Bulgarian Chemical Communications, Volume 47, Special issue C (pp. 105–111) 2015

Mixed cobalt-copper ferrite-type materials: synthesis and photocatalytic efficiency in degradation of Reactive Black 5 dye under UV-light irradiation

K. L. Zaharieva[1]*, K. I. Milenova[1], V. Rives[2], R. Trujillano[2], Z. P. Cherkezova-Zheleva[1], A. E. Eliyas[1], M. P. Tsvetkov[3], B. N. Kunev[1], I. G. Mitov[1]

[1] *Institute of Catalysis, Bulgarian Academy of Sciences, Acad. G. Bonchev St., Bldg. 11, 1113 Sofia, Bulgaria*
[2] *GIR-QUESCAT, Dpto. Química Inorgánica, Universidad de Salamanca, 37008-Salamanca, Spain*

Received: October 5, 2015; Revised October 20, 2015

Mixed cobalt-copper ferrite-type materials having different compositions were prepared using a coprecipitation technique and mechanochemical or microwave treatment. Various physicochemical methods, such as powder X-ray diffraction, Mössbauer and FTIR spectroscopy, single point BET method, porosity investigations, and temperature-programmed reduction, were used for characterization of the obtained ferrite-type samples. The photocatalytic activities of the so synthesized cobalt-copper ferrite-type materials were examined in oxidative degradation of Reactive Black 5 (RB5) dye as model contaminant in aqueous solution under UV-A light illumination. Photocatalytic activity tests established that microwave treatment of coprecipitated $Co_{0.25}Cu_{0.25}Fe_{2.5}O_4$ sample leads to a higher degree of degradation of RB5 dye (98%) compared to that of coprecipitated (96%) and mechanochemically treated (73%) materials. Mechanochemical treatment enhanced the conversion degree of RB5 dye after 120 min of illumination: 77 and 78% for $Co_{0.5}Cu_{0.5}Fe_2O_4$ and $Co_{0.4}Cu_{0.1}Fe_{2.5}O_4$, respectively, compared with matching coprecipitated samples (48% and 52%), accordingly. An enhancement of photocatalytic efficiency of prepared cobalt-copper ferrites upon decreasing the cobalt content was established. The photocatalytic properties of obtained mixed cobalt-copper ferrite-type samples were affected by the degree of incorporation of metal ions in the magnetite-type structure and by applied preparation methods.

Keywords: mixed cobalt-copper ferrite-type materials, mechanochemical and microwave treatment, Reactive Black 5 dye.

INTRODUCTION

Studies of nanodimensional ferrites properties have attracted attention in last years because of their significance in the fundamental understanding of physical processes as well as due to their various technological applications [1]. Spinel ferrites possess very interesting catalytic properties compared with single component metal oxides. The catalytic activities of spinel ferrites depend on various factors such as particle size, redox properties of metal ions and their distribution between the tetrahedral (A) and octahedral (B) coordination sites [2]. Investigations of the preparation and properties of cobalt-copper (copper-cobalt) ferrites [1,3–5] and substituted cobalt nanoferrites $CoM_xFe_{2-x}O_4$ ($M=Cr^{3+}$, Ni^{2+}, Cu^{2+}, Zn^{2+}; $0.2 \leq x \leq 1.0$) [2] of different compositions have been carried out by many researchers [1–5].

The goals of the present work were synthesis, physicochemical characterization, and comparison of photocatalytic activities of mixed cobalt-copper ferrite-type materials of different compositions in degradation of Reactive Black 5 dye as model pollutant in aqueous solution under UV-A light irradiation.

