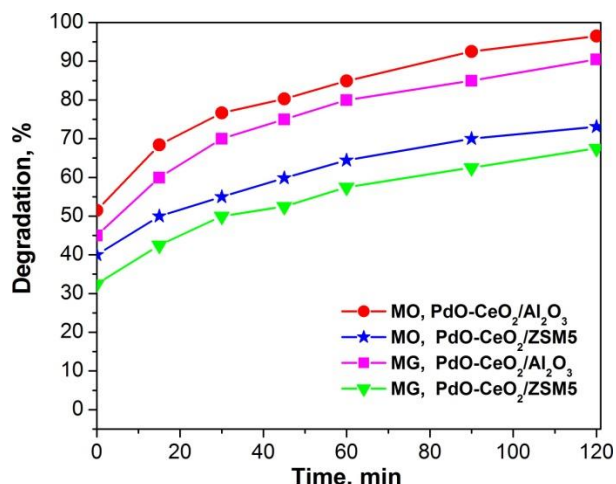

Fig. 5. Photocatalytic degradation of MO (λ_{max} = 464 nm) and MG (λ_{max} = 615 nm) dyes on investigated catalysts.

In Table 2 are presented the adsorption capacities and apparent rate constants of investigated photocatalytic systems. It is obvious the existed correlation between the adsorption capacities, degree of degradation and apparent rate constants for investigated dye solutions on PdO-CeO₂/Al₂O₃ and PdO-CeO₂/ZSM5 photocatalysts.

Table 2. Calculated adsorption capacities and apparent rate constants of investigated photocatalytic systems.

Sample	Adsorption capacity, mg/g	k (10^{-3} min^{-1})
MG, PdO-CeO/ZSM5	0.065	5.8
MO, PdO-CeO/ZSM5	0.080	6.6
MG, PdO-CeO/Al₂O₃	0.090	13.9
MO, PdO-CeO/Al₂O₃	0.103	21.0

The apparent rate constants (pseudo first order kinetics) have been calculated using logarithmic linear dependence of the concentrations ratio on the time:

$$-\ln\left(\frac{C}{C_0}\right) = k.t$$

and the results are shown on Fig. 6. PdO-CeO₂/Al₂O₃ sample exhibits better photocatalytic

properties in comparison with PdO-CeO₂/ZSM5 one. Existing synergism between supported active phases PdO, CeO₂ and the carrier Al₂O₃ is a possible explanation of registered higher photocatalytic activity. The role of γ-Al₂O₃ support is important, because of its unique surface properties - Brønsted and Lewis acid and base sites [22] which can promote photocatalytic activity of supported materials [23, 24].

The presence of particles of PdO as the photoelectron trapping centers reduces the e-/h+ pair recombination rate and increases the lifetime of charge carrier [25, 26]. In article [27] was described mechanism of photodegradation of MO on CeO₂ under UV light irradiation. It was discovered that low-coordinate surface cerium cations played important role in the photocatalytic reaction.

From the XPS results we can conclude that the more Ce³⁺ states exist on the surface of PdO-CeO₂/Al₂O₃ catalysts which explains its higher photocatalytic activity. We can suppose that during photocatalytic reaction, electrons in the valence band of Ce₂O₃ are excited. At the same time, the transfer of electrons from CeO₂ to Ce₂O₃ occurs, also. Then the electrons react with the adsorbed oxygen molecules to form superoxide radicals, which are responsible for the degradation/oxidation of organic pollutants [28].
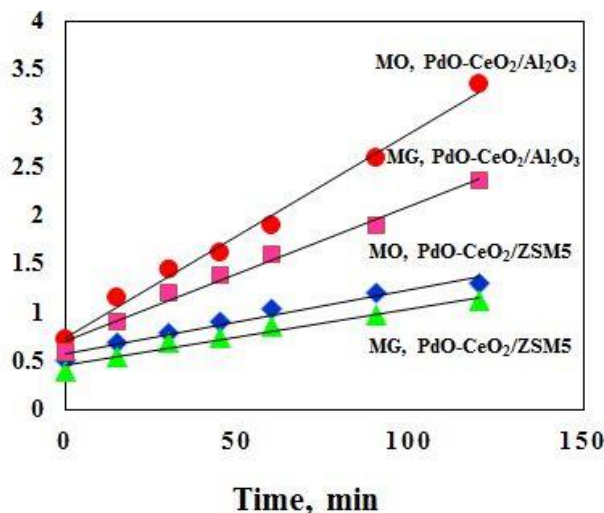

Fig.6. Dependence of $-\ln\left(\dfrac{C}{C_0}\right)$ versus illumination time on investigated photocatalysts.

CONCLUSION

Impregnation method was used for synthesis of PdO-CeO₂/Al₂O₃ and PdO-CeO₂/ZSM5 powders. Photocatalytic behaviour of the catalysts was

compared for degradation of two organic dyes under UV-light. As model pollutants were used textile dyes: Malachite Green and Methyl Orange.

The XRD and XPS confirmed existence of PdO and CeO_2. It was established correlation between the adsorption capacities, degree of degradation and apparent rate constants of investigated dyes on PdO-CeO₂/Al₂O₃ and PdO-CeO₂/ZSM5 samples. The higher photocatalytic activity was shown by PdO-CeO₂/Al₂O₃ sample in comparison with PdO-CeO₂/ZSM5. The possible reasons were synergism between mixed oxides PdO-CeO₂ and the support Al₂O₃ and existence of higher amount of Ce^{3+} states on the surface of PdO-CeO₂/Al₂O₃ catalysts.

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СРАВНЕНИЕ НА ФОТОКАТАЛИТИЧНОТО ПОВЕДЕНИЕТО ПОД УВ-СВЕТЛИНА НА PdO-CeO$_2$/Al$_2$O$_3$ И PdO-CeO$_2$/ZSM5 ЗА РАЗГРАЖДАНЕ НА ОРГАНИЧНИ БАГРИЛА

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(Резюме)

Прахообразни образци от PdO-CeO$_2$/Al$_2$O$_3$ и PdO-CeO$_2$/ZSM5 бяха приготвени чрез метода на импрегниране и приложени за фоторазлагането на водни разтвори на багрила от Малахитово Зелено и Метил Оранж под УВ светлина. За физикохимичното охарактеризиране на пробите бяха използвани следните методи - ААА, BET, XRD, SEM и XPS. Установено е, че съдържанието на паладий и церий в двата изследвани фотокатализатора е около 4.3 и 3 тегл. %, специфичната повърхност за PdO-CeO$_2$/Al$_2$O$_3$ е 133 m^2/g докато тази при образец PdO-CeO$_2$/ZSM5 е 188 m^2/g. Скоростните константи на изследваните багрила са в следния ред: MO, PdO-CeO/Al$_2$O$_3$ (21.0 x10^{-3}min^{-1}) > MG, PdO-CeO/Al$_2$O$_3$ (13.9 x10^{-3}min^{-1}) > MO, PdO-CeO/ZSM5 (6.6 x10^{-3}min^{-1}) > MG, PdO-CeO/ZSM5 (5.8 x10^{-3}min^{-1}).