

CoO/Al₂O₃, CuO/Al₂O₃ AND NiO/Al₂O₃ CATALYSTS FOR PHOTODEGRADATION OF MALACHITE GREEN DYE UNDER UV-IRRADIATION

CoO/Al₂O₃, CuO/Al₂O₃ И NiO/Al₂O₃ КАТАЛИЗАТОРИ ЗА ФОТОРАЗГРАЖДАНЕ НА МАЛАХИТОВО ЗЕЛЕНО БАГРИЛО ПОД УВ ОБЛЪЧВАНЕ

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Abstract: CoO, CuO or NiO supported on Al₂O₃ photocatalysts were prepared by impregnation and then calcination at 400°C for 3 hours. The obtained samples were physico-chemically studied by Powder X-ray diffraction analysis, X-ray photoelectron spectroscopy and Scanning electron microscopy. The photocatalytic oxidative degradation of aqueous solution of Malachite Green (MG) dye as pollutant using CoO, CuO or NiO supported on Al₂O₃ under UV irradiation was tested. The results determined that the highest degree of degradation of MG dye after 120 minutes was achieved using NiO/Al₂O₃ photocatalyst (82%) than that the other materials CuO/Al₂O₃ (64%), CoO/Al₂O₃ (59%) and Al₂O₃ (50%). The calculated apparent rate constants increasing in the order: Al₂O₃ ($2.7 \times 10^{-3} \text{ min}^{-1}$) < CoO/Al₂O₃ ($3.9 \times 10^{-3} \text{ min}^{-1}$) < CuO/Al₂O₃ ($4.1 \times 10^{-3} \text{ min}^{-1}$) < NiO/Al₂O₃ ($8.4 \times 10^{-3} \text{ min}^{-1}$).

Keywords: NiO, CuO, CoO, Al₂O₃, MALACHITE GREEN, PHOTOCATALYST, DEGRADATION

1. Introduction

Latest industrial development has ameliorated living standards but due to insufficient environmental monitoring, the continuous discharge of many industrial pollutants (organic compounds derived from synthetic dyes and etc.) is causing major environmental problems. Since these pollutants are carcinogenic at trace levels for aquatic and non-aquatic organisms, a wide range of remediation techniques as: biological, physical, and chemical methods have been applied for water decontamination [1-4]. Photocatalysis is widely used to describe the process based on a series of light-induced redox reactions occurring when a semiconductor (e.g. TiO₂, ZnO, SnO₂, WO₃), interacts with light in order to generate reactive species. This can lead to the photodegradation of the dye pollutants [2]. The challenge for the recent researchers is to create new and effective photocatalysts, applying appropriate synthesis methods by modifying the structure or properties of supports (to achieve more active sites, which may promote the reaction with the reactants) and introduce other elements homogeneously distributed on the support [5]. Non-reactive solid supports such as alumina may significantly control the photochemical reactivity of adsorbed molecules due to electronic interaction between the molecules and the surfaces [6]. The excellent dispersing ability of the alumina surface is much more pronounced in the supported photocatalysts [7]. Al₂O₃ was used as a catalyst for the photomineralization of hazardous organic molecules [2, 8]. Introduction of some transition metals, such as Cr, V, Fe, Cu, Mn, Co, Ni, Mo etc. may lead to higher catalytic activity [4]. Karunakaran et al. (ref. [6]) concluded that the presence of a semiconductor like (TiO₂, ZnO, CuO and other) with Al₂O₃ (insulator) lead to synergism between them, which improved their photocatalytic performance. The iron oxide supported on alumina was studied in photo-assisted Fenton degradation of different textile dyes [5]. 2-phenyl-4-(1-naphthyl) quinolinium supported on silica-alumina photocatalyst was examined for H₂O₂ production [9]. The impact of surface of Al₂O₃/TiO₂ [10] and Al₂O₃-Fe₂O₃ catalysts [11] on the photodegradation of organic pollutants was discussed in details. Cobalt oxide as photocatalyst was applied for reaction of photocatalytic water-splitting [12]. Cobalt oxide supported on carbon was used for degradation reaction of Methyl Orange [13]. Properties of CuO-CoO/Al₂O₃ catalysts were investigated for NO reduction by CO [14]. CuO was used as semiconductor photocatalysts for the degradation of dyes [15]. Films of CuO [16] and nickel oxide powders [17] were evaluated as photocatalysts for degradation of Rhodamine B dye. Photocatalytic activity of pure

CuO for H₂ evolution reaction was discussed in [18]. Many researchers had anticipated the reaction of CuO on different adsorbents like activated alumina in wastewater treatments [15]. Series of NiO photocatalysts have been investigated in the degradation of Methylene Blue [19].