EXPERIMENTAL

Mixed Co-Cu ferrite-type samples having different stoichiometric compositions: $Co_{0.25}Cu_{0.25}Fe_{2.5}O_4$ (A), $Co_{0.4}Cu_{0.1}Fe_{2.5}O_4$ (B), and $Co_{0.5}Cu_{0.5}Fe_2O_4$ (C) were synthesized by a coprecipitation procedure using 0.03 M aqueous solutions of $CoCl_2.6H_2O$ (Alfa Aesar), $CuCl_2.2H_2O$ (Valerus, p.a.), $FeCl_2.4H_2O$ (Sigma Aldrich, p.a.), and/or $FeCl_3.6H_2O$ (P.P.H. STANLAB s.j) mixed at appropriate ratios. A pH value of 12.5 of the mixture was reached by adding dropwise 0.3 M NaOH under continuous stirring. After coprecipitation, the mixture was stirred for another hour. The obtained precipitates were centrifuged and washed with distilled water until neutral reaction (pH = 7) was achieved. The prepared samples were then sonicated for 5 min. The products were dried in air at room temperature. Coprecipitated ferrite-type samples were mechanochemically treated in a high-energy planetary ball mill (model PM 100, Retsch, Germany). The mechanochemical process was carried out in tungsten carbide vessels of 250-ml volume at a milling speed of 400 rpm for 210 min under argon. The mass ratio of powder amount to applied balls was 1:46. The mechanochemically treated materials were denoted as follows: $Co_{0.25}Cu_{0.25}Fe_{2.5}O_4$ as D,

---

* To whom all correspondence should be sent
E-mail: zaharieva@ic.bas.bg

$Co_{0.4}Cu_{0.1}Fe_{2.5}O_4$ like E, and $Co_{0.5}Cu_{0.5}Fe_2O_4$ as F. The coprecipitated sample A was also microwave-treated at 120°C for 2 h using a microwave apparatus (Milestone Ethos Plus High Performance Microwave Labstation). Afterwards the $Co_{0.25}Cu_{0.25}Fe_{2.5}O_4$ material, labelled as G, was centrifuged and dried at 100°C for 4 h and 30 min.

The structure, phase composition, and magnetic behaviour of the prepared cobalt-copper ferrite-type samples were investigated by several physico-chemical methods.

Powder X-ray diffraction (PXRD) analysis was carried out on a Siemens D-500 diffractometer at 40 kV and 30 mA, using CuKα filtered radiation (λ = 1.5418 Å).

Mössbauer spectroscopy measurements of the synthesized materials were carried out on a Wissenschaftliche Elektronik GmbH apparatus by working at a constant acceleration mode and applying a $^{57}Co/Rh$ source (activity ≈50 mCi) and α-Fe standard. Hyperfine interaction parameters of Mössbauer spectral components: isomeric shift (IS), quadrupole splitting (QS), hyperfine effective magnetic field at the sites of iron nuclei (H_{eff}), line widths (FWHM), and component relative weights (G) were determined by computer fitting.

A FTIR spectroscopic study was performed using the KBr pellet technique on a Perkin Elmer Spectrum One apparatus by averaging 50 spectra with a nominal resolution of 4 cm^{-1}.

A Micromeritics Gemini VII 2390t surface area analyser was used to record nitrogen adsorption-desorption isotherms for specific surface area and porosity assessment. The investigated materials were degassed beforehand in a Micromeritics Gemini Flow Prep 060 degassing unit for 2 h at 110°C under continuous nitrogen flow.

Temperature-programmed reduction (TPR) experiments were conducted in a Micromeritics TPR-TPD 2900 apparatus by applying a 5-vol.% H_2/Ar mixture (from L'Air Liquide, Spain) at a heating rate of 10 $grad.min^{-1}$. The amount of tested material was selected to satisfy resolution conditions reported by Malet and Caballero [6].

