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Enhancement of the photocatalytic ability of alumina by mechanochemical activation and silver doping

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In the present paper the photocatalytic ability of commercial alumina, 5 wt% Ag supported Al_2O_3 synthesized by impregnation and the respective mechanochemically activated (MCA) materials was investigated for degradation of aqueous solutions of Malachite Green (MG) and Reactive Black 5 (RB5) dyes as model contaminants under UV light. The Powder X-ray diffraction analysis and FT-IR spectroscopy were used to establish the phase composition and structure of the prepared samples. The photocatalytic tests determined that the presence of Ag dopant and especially the mechanochemical treatment lead to lower degree of crystallinity, decreasing the mean crystallite size and enhancement of the photocatalytic activity of the investigated materials. The degrees of degradation of the two tested dyes decrease as follows: Ag-Al_2O_3, MCA, RB5 (99%) > Ag-Al_2O_3, MCA, MG (98%) > Al_2O_3, MCA, MG (92%) > Al_2O_3, MCA, RB5 (91%) > Ag-Al_2O_3, RB5 (72%) > Ag-Al_2O_3, MG (67%) > Al_2O_3, MG (47%) > Al_2O_3, RB5 (41%).

Keywords: mechanochemical activation, dopant, photocatalytic efficiency, Malachite Green, Reactive Black 5.

INTRODUCTION

Mechanical treatment leading to enhancement of the reactivity of solids has been known in the ceramics industry, as a method for generating various defects and new surfaces [1]. Aluminium oxide (Al_2O_3), also known as alumina, has several thermodynamically stable transitional phases as gamma alumina (γ-Al_2O_3), delta alumina (δ-Al_2O_3), kappa alumina (κ-Al_2O_3), theta alumina (θ-Al_2O_3) and alpha alumina (α-Al_2O_3). The γ-Al_2O_3 (activated alumina) has been widely used as a catalyst supports, catalysts, dehydrators and adsorbents due to its good porosity, large specific surface area, acid-base and adsorbability characteristics [2]. Heterogeneous and homogeneous photocatalyses have played an important role in many photochemical conversion processes, and have been extensively investigated over the last two decades [3]. Li Hua et al. treated Methyl Orange, Direct Brown and Direct Green azo dyes by catalytic wet air oxidation using CuO/γ-Al_2O_3 composite catalysts synthesized by consecutive impregnation [4]. Lung-Chuan Chen et al. established that incorporating of Ag in TiO_2/γ-Al_2O_3 significantly increased the rate of photo decolorization of Methyl Orange [5]. Yan Liu et al. revealed that Acid Orange 52, Acid Orange 7 and Reactive Black 5 azo dyes can be efficiently degraded with Fe_2O_3/γ-Al_2O_3 and Fe_2O_3–CeO_2/γ-Al_2O_3 catalysts in a catalytic wet peroxide oxidation under standard atmospheric conditions [6]. Sung-Chul Kim et al. proved the high activities of Pd–Pt/Al_2O_3 bimetallic catalysts toward the wet oxidation of the reactive dyes in the presence of 1% H_2 together with excess oxygen [7].

The goal of the present study is a comparative investigation of the photocatalytic efficiency of commercial alumina and Ag supported Al_2O_3 photocatalytic materials prepared by impregnation for degradation of aqueous solutions of Malachite Green and Reactive Black 5 dyes as model

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pollutants. The influence of mechanochemical treatment on the photocatalytic properties of Al_2O_3 and Ag supported Al_2O_3 samples was also studied.

EXPERIMENTAL

For the preparation of Ag-Al_2O_3 photocatalyst, commercial γ-Al_2O_3 (Valerus Co.) was used. The alumina powder was impregnated with aqueous solutions of $AgNO_3$ under heating and stirring in accordance to achieve 5 wt% silver.

One part of the commercial alumina and Ag supported Al_2O_3 samples were mechanochemically activated using a high-energy planetary ball mill model PM 100 (Retsch, Germany). The mechanochemical activation (MCA) was performed in an agate milling container of 80 ml volume at milling speed 390 rpm for milling time interval of 20 minutes using air atmosphere. The weight ratio between the balls to sample was 13:1.

