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MECHANOCHEMICAL SYNTHESIS OF NANOSIZED MIXED OXIDES

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Abstract: *Fe_2O_3-ZnO nanosized mixed oxides samples were successfully synthesized using a simple mechanochemical method. The composites were characterized by X-ray diffraction (XRD), Fourier transform infrared, and UV-visible diffuse reflectance spectroscopies The pattern of XRD shows broadening in the diffraction peaks, indicating a decrease in the particle size of the samples with milling time.*

Keywords: *nanotribology, mechanochemistry, ball-milling, X-ray diffraction*

1. INTRODUCTION

The mixed oxides find application catalysts and support for catalysts, batteries, magnetic materials and gas sensors [1, 2]. The mixed metals oxides are used in the chemical and pharmaceutical industry. The catalytic activity of mixed oxide systems is usually higher than that of the individual oxide components. The research work is aimed at achieving the maximal efficiency. In order to achieve this aim two strategies are applied in general: modification of the method of preparation and addition of dopants. The mixed oxides are usually obtained in the form of powders and these represent a substantial part of the industrial catalysts due to their low price, easiness of regeneration and their selective action. They are prepared by the sol-gel method [3], solid state reaction method [4], co-precipitation [5], citric acid method [6], solution-combustion method [7-8], thermal decomposition method [9], mechanochemical processing [10-12], gas-phase flame synthesis and aerogel method [13]. Mechanochemical processing is a method for production of nanosized materials [11]. Its main advantage is the option to synthesize nanopowders at low temperatures by a simple one-step procedure of milling. Mechanochemistry is generally performed in high-energy ball mills using powder reactant mixtures. In this work we report on Fe2O3-Zno mixed oxides formation during milling in a planetary ball mill.

2. EXPERIMENTAL

Mechanochemical synthesis of Fe_2O_3-ZnO mixed oxides was performed in a laboratory planetary mill Pulverisette 6 (Fritsch, Germany) by high-energy milling of hematite and ZnO. The following experimental conditions were applied for the mechanochemical synthesis: loading of the mill, 50 balls of 10 mm in diameter; material of milling chamber and balls was tungsten carbide; volume of milling chamber, 250 ml; room temperature; rotational speed of the mill planet carrier 400 min^{-1}; milling time, 20 min.

X-ray powder diffraction patterns (XRD) of the samples were registered at room temperature with a TUR M62 apparatus with PC management and data accumulation, using HZG-4 goniometer with CoK_α radiation. The XRD lines were identified by comparing the measured patterns to the JCPDS data cards.

Specific surface area was determined by the low temperature nitrogen adsorption method in a Gemini 2360 sorption apparatus (Micromeritics, USA).

The phase evolution during high energy ball milling was followed by Nicolet 6700 FTIR spectrometer (thermo Electron Corporation, USA).

The method of dilution of the studied sample in KBr at concentration 0.5 % was used.

The diffuse reflectance UV–vis spectra were taken with a Thermo Evolution 300 UV-Vis Spectrophotometer equipped with a Praying Mantis device with Spectralon as the reference. Spectralon is a fluoropolymer, which has the highest diffuse reflectance of any known material or coating over the ultraviolet, visible, and near-infrared regions of the spectrum.

3. RESULTS AND DISCUSSION

Textural properties of initial hematite and rutile and mechanochemically synthesized mixed oxides are presented in Table 1.

Table 1. Samples composition and textural properties

Sample code	Chemical composition [%]		Specific surface area, m^2g^{-1}	Pore volume
	Fe_2O_3	ZnO		
ZnO	0.0	100.0	5.5	0.004
ZnO-MA	0.0	100.0	3.0	0.002
0.3 FZ	0.3	99.7	5.3	0.004
4.3 FZ	4.3	95.7	5.4	0.004
14.3 FZn	14.3	85.7	5.3	0.004
66 FZ	66.0	33.0	6.6	0.005

The XRD patterns of the Fe_2O_3-ZnO mixed oxides with different iron content are presented in Fig. 1.