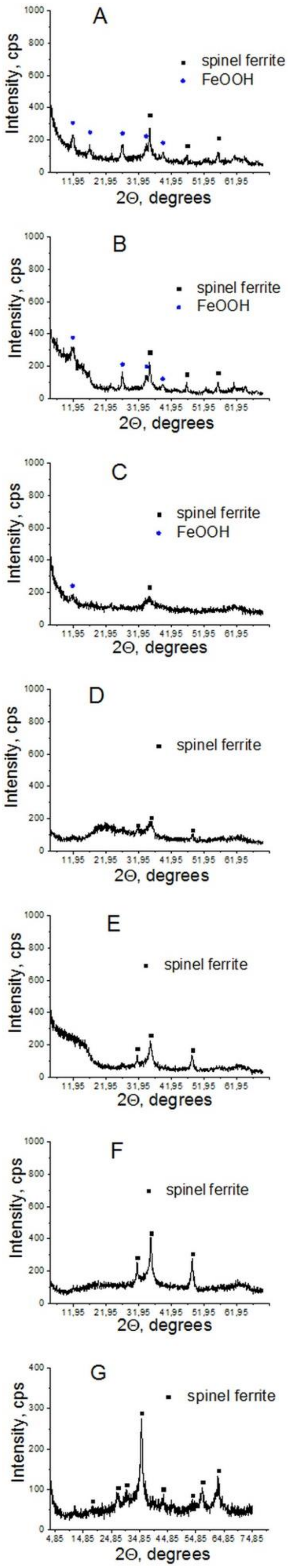
Synthesized materials were tested for photocatalytic activity in oxidative degradation of Reactive Black 5 (RB5) dye under UV-A polychromatic illumination (18-W lamp with maximal emission at 365 nm). The reaction course was followed using a CamSpec M501 UV-Vis spectrophotometer in the wavelength range from 200 to 800 nm. The initial concentration of the used RB5 dye solution was 20 ppm. The investigated systems reached an equilibrium state in the dark for about 30 min before switching on the UV illumination. The photocatalytic tests were carried out in a semi-batch suspension photocatalytic reactor upon feeding air through two frits to create a large stoichiometric excess of oxygen.

RESULTS AND DISCUSSION

PXRD patterns of coprecipitated, mechanochemically and microwave-treated mixed cobalt-copper ferrite-type materials are shown in figure 1. The spinel non-stoichiometric ferrite (PDF-22-1086; PDF-34-0425; PDF-75-0449) and additional iron oxyhydroxide (PDF-75-1594) phases are identified in the PXRD diagrams of coprecipitated samples A, B, and C. Formation of single spinel non-stoichiometric ferrite phases (PDF-22-1086; PDF-34-0425; PDF-75-0449) is observed in the investigated samples both after mechanochemical (D, E, F) and microwave (G) treatment.

Mössbauer data are presented in figure 2. Doublet or doublet and sextet components are observed in the spectra at room temperature (RT) with the so prepared cobalt-copper ferrite-type materials A, B, C, D, E, F, and G. Mössbauer spectra at liquid nitrogen temperature (LNT) were recorded to establish the nature of doublet and sextet lines. A superposition of sextet and doublet components is derived from the LNT spectra of all studied samples. Estimation of the spectra pointed to existence of iron ions in a ultradispersed ferrite phase of superparamagnetic (SPM) behaviour and sizes below 10 nm, and/or ferrite particles of sizes below 20 nm showing a collective magnetic excitation (CME) behaviour for the A, B, C, D, E, F, and G samples and iron ions belonging to an intermediate phase of iron oxyhydroxide with the A, B, and C materials [7].

FTIR spectra of the obtained mixed cobalt-copper ferrite-type samples are displayed in figure 3. The bands positioned below 700 cm^{-1} are assigned to vibrations of ions in the crystal lattice [8]. The vibrations recorded around 3400 cm^{-1} and 1625–1633 cm^{-1} are due to the O-H stretching and H-O-H bending modes of free or absorbed water molecules [1]. The bands at about 1352–1368 cm^{-1} and 1464–1475 cm^{-1} are ascribed to vibrations of carbonate (CO_3^{2-}) and hydroxycarbonate (HCO_3^{-}) species [9] adsorbed on the surface. Adsorption of atmospheric CO_2 could explain the presence of these species.