The present paper deals with synthesis of CoO/Al₂O₃, CuO/Al₂O₃ and NiO/Al₂O₃ powders, prepared by impregnation of previously prepared alumina containing support. They were physicochemically characterized and tested in the photodegradation of Malachite Green dye under UV-irradiation.

2. Experimental

2.1. Synthesis of the samples

The Al₂O₃ powder was prepared after precipitating aluminium hydroxide. Then it was mixed with bentonite in respect to obtain composite Al₂O₃: bentonite (90:10) and compressed in tablets. The powder was calcined at 800°C for 8h to obtain γ-Al₂O₃ (the composite material was synthesized at University of Chemical Technology and Metallurgy, Sofia, with assistance of Assoc. Prof. Nikoleta Kassabova). In order to obtain photocatalytic systems, with active phase NiO, CuO or CoO were used the corresponding water solutions of: Ni(NO₃)₂·6H₂O, Cu(NO₃)₂·3H₂O and Co(NO₃)₂·6H₂O calculated to give 10 wt % content with respect to Ni, Cu or Co amount. The carrier was impregnated with the aqueous nitrate solutions under heating and constant electromagnetic stirring. Then the samples were dried at 100 °C and after that calcined at temperature 400 °C for 3 hours. The prepared photocatalysts was named as: Al₂O₃ as P1; CoO/Al₂O₃ as P2; CuO/Al₂O₃ as P3; NiO/Al₂O₃ as P4.

2.2. Powder X-ray diffraction analysis (PXRD)

The powder X-ray diffraction patterns were recorded on a Bruker D2 Phaser diffractometer within the range of 2θ values between 5° and 75° using Cu Kα radiation (λ = 0.154056 nm) at 40 kV. The phases were determined by using of JCPDS database (Powder Diffraction Files, Joint Committee on Powder Diffraction Standards, Philadelphia PA, USA, 1997).

2.3. Scanning electron microscopy (SEM)

SEM studies were performed on a JSM – 5510 JEOL scanning electron microscope. For morphology observations of the samples the accelerating voltage 10 kV was used.

2.4. X-ray Photoelectron spectroscopy (XPS)

The XPS analyses were performed on a Kratos AXIS Supra with a monochromatic Al X-ray source. Each analysis started with a survey scan from 0 to 1200 eV pass energy of 160 eV at steps of 1 eV with 1 sweep. For the high resolution analysis the number of sweeps was increased, the pass energy was lowered to 20 eV at steps of 100 meV. The X-ray Photoelectron spectroscopy method was used for the investigation of the surface states of Cu;Co;Ni loaded photocatalysts over precursor Al_2O_3 :bentonite. The C1s, O1s, Al2p, Si2p, Co2p, Cu2p as well as Ni2p photoelectron lines were recorded and the obtained spectra were discussed. The surface concentrations of the constituent elements in the investigated catalysts have been calculated, too.

2.5. Photocatalytic investigations

Synthesized samples were investigated for period of 2 hours in the oxidative degradation of Malachite Green (MG) dye in a semi-batch photocatalytic reactor. UV light irradiation was used with power 18 W and maximal emission at 365 nm. In the beginning of the process the concentration of MG dye solutions was 5 ppm ($\lambda_{\text{max}} = 615 \text{ nm}$) accordingly, with catalyst loading 1g/l. Before switching on the UV illumination investigated systems were equilibrated in the dark for about 30 min. All activity tests were run out at a constant stirring rate using continuous air flow at room temperature. To examine the photocatalytic activity of materials, sample aliquots of the suspension have been taken out of the reaction vessel at regular time intervals (powder was separated from the aliquot solution by centrifugation). The absorbance of investigated solutions was measured on UV-1600PC Spectrophotometer (wavelength range from 200 to 800 nm). The degree of degradation is estimated using dependence $(C-\text{Co}/\text{Co}) \times 100$, where Co and C are initial concentration before turning on the illumination and residual concentration of the dye solution after illumination for selected time interval.

