CHARACTERIZATION AND PHOTOCATALYTIC INVESTIGATION ON COPPER OXIDE CONTAINING CATALYST

ОХАРАКТЕРИЗИРАНЕ И ФОТОКАТАЛИТИЧНО ИЗСЛЕДВАНЕ НА КАТАЛИЗАТОР СЪДЪРЖАЩ МЕДЕН ОКИЦИД


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Abstract: New type of photocatalyst containing copper oxide hydrate crystalline phase and additional amount of copper sulfate hydroxide was prepared by thermal decomposition of copper sulfate. The EPR detected presence of Cu2+ ions. Photocatalytic degradation of two different model pollutants Reactive Black 5 (RB5) and Malachite Green (MG) in aqueous solution under UV illumination was investigated. The copper oxide containing catalyst showed four times higher photocatalytic activity with respect to RB5 than to MG dye. The catalyst exhibited much higher adsorption capacity to RB5 than to MG dye. The degree of degradation of MG dye is 18%, rate constant is 1.7x10^{-4} min^{-1} while the degree of degradation of RB5 dye is 90%, rate constant is 8x10^{-3} min^{-1} after 2 hours of illumination.

Keywords: COPPER OXIDE, REACTIVE BLACK 5, MALACHITE GREEN, PHOTOCATALYSIS, WASTEWATERS

1. Introduction

CuO is p-type semiconductor with a narrow band gap of 1.21–1.51 eV and monoclinic structure [1]. It is an interesting multifunctional material due to its promising applications in gas sensors [2,3], magnetic storage media [4], lithium ion batteries [5], and solar cells [6] due to its photoconductive and photochemical properties. In most reports composite photocatalyst for dye degradation such as: CuO/SnO2, CuO/ZnO, CuO/Br2O3, CuO/SiO2, CuO/zeolite [7], CuO/graphene [8], chitosan anchored copper oxide [9] were used but in recent years also pure CuO was studied [10]. CuO was tested as an adsorbent in the Methylene Blue dye decolorization process [11]. Cu-core/CuSO4-shell nanoparticles exhibited higher photocatalytic efficiency than Cu nanoparticles and these results proved that CuSO4-shell has significant effect on the degradation of Methylene Blue [12]. Enormous amounts of environmental pollutants, effluents of colored dyes having carcinogenic effect are discharged by the textile and paper industries [13]. These dye pollutants are chemically stable, so technologies relating to direct UV photolysis and hydrogen peroxide oxidation are not effective in removing the color dyes. At present, the photocatalytic method attracts considerable attention due to its effective decolorization of dyes [14]. Malachite Green (MG) has now become a highly controversial compound due to the risks it poses to the consumers of treated fish, including its effects on the immune system and reproductive system and its genotoxic carcinogenic properties [15]. The photocatalytic efficiencies of cerium-cadmium oxide [16], ZnS-Cds [17], bismuth oxide [18], TiO2 [15], CuO supported on HY zeolite [19] and other catalysts were tested by using them in the photocatalytic degradation of Malachite Green dye. Sonophotolytic degradation of azo dye Reactive Black 5 (RB5) in an ultrasound/UV/ferric system was examined [20] as well as the efficiency of the Fe3O4/FeC2O4 magnetic catalyst in the catalytic wet peroxide oxidation of reactive azo dye RB5 [21]. Our previous research has shown high photocatalytic activity of TiO2 films in the degradation of RB5 dye under UV light [22].

The aim of this article is to characterize by PXRD, XPS and EPR analysis copper oxide containing catalyst synthesized by thermal decomposition of copper sulfate. Because of its recent application in photocatalysis we set ourselves the task to examine its photocatalytic properties in regard to oxidative degradation of two hazardous textile dyes- Reactive Black 5 and Malachite Green.

2. Experimental

2.1. Synthesis of the samples

For preparation of CuO containing sample we used CuSO4.5H2O as starting reagent. The suspension of copper sulfate and water was magnetically stirred upon heating for about 1h. After that the obtained sample was dried at 100°C for 12 h. The finally obtained powder was annealed for 3 h at 500°C in air.

2.2. Powder X-ray diffraction analysis (PXRD)

The PXRD of the obtained photocatalyst was carried out using a TUR M62 apparatus, Germany with PC control and data acquisition, using HZG-4 goniometer and CoKα radiation. The presence of the phases registered in PXRD pattern was established by using of JCPDS database (Powder Diffraction Standards, Philadelphia PA, USA, 1997).

2.3. Electron paramagnetic resonance (EPR)

The EPR spectrum was recorded on JEOL JES-FA 100 EPR spectrometer operating in the X-band with standard TE011 cylindrical resonator. Spectra were recorded at room temperature.

2.4. X-ray photoelectron spectroscopy (XPS)

The X-ray photoelectron spectroscopy (XPS) studies were performed in a VG Escalab II electron spectrometer using AlKα radiation with energy of 1486.6 eV under base pressure 10^{-7} Pa and a total instrumental resolution of 1eV. The binding energies (BE) were determined utilizing the C 1s line from an adventitious carbon as a reference with energy of 285.0 eV. The accuracy of measuring the binding energy was 0.2 eV. The O 1s, Cu2p and S2p, photoelectron lines were recorded and corrected by subtraction of a Shirley’s-type of background and quantified using the peak area and Scofield’s photoionization cross-sections.