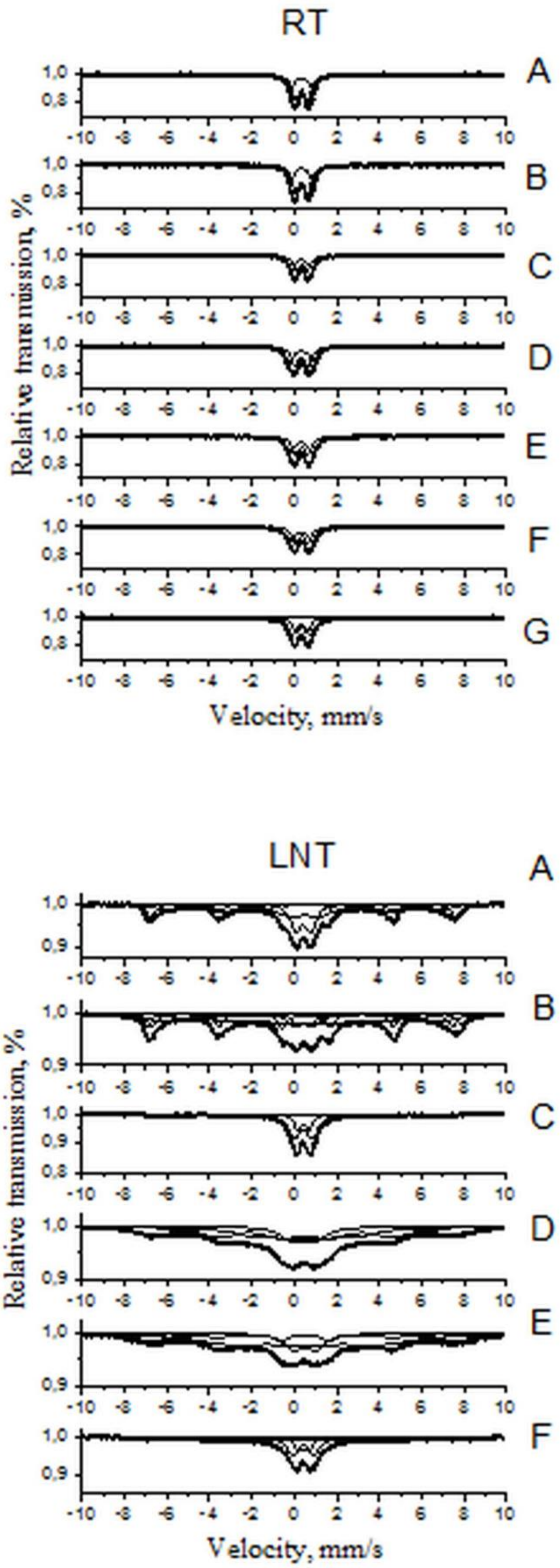


Fig. 1. PXRD patterns of synthesized mixed cobalt-copper ferrite-type materials.

Fig. 2. Mössbauer spectra of prepared mixed Co-Cu ferrite-type samples at room (RT) and liquid nitrogen (LN) temperature.

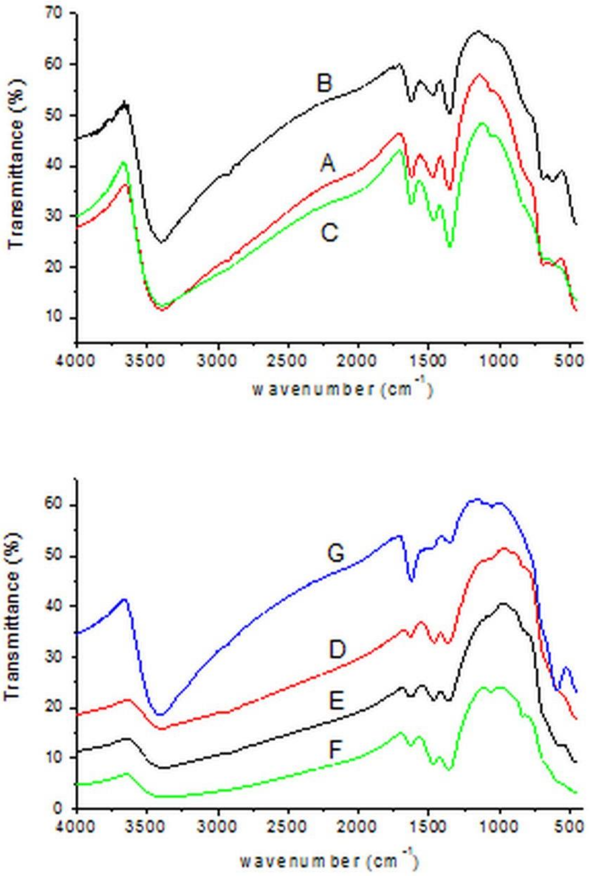


Fig. 3. FTIR spectra of obtained mixed cobalt-copper ferrite-type samples.