3. Results and discussions

Figure 1 illustrates Powder X-ray diffraction patterns of the investigated materials. The presence of $\gamma\text{-Al}_2\text{O}_3$ (PDF-29-1486), SiO_2 (PDF-87-2096) were established in all the samples – P2, P3 and P4. Additionally CuO (PDF-44-0706) for P3 and Co_3O_4 (PDF-42-1467) for P4 samples are observed in the PXRD spectra.

The Survey spectra are shown in Figure 2 for the illustration of the constituent elements in the catalysts. The position of O1s and Al2p photoelectron peaks at 531.5 eV and 74.5eV, respectively indicate that the support of the studied catalysts is Al_2O_3 . The small quantities of silicon on their surfaces have been detected, also. The binding energy of Si2p peak at around 103.2 eV, is typical for SiO_2 . This is in coincidence with the XRD results.

The binding energies of Ni2p, Cu2p as well as Co2p photoelectron peaks and the shape of the peaks shows that the loaded elements exist on the surface as oxide, NiO, CuO and CoO as well.

It should be mentioned, that the calculated quantity of Ni, Cu and Co is different and follow the order $\text{Cu} > \text{Ni} > \text{Co}$ although the equal quantity used during the synthesis of the final catalyst.

Figure 3 presents SEM pictures of the three samples: A) P4; B) P3 and C) P2 at two different magnifications (x 1.000 and 8.000).

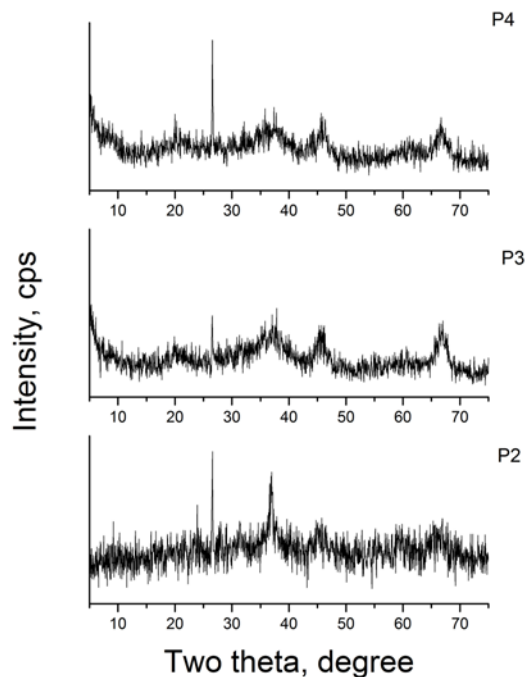


Fig. 1 PXRD patterns of $\text{CoO}/\text{Al}_2\text{O}_3$, $\text{CuO}/\text{Al}_2\text{O}_3$ and $\text{NiO}/\text{Al}_2\text{O}_3$ photocatalysts.

The SEM observations of NiO supported photocatalyst (Figure 3A) revealed typical layered material. The micrographs presented “plates-like” structures joined in aggregate. In the bigger magnification morphology observations of the sample P4 also demonstrated presence of bulk aggregates with irregular shape and also smaller particles on them.

The SEM images of $\text{CuO}/\text{Al}_2\text{O}_3$ (Figure 3B) were consistent from “flake-like” pieces and other bigger particles, with different sizes, and thin ones stuck to their surface. In the bulk and between the different stones were observed fibrous particles. In the larger augmentation it can be seen that the investigated material in some places also revealed porous “spider web-like” structure.

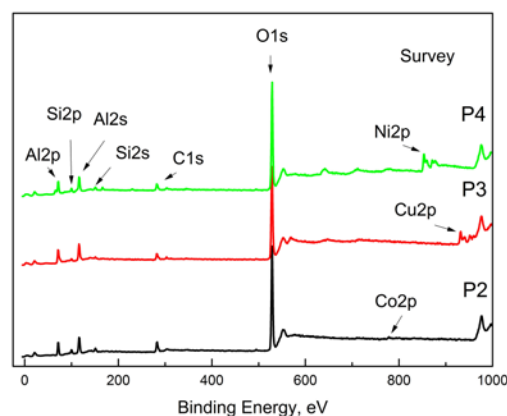


Fig. 2 XPS of $\text{NiO}/\text{Al}_2\text{O}_3$, $\text{CoO}/\text{Al}_2\text{O}_3$, $\text{CuO}/\text{Al}_2\text{O}_3$ samples.