The Powder X-ray diffraction analysis (PXRD) and FT-IR spectroscopy were used for physicochemical characterization of the samples. The PXRD spectra of the samples were collected using Philips PW 1050 with CuK_α-radiation. The phases were determined using the JCPDS database. FT-IR spectroscopy was carried out on a Fourier infrared spectrometer Bruker-Vector 22. The obtained materials using KBr tablets were studied in the 400-4000 cm^{-1} range.

The photocatalytic activity of the samples (0.15g catalyst in 150 ml water solution of the dye) was investigated in a semi-batch photocatalytic reactor under constant stirring, at room temperature, for the oxidative degradation of Malachite Green (5 ppm) or Reactive Black 5 (20 ppm) dyes. The first half an hour of the tests was carried out in the dark, without illumination in order to obtain adsorption-desorption equilibrium. After that UV illumination (power 18 W, λmax = 365 nm) was switching on for period of 2 hours. The photocatalytic degradation was evaluated by taking aliquote of the solution after centrifugation and measuring the adsorbance by means of UV-1600PC Spectrophotometer (wavelength range from 200 to 800 nm). The degree of the model dye degradation was calculated using the dependence (Co-C/Co) x100, 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.

RESULTS AND DISCUSSION

The Powder X-ray diffraction patterns of the commercial alumina, Ag supported Al_2O_3 and respective mechanochemically treated materials are presented in Fig 1. The presence of only one γ-Al_2O_3 phase (PDF-49-0134; 29-1486) was registered in the spectra of the commercial Al_2O_3 and mechanochemically activated alumina samples. The γ-Al_2O_3 (PDF-49-0134) and the additional silver crystallographic phase (PDF-04-0783) were established for Ag supported Al_2O_3 and the mechanochemically treated Ag supported alumina materials. The lower degree of crystallinity was determined for mechanochemically treated samples. The calculated mean crystallite size of Al_2O_3 using PowderCell 2.4 program [8] are 16, 14, 15 and 14 nm for commercial Al_2O_3, Al_2O_3, MCA, Ag supported Al_2O_3 and Ag supported Al_2O_3, MCA. The results established that the presence of silver dopant or mechanochemical activation lead to decreasing of the average crystallite size of Al_2O_3.

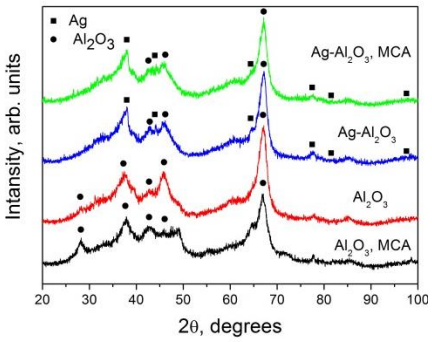

Fig. 1. PXRD patterns of the investigated materials.

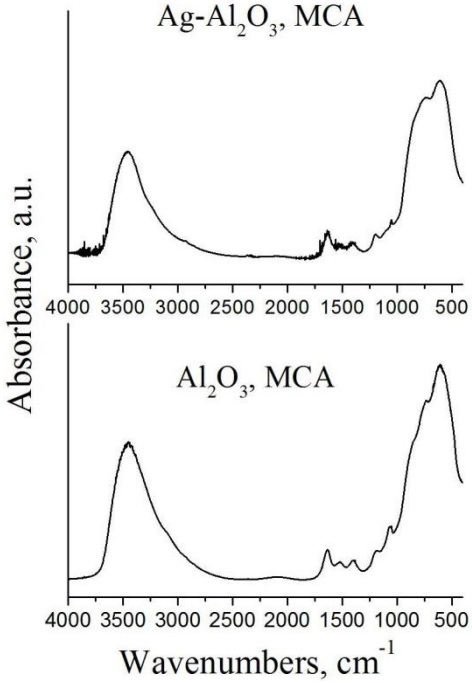

Fig. 2. FT-IR spectra of the studied samples.