Figure 4 shows N_2 adsorption-desorption isotherms at –196°C for the synthesized cobalt-copper ferrite-type samples. The adsorption branch in the three isotherms of mechanochemically treated materials D, E, and F belongs to Type II of the IUPAC classification [10]. They display hysteresis loops of type H3 that is typical of non-rigid aggregates of plate-like particles giving rise to slit-shaped pores [11]. Sample F has a notably higher specific surface area value (92 $m^2.g^{-1}$) compared to the mechanochemically treated samples D and E, 37 and 51 $m^2.g^{-1}$, respectively. The shape of the isotherm of coprecipitated sample C shows a hysteresis loop similar to the H2 type. This hysteresis type has been found for disordered materials of indefinite pore size distribution and shape. On the other hand, the isotherms of samples A, B, and G are similar to those of type IV in the IUPAC classification that is typical of mesoporous materials. Data in table 1 show that the surface area values of the coprecipitated materials are much higher than those of mechanochemically treated series are. Table 1 summarizes values of total specific surface area (S_{BET}), external surface area (S_t), micropore volume (V_{MP}), and average pore diameter (D_p) calculated from the N_2 adsorption-desorption isotherms at –196°C.

Table 1. Values of total specific surface area (S_{BET}), external surface area (S_t), micropore volume (V_{MP}), and pore diameter (D_p) calculated from isotherms of N_2 adsorption-desorption at –196°C.

Sample	S_{BET} $m^2.g^{-1}$	S_t $m^2.g^{-1}$	V_{MP} $cm^3.g^{-1}$	D_p nm
D	37	27	0.005	4.2
E	51	44	0.004	4.2
F	92	84	0.005	4.2
B	192	192	0.000	5.5
G	204	204	0.000	4.0
A	224	224	0.000	4.7
C	286	286	0.000	3.0

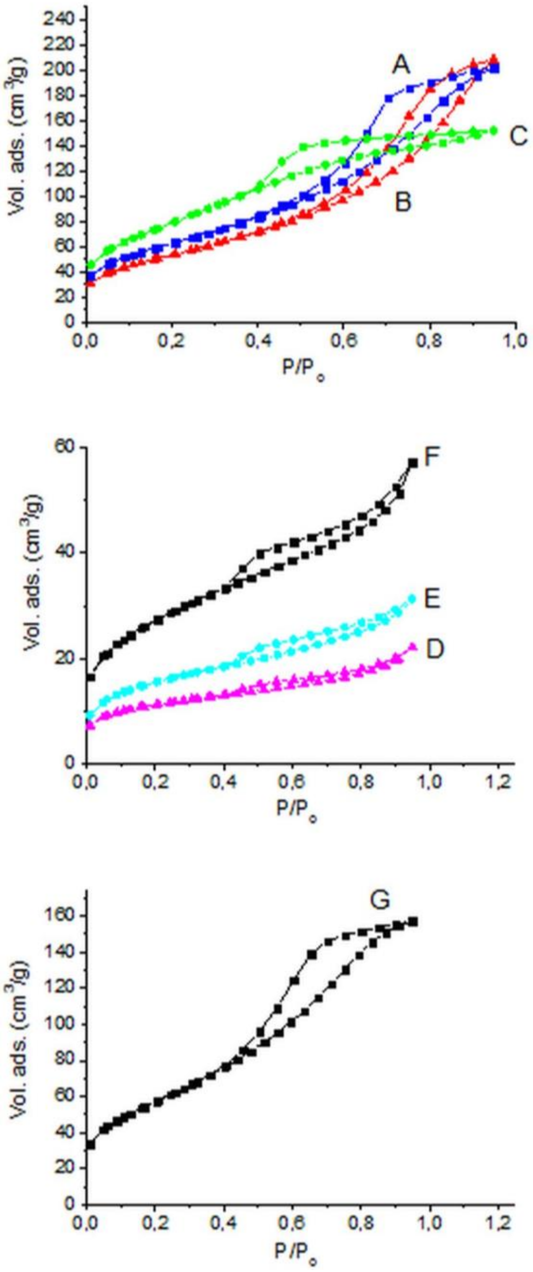


Fig. 4. Nitrogen adsorption-desorption isotherms of prepared mixed cobalt-copper ferrite-type materials measured at –196°C.