2.5. Catalytic activity tests

The photocatalytic activities of the prepared samples were measured in oxidative degradation of both Reactive Black 5 (RB5) dye and Malachite Green (MG) under UV light. The photocatalytic
studies were performed using UV-Vis absorbance spectrophotometer in the wavelength range from 200 to 800 nm and a polychromatic UV-A lamp illumination (18W) with maximum emission at 365 nm. The initial concentration of the used RB5 and Malachite Green dye solutions was 20 ppm and 5 ppm respectively. The photocatalytic tests were carried out under slightly acidic pH=6. Before switching on illumination, the catalyst and dye solution were stirred for 30 min in dark to achieve adsorption equilibrium. The degree of degradation of the dyes is calculated using equation (1), where C0 is the initial concentration (based on absorbance) of the dye, C is the residual concentration after 120 min of illumination.

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\text{Degradation}[\%] = \left[ \frac{C_0 - C}{C_0} \right] \times 100
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1. Results and discussions

Figure 1 represents powder X-ray diffraction spectrum of the obtained copper oxide containing photocatalyst. The PXRD results established the presence of copper oxide hydrate phase (CuO.3H2O) (PDF-36-0545) and additional amount of copper sulfate hydroxide (Cu3(SO4)(OH)4) (PDF-76-1621). The incomplete thermal decomposition of the starting material copper sulfate is the possible reason for existence of intermediate precursor phase copper sulfate hydroxide registered in the PXRD pattern of prepared copper oxide containing catalyst.

Figure 2 illustrates the results of electron paramagnetic resonance method. EPR spectrum of CuO containing catalyst at room temperature is consisting of an asymmetric line with g factor 2.24 most probably due to interacting Cu²⁺ ions in clusters [23, 24]. The effect of dipolar interaction between Cu²⁺ ions leads to broadening of individual lines. For this reason the hyperfine structure due to I=3/2 of Cu²⁺ ion cannot be seen.

The XPS Cu 2p spectrum of the catalyst sample is shown in Figure 3. The “shake-up” satellite located at 944 eV position and a peak at 935.5 eV are clearly visible. The “shake-up” satellite is an evidence of Cu (II) ions [25], while the peak at 935.5 eV coincides with the known CuSO₄ peak position at 935.4 eV [26]. A low intensity peak at 933.6 eV is typical of the CuO peak [26]. The results indicate incomplete transformation of CuSO₄ into CuO, most probably due to the low temperature of treatment.

Figure 4 represents the course of the photocatalytic reaction as dye concentration decrease with the time of illumination of both investigated model pollutants on the CuO containing photocatalyst. The prepared photocatalyst showed four times higher photocatalytic activity to RB5 than MG dye. It has to be noted that the catalyst exhibited much higher adsorption capacity with respect to RB5 than MG for 30 min in dark. The degree of discoloration after 2 hours irradiation for MG is 18%, while for RB5 dye is 90% (Figure 5).

Figure 6 show the dependences of –ln(C/C₀) as a function of time t under UV light illumination. The dependence shows that the copper containing catalysts exhibit higher photoactivity to Reactive Black 5 than MG dye in the first 15 minutes of illumination. The photocatalyst has very low activity in degradation of Malachite Green probably due to the difference in the size of conjugated system of C=C and C-C bonds in the molecular structure of the both dyes and different bond scission energies. The rate constants and degree of degradation for the dyes over CuO containing photocatalyst after 120 minutes of UV irradiation are represented in Table 1. The rate constants k after 2 hours for MG and RB5 are 1.7x10⁻³ min⁻¹ and 8x10⁻³ min⁻¹, respectively. Rate constants were calculated using the equation –ln(C/C₀) = kt on the basis of the slope of the linear logarithmic function.
In our case probably the same effect of the presence of copper sulphate plays positive role in the photocatalytic degradation. The results obtained in this article for copper containing photocatalysts are in accordance with our previous studies on ZnO films [29].

4. Conclusions

Photocatalyst containing hydrated copper oxide crystalline phase and additional amount of copper sulfate hydroxide was prepared by thermal decomposition of copper sulfate. The performed PXRD and XPS studies confirmed the presence of copper oxide and some quantity of copper sulfate hydroxide phases. The EPR analysis detected the existence of Cu$^{2+}$ ions in obtained material. The copper oxide containing photocatalyst showed strong difference in its photocatalytic behaviour with respect to the two model dyes, due to differences in their structure and physicochemical properties. The photocatalyst possess much higher adsorption capacity and selectivity to degrade the double diazo bond in RB5 in comparison to the two single carbon-carbon bond in MG. We can recommend copper oxide containing material as relatively new cheap alternative to the already used photocatalysts for degradation of textile azo dyes.

Acknowledgements

The authors gratefully acknowledge financial support by National Science Fund, Ministry of Education and Sciences of Bulgaria (Contract DFNI - T02 16).

References