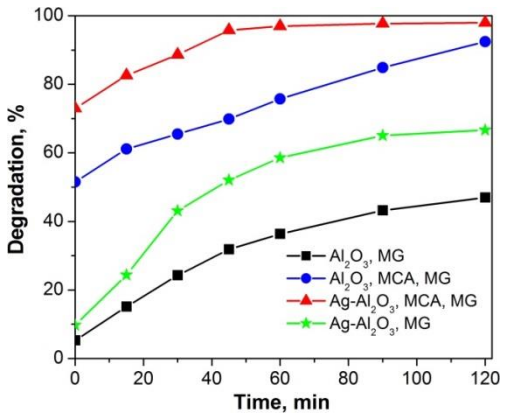

Fig. 3. Degree of degradation of MG dye as a function of the time of UV illumination.

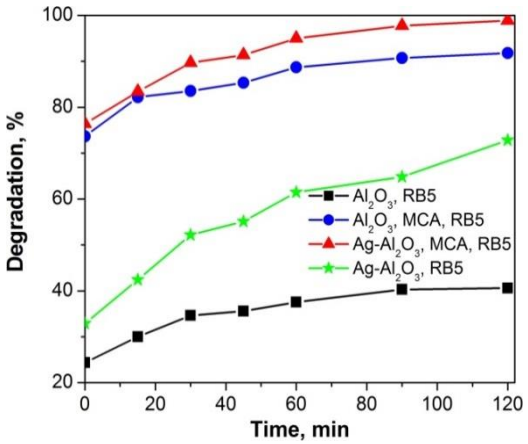

Fig. 4. Degree of degradation of RB5 dye as a function of the time of UV illumination.

FT-IR spectra of mechanochemically treated commercial alumina and Ag supported Al_2O_3 samples are displayed in Fig. 2. The absorption bands at around 3450 and 3472 cm^{-1} could be due to the presence of -OH species, showing the presence of Al-OH bond in the samples. The band at around 1636 cm^{-1} corresponds to the H-O-H angle bending vibration of weakly bound molecular water [9]. The peaks at around 609 and 611 cm^{-1} were attributed to Al–O stretching mode [9-11]. The absorption band at around 1400 cm^{-1} could be attributed to the presence of carbon-hydrogen (CH_3), - carbon (C-C) and -oxygen (C=O) deformations. The peaks at around 1518; 1187-1189 and 1050-1065 cm^{-1} may be due to the presence of others impurities in the investigated samples [9]. The results obtained by FT-IR spectroscopy are in agreement with the PXRD analysis.

Figs. 3 and 4 present the degree of degradation of MG and RB5 dyes as a function of the time of illumination under UV light. After the mechanochemical activation of Ag/Al_2O_3 photocatalyst, the degradation degree of RB5 dye reached 99% and of MG dye 98%, while Al_2O_3, MCA photocatalyst showed 92% and 91% for RB5 and MG dyes accordingly. The photocatalytic activity for the degradation of MG and RB5 dyes on Ag supported Al_2O_3 samples was 72 and 67%. The commercial alumina samples exhibited lower photocatalytic efficiency for degradation of the MG and RB5 dyes: 47% and 41% respectively. The comparison data of apparent rate constants of all investigated catalysts for both dyes was exhibited in Fig. 5. The presented apparent rate constants were calculated using linear dependence $-\ln(C/C_0) = k.t$. The photocatalytic efficiency of the investigated samples for degradation of MG dye (based on rate