Figure 5 discloses TPR curves of the obtained ferrite-type samples and reduction temperature ranges from 200 to 800°C. All curves have two reduction peaks between 200 and 350°C that could be attributed to reduction of Co^{2+} and Cu^{2+} species to metallic cobalt and copper phases, respectively. At temperatures between *ca*. 350°C and end of reduction, the curve has several overlapping effects due to the reduction of Fe_2O_3. The TPR curves of samples C and F indicate a lower H_2 consumption in this interval, as it could be expected in advance due to a lower iron content in these samples. TPR curves belonging to samples of similar compositions show similar shapes, the shifts in temperature of the effects found for the reduction steps being due to differences in dispersion of the species formed depending on synthesis method used.

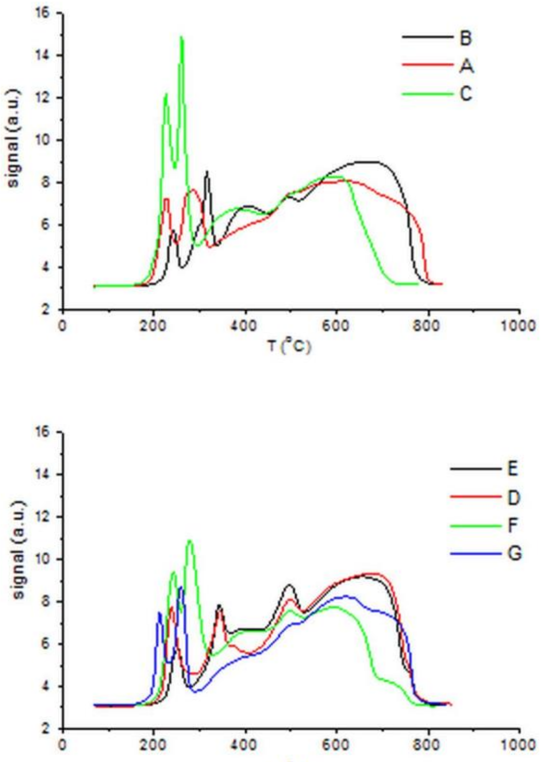


Fig. 5. TPR profiles of synthesized mixed cobalt-copper ferrite-type materials.

Table 2 summarizes ratios of hydrogen amount experimentally consumed during TPR analysis to theoretically needed amount for complete reduction of the cations, calculated from the content of each metal cation obtained by element chemical analysis of the samples. Experimental H_2 consumption values agree well with the calculated ones and a slight deviation is within the experimental error inherent to this technique [12].

The results obtained by PXRD, Mössbauer and FTIR spectroscopy, specific surface area, porosity measurements, and temperature-programmed reduction are in complete agreement.

Table 2. Ratio of experimental to calculated H_2 consumption based on TPR analysis.

Sample	Exp./calc. amount of consumed H_2
A	1.1
B	1.0
C	0.8
D	1.0
E	1.1
F	1.0
G	1.1

Prior to testing the photocatalytic activities of the samples, the adsorption capacities of the samples (mg dye/mg catalyst) were juxtaposed after 30 min of adsorption time interval in the dark (sufficient to reach adsorption-desorption): 0.02 (A), 0.04 (B), 0.04 (C), 0.06 (D), 0.07 (E), 0.07 (F), and 0.12 (G). Different starting points in figure 6 are due to different adsorption capacities of the samples, however, experimental runs were carried out at one and the same initial concentration, C_0 = 20 ppm. Figure 6 represents comparatively the course of the photocatalytic reaction with time interval of illumination of the RB5 aqueous solution. Photocatalytic testing results established that the conversion degrees of RB5 dye after 120 min over the mechanochemically treated photocatalysts E (78%) and F (77%) are higher than those over samples B (52%) and C (48%) prepared by coprecipitation. An enhancement of the degree of degradation of RB5 dye using the microwave-treated sample G (98%) as photocatalyst is also observed if compared with the coprecipitated sample A (96%) and the mechanochemically treated one D (73%).