The SEM photographs of $\text{CoO}/\text{Al}_2\text{O}_3$ sample (Figure 3C) showed aggregates with almost smooth surface, maybe it was flip off between two grains. It also composed of different little particles like flakes, tiny spots situated on angular species. Some of the broken off pieces had pores. Consequently the pictures also exposed dissimilar pores, according to size, between the particles. On the major magnification common nature of P2 sample displayed that separate grains were sintered.

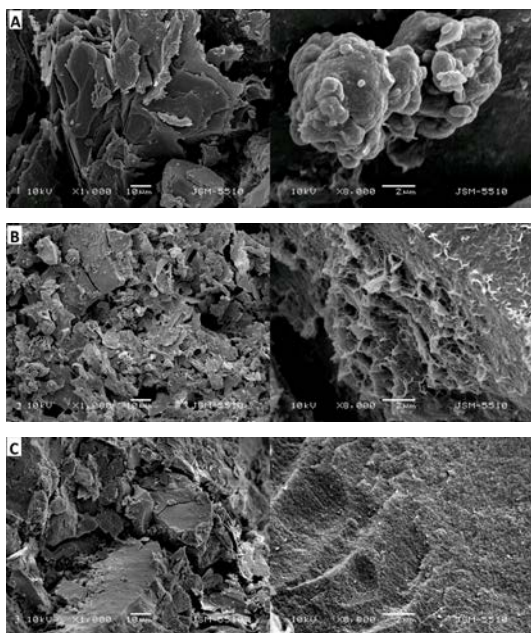


Fig. 3 SEM pictures of samples: A) P4; B) P3 and C) P2 at different magnifications.

Photocatalytic activities of investigated catalysts were tested for degradation of textile dye Malachite Green under UV-light illumination. The results of dark period before switch on the lamp showed that the absorption capacity of alumina containing support is lower than the supported materials. Absorption increases slightly with adding of active phase CoO, CuO or NiO and it is in the following order: P1<P2<P3<P4 (Figure 4). Figure 4 also represents the degradation degree of the MG dye solution, the supported photocatalysts P2-P4 showed better extent of degradation of MG dye then the support P1.

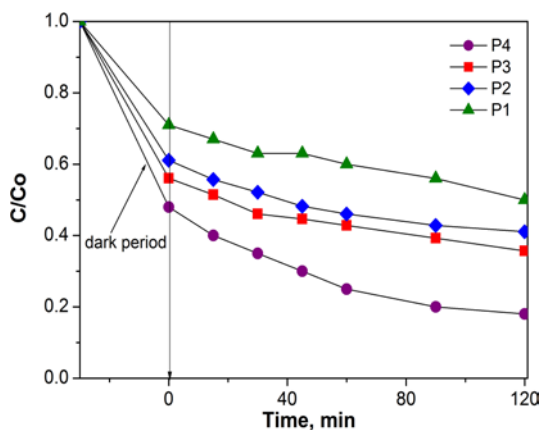


Fig. 4 Degradation degree of the MG dye solution under UV-A illumination over investigated samples; where C0 is initial concentration of the dye, C is the dye concentration after illumination.

On Figure 5 is shown degree of degradation of P1-P4 catalysts after 120 min time of illumination, which varied in the range of 59-82% for impregnated systems and 50% for the support. Among the investigated photocatalysts NiO/Al2O3 showed the highest photocatalytic performance, which is 35% enhancement in comparison to this of Al2O3 sample.

It can be seen from Figure 6 that the reaction course of MG dye degradation as a function of the time of illumination of investigated photocatalysts, follows pseudo first order kinetics. The apparent rate constants k is estimated using logarithmic linear dependence: -ln(C/C0) = k.t. The values of rate constants and degree of

degradation of MG dye for 120 minutes illumination are given in Table 1. Apparent rate constants of supported photo-catalysts were (3.9-8.4 x10⁻³, min⁻¹), while for the support was (2.7 x10⁻³, min⁻¹). Increasing of absorption was in accordance with enhancement degree of degradation and apparent rate constants.