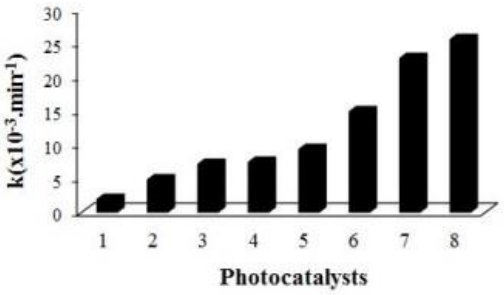

Fig. 5. Comparison data of apparent rate constants of: **1**-Al_2O_3, RB5; **2**-Al_2O_3, MG; **3**-Ag-Al_2O_3, RB5; **4**-Ag-Al_2O_3, MG; **5**-Al_2O_3, MCA, RB5; **6**-Al_2O_3, MCA, MG; **7**- Ag-Al_2O_3, MCA, MG; **8**- Ag-Al_2O_3, MCA, RB5 photocatalysts in degradation of RB5 and MG dyes.

constants) is: Ag-Al_2O_3, MCA ($22.8x10^{-3}$ min^{-1})> Al_2O_3, MCA ($14.9x10^{-3}$ min^{-1}) > Ag-Al_2O_3 ($7.4x10^{-3}$ min^{-1})> Al_2O_3 ($4.8x10^{-3}$ min^{-1}). The RB5 photodegradation decreases in the following order: Ag-Al_2O_3, MCA ($25.6x10^{-3}$ min^{-1})> Al_2O_3, MCA ($9.3x10^{-3}$ min^{-1}) > Ag-Al_2O_3 ($7.1x10^{-3}$ min^{-1})> Al_2O_3 ($1.9x10^{-3}$ min^{-1}).The highest rate constant belongs to Ag-Al_2O_3, MCA. We can conclude that the silver doping influenced catalytic activity to some extent, whereas mechanochemical activation increased it significantly. It is well-known that the mechanical energy obtained during milling can have effects such as generating new interfaces and crystal defects, changes in particle size and amorphization [12]. In our study the mechanochemically treated samples possess lower degree of crystallinity and decreased average crystallite size which leads to higher photocatalytic activity. Similar effects have been established for mechanochemically activated Ag/ZnO particles [13].

CONCLUSIONS

The obtained photocatalytic results show that both the silver doping and mechanochemical activation of Al_2O_3 lead to enhancement in the photocatalytic properties of the investigated materials in the oxidative degradation of aqueous solutions of MG and RB5 dyes under UV light. The mechanochemical activation improves significantly the photocatalytic efficiency of the studied samples. The mechanochemically activated Ag supported Al_2O_3 shows the highest photocatalytic activity for the oxidative degradation of the model pollutants, compared to the other tested materials.

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ПОВИШАВАНЕ НА ФОТОКАТАЛИТИЧНАТА СПОСОБНОСТ НА АЛУМИНИЕВ ОКСИД ЧРЕЗ МЕХАНОХИМИЧНА АКТИВАЦИЯ И ДОТИРАНЕ СЪС СРЕБРО

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(Резюме)

В настоящата статия е изследвана фотокаталитичната способност на търговски алуминиев оксид, дотиран с 5 тегловни % сребро Al_2O_3 синтезиран чрез импрегниране и съответните механохимично активираните (МХА) материали бяха изследвани за разграждането на водни разтвори на Малахитово Зелено (МЗ) и Реактивно Черно 5 (РЧ5) багрила като моделни замърсители под действието на УВ светлина. Рентгенофазов анализ и инфрачервена спектроскопия с фурие трансформация бяха използвани за установяване на фазовия състав и структурата на получените проби. Фотокаталитичните тестове определиха, че присъствието на Ag като допант и особено механохимичната обработка водят до по-ниска степен на кристалност, намаляване на средния размер на кристалитите и повишаване на фотокаталитичната активност на изследваните материали. Степента на разграждане на двете тествани багрила намалява както следва: Ag-Al_2O_3, МХА, РЧ5 (99%) > Ag-Al_2O_3, МХА, МЗ (98%) > Al_2O_3, МХА, МЗ (92%) > Al_2O_3, МХА, РЧ5 (91%) > Ag-Al_2O_3, РЧ5 (72%) > Ag-Al_2O_3, МЗ (67%) > Al_2O_3, МЗ (47%) > Al_2O_3, РЧ5 (41%).