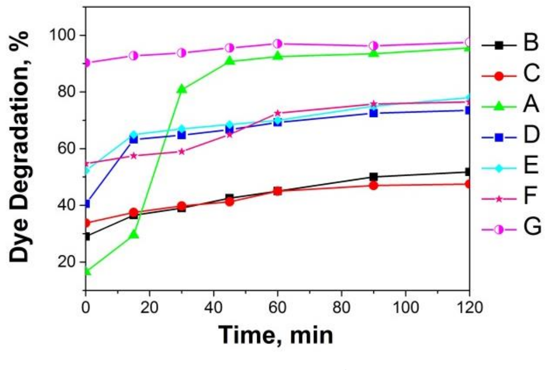


Fig. 6. Conversion degrees of RB5 dye solution determined as $[(C_0–C)/C_0]\times100\%$, where C_0 is the initial concentration (20 ppm) of RB5 dye before switching on the illumination and C is the current concentration with course of time (maximum absorbance at 599 nm azo bond (-N=N-) under UV-A illumination over mixed cobalt-copper ferrite-type photocatalysts.

An improvement of photocatalytic efficiency of the mixed cobalt-copper ferrite-type materials is achieved upon lowering the content of cobalt in the magnetite-type host structure. In the general case, the photocatalytic activities are correlating with adsorption capacity: the higher the capacity, the higher the activity with the exception of sample A. In spite of its lowest adsorption capacity, the latter sample is being activated in the course of the photocatalytic test reaching almost the same activity as that of sample G. The mechanism of this activation is not clear yet and it has to be elucidated in a future study. This effect is due to some adsorbed admixture that has remained on the surface after synthesis. In the course of the photocatalytic activity testing, under the effect of the illumination energy the adsorbed amount is being desorbed during the irradiation. Thus, the activation is probably enhancing liberation of adsorption sites, which is evident by a sharp increase in conversion degree with time.

CONCLUSIONS

Mixed cobalt-copper ferrite-type materials were successfully synthesized using coprecipitation and mechanochemical or microwave treatment. Powder X-ray diffraction data established the presence of spinel ferrite and an iron oxyhydroxide phase in the coprecipitated samples. The single ferrite phase was obtained after mechanochemical or microwave treatment of the mixed cobalt-copper ferrite-type materials. Superparamagnetic and collective magnetic excitation properties of the prepared ferrite powders were estimated by Mössbauer spectroscopy at both room and liquid nitrogen temperature. A coprecipitated $Co_{0.5}Cu_{0.5}Fe_2O_4$ sample exhibited the highest specific surface area of 286 $m^2.g^{-1}$, which was larger than that of other cobalt-copper ferrite-type materials. A microwave-treated $Co_{0.25}Cu_{0.25}Fe_{2.5}O_4$ sample exposed a specific surface area of 204 $m^2.g^{-1}$, being higher than that of a mechanochemically treated counterpart (S_{BET} = 37 $m^2.g^{-1}$). Photocatalytic studies proved that the mechanochemical treatment leads to an improved degradation conversion degree of RB5 dye after 120 min, 77 and 78% for the $Co_{0.5}Cu_{0.5}Fe_2O_4$ and $Co_{0.4}Cu_{0.1}Fe_{2.5}O_4$ samples, respectively, compared with coprecipitated $Co_{0.5}Cu_{0.5}Fe_2O_4$ (48%) and $Co_{0.4}Cu_{0.1}Fe_{2.5}O_4$ (52%) materials. In the case of microwave-treated $Co_{0.25}Cu_{0.25}Fe_{2.5}O_4$ sample the degree of discoloration (98%) was higher than that of coprecipitated $Co_{0.25}Cu_{0.25}Fe_{2.5}O_4$ (96%) and mechanochemically treated $Co_{0.25}Cu_{0.25}Fe_{2.5}O_4$ (73%) samples. The results indicate that the photocatalytic efficiency of synthesized cobalt-copper ferrites is dependent on the degree of incorporation of metal ions in the magnetite type structure and on the preparation conditions. Decreasing the cobalt content in the ferrite-type materials leads to an increase in photocatalytic activity. The present study shows that mixed cobalt-copper ferrite-type materials can find potential application to purification of polluted waters containing azo dyes.

Acknowledgements: Financial support by Bulgarian Science Fund through contract DFNI-T02-17/2014 is gratefully acknowledged.