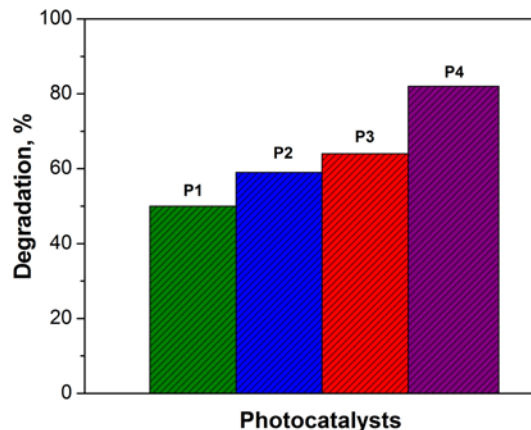


Fig. 5 Degree of degradation of the MG dye solution after 120 min under UV-A illumination over investigated samples.

Table 1: Apparent rate constants and degradation conversion degrees (120min) of investigated photocatalysts regarding MG dye.

Samples	k x10 ⁻³ ,min ⁻¹	Degradation, %
P4	8.4	82
P3	4.1	64
P2	3.9	59
P1	2.7	50

In our previous work we found out that alumina based samples, which contain α-Al2O3, θ-Al2O3 and Ca3Al2O6 showed 29% photocatalytic degree of degradation of Reactive Black 5 textile dye and after mechanochemical activation the degree of degradation increased up to 40% [20]. Some researchers reported the existence of unusual synergism when an insulator is present along with a semiconductor like TiO2, ZnO, ZnS, Fe2O3, CdO, CuO and Nb2O5 [6]. Probably, in our case CuO, CoO and NiO supported on γ-Al2O3 composites show synergistic photocatalytic effect and as result of it comes the enhanced dye photodegradation degree.

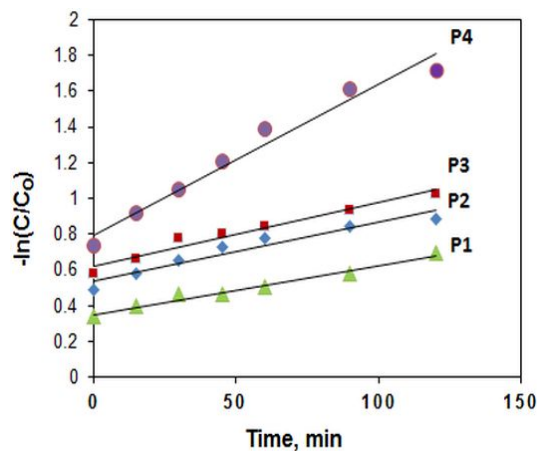


Fig. 6 Reaction course as a function of the time of illumination -ln(C/C0) of the alumina supported photocatalysts.

In conclusion we can state that all active semiconducting phases (CoO, CuO or NiO) exert considerable catalytic photodegradation

of MG dye, whereupon NiO/Al₂O₃ photocatalyst is superior to the other two systems. In this case both the alumina and the semiconductor particles are likely to be present in the agglomerates. This could lead to the transfer of holes from the illuminated semiconductor to the dye molecule, adsorbed on the Al₂O₃ surface, resulting in effective separation of the electron-hole pairs and higher rate of photoreaction.

4. Conclusions

The NiO/Al₂O₃, CuO/Al₂O₃ and CoO/Al₂O₃ photocatalytic systems were synthesized by impregnation method. The SEM pictures showed particles and aggregates with sizes around 0.2-80 μm. The materials were tested as catalysts for photodegradation of toxic pollutant Malachite Green dye under UV light. Photocatalytic degradation of MG dye on Al₂O₃ samples was 50%. In the case of NiO, CuO and CoO supported Al₂O₃ photocatalysts the degradation rate increases to some extent due to the synergism between insulating support and semiconducting oxide. The best photocatalytic efficiency was manifested by the NiO supported on γ-Al₂O₃ (degradation rate 82%), which correlates with its highest adsorption capacity and respectively specific surface area.

Acknowledgements

The financial support by National Science Fund, Ministry of Education and Sciences of Bulgaria (Contract DFNI – T-02-16) is acknowledged.

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