REFERENCES

1. J. Balavijayalakshmi, N. Suriyanarayanan, R. Jayaprakash, V. Gopalakrishnan, *Phys. Procedia*, **49**, 49 (2013).
2. S. Jauhar, S. Singhal, *Ceram. Int.*, **40**, 11845 (2014).
3. Y. Pu, X. Tao, J. Zhai, J.-F. Chen, *Mater. Res. Bull.*, **45**, 616 (2010).
4. I. Ahmad, T. Abbas, M. U. Islam, A. Maqsood, *Ceram. Int.*, **39**, 6735 (2013).
5. N. Velinov, K. Koleva, T. Tsoncheva, D. Paneva, E. Manova, K. Tenchev, B. Kunev, I. Genova, I. Mitov, *Cent. Eur. J. Chem*., **12**, 250 (2014).
6. P. Malet, A. Caballero, *J. Chem. Soc. Faraday Trans.*, **84**, 2369 (1988).
7. U. Schwertmann, R. Cornell, Iron Oxides in the Laboratory, Weinheim, New York, 1991.
8. H. Emadi, A. Nemati Kharat, *J. Ind. Eng. Chem.*, **21**, 951 (2015).
9. F. A. Miller, C. H. Wilkins, *Anal. Chem.*, **24**, 1253 (1952).
10. K. S. W. Sing, D. H. Everett, R. A. W. Haul, L. Moscou, R. A. Pierotti, J. Rouquerol, T. Siemieniewska, *Pure Appl. Chem*., **57**, 603 (1985).
11. S. Lowell, J. Shields, M. A. Thomas, M. Thommes, Characterization of Porous Solids and Powders: Surface Area, Pore Size and Density, Springer Netherlands, 2010.
12. S. P. Newman, W. Jones, *New J. Chem.*, **22**, 105 (1998).

СМЕСЕНИ КОБАЛТ-МЕДНИ МАТЕРИАЛИ ОТ ФЕРИТЕН ТИП – СИНТЕЗ И ФОТОКАТАЛИТИЧНА АКТИВНОСТ В РАЗГРАЖДАНЕТО НА РЕАКТИВНО ЧЕРНО 5 БАГРИЛО ПРИ УВ ОБЛЪЧВАНЕ

К. Л. Захариева[1]*, К. И. Миленова[1], В. Ривес[2], Р. Трухиляно[2], З. П. Черкезова-Желева[1], Ал. Ел. Елияс[1], М. П. Цветков[3], Б. Н. Кунев[1], Ив. Г. Митов[1]

[1] Институт по катализ, Българска академия на науките, ул. „Акад. Г. Бончев“, бл. 11, 1113 София, България
[2] ПИГ-ХТТМХК, Департамент по неорганична химия, Университет на Саламанка, 37008-Саламанка, Испания
[3] Институт по физикохимия, Българска академия на науките, ул. „Акад. Г. Бончев“, бл. 11, 1113 София, България

Постъпила на 5 октомври 2015 г.; Преработена на 20 октомври 2015 г.

(Резюме)

Смесени кобалт-медни материали от феритен тип с различен състав бяха получени използвайки техника на съутаяване и механохимична или микровълнова обработка. Различни физикохимични методи като рентгенова дифракция и Мьосбауерова спектроскопия, инфрачервена спектроскопия с Фурие трансформация, БЕТ метод за специфичната повърхност, порьозността и температурно-програмирана редукция бяха използвани за охарактеризиране на получените проби от феритен тип. Фотокаталитичните активности на синтезираните кобалт-медни материали от феритен тип бяха изследвани в окислителното разграждане на Реактивно Черно 5 (РЧ5) багрило като моделен замърсител във воден разтвор при облъчване с УВ-А светлина. Фотокаталитични опити установиха, че микровълновата обработка на утаена проба $Co_{0.25}Cu_{0.25}Fe_{2.5}O_4$ води до по-висока степен на разграждане на РЧ5 багрилото (98%) в сравнение с тази при използване на утаения (96%) и механохимично обработения (73%) материал. Механохимичната обработка повишава степента на разграждане на РЧ5 багрилото след 120 мин осветяване: 77% и 78% за $Co_{0.5}Cu_{0.5}Fe_2O_4$ и $Co_{0.4}Cu_{0.1}Fe_{2.5}O_4$, в сравнение със съответните утаени проби (48% и 52%). Установено е подобрение на фотокаталитичната способност на получените кобалт-медни ферити с намаляване съдържанието на кобалт в материала. Фотокаталитичните свойства на получените смесени кобалт-медни проби от феритен тип зависят от степента на внедряване на металните йони в магнетитовия тип структура и от използваните методи за получаване.