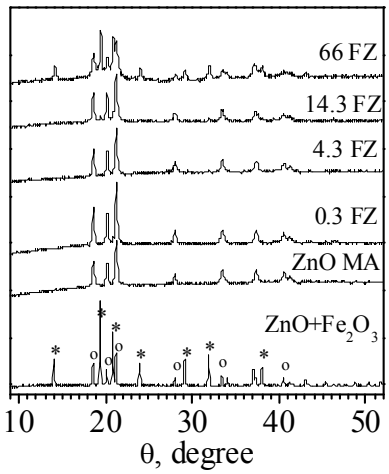

Figure 1. XRD patterns of the Fe_2O_3-ZnO sample. The mark (*) indicated the peaks corresponding to Fe_2O_3, and the marks (o) – peaks corresponding to ZnO.

The XRD diagram marks as ZnO+Fe_2O_3 corresponds to the starting mixture with molar ratio ZnO:Fe_2O_3 = 1:1 before milling. All the diffraction peaks of mechanical activated zinc oxide and 0.3 FZ sample can be well indexed to the hexagonal phase ZnO (JCPDS card no. 36-1451. A decrease in the reflection intensity was observed during milling. As milling proceeds broadening of diffraction peaks is observed due to grain size reduction.

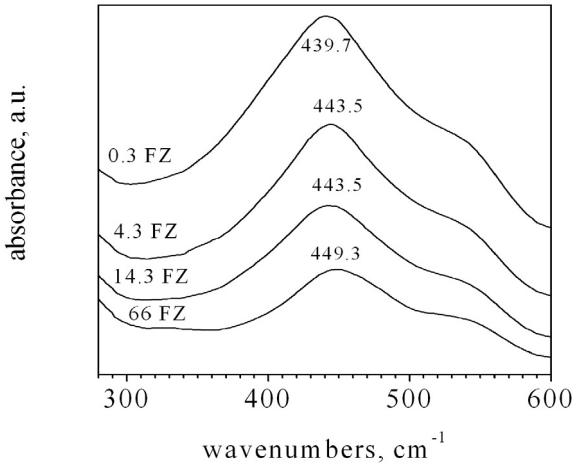

Figure 2. FTIR spectra of the Fe_2O_3-ZnO mixed oxides

Figure 2 shows the IFTR spectra the mechanically activated Fe_2O_3-ZnO mixed oxides. All the samples show prominent absorption band and shoulder at about 440 $cm^{-}1$ and 550 cm^{-1}, respectively. Slight variation with increasing of iron content in the samples is due to grain size influence the band position. The band at lower frequency of 440 cm-1 corresponds to M-O stretching vibration in octahedral site. This shift can be result of higher content of oxygen vacancies present in the structure and created during mechanical activation [14].

The diffuse reflectance of the ZnO and Fe_2O_3-ZnO mixed oxides are shown in Fig. 3. The spectra of the samples in UV region exhibit an absorption peak at about 220-250 nm attributable to isolated, tetrahedral coordinated species.

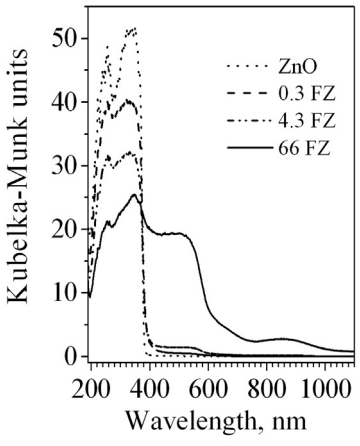

Figure 3. UV-vis diffuse reflectance spectra of ZnO and Fe_2O_3-ZnO mixed oxides

The samples with larger iron content show intense absorption in wide wavelength range from UV to visible light with absorption tail extending into infrared region. This means that Fe component was physically connected to the external surface of ZnO structure. The peak with maximum centred at

about 260 nm is related to isolated Fe^{3+} cations, while the second band at about 350 nm corresponds to small oligonuclear $(FeO)_n$ species. At higher iron content the peak around 520 nm is observed indicating the presence of iron oxide particles.

This peak can be assigned to symmetrical and spin forbidden d-d transitions of Fe^{3+} [15]. When the sample contains small iron content (sample 0.3 FZ), the band slightly shifts to the right without tail broadening. This means that the Fe component was well inserted inter the framework of the ZnO structure.

In a ball mill intense mixing takes place and reactants are brought into intimate contact with each other. Grinding reduces the particle size and increases the surface area available for reaction. New reactive surfaces are exposed during particle fracture and the introduction of dislocations increases the surface reactivity. At the point of contact between two grinding balls during a collision event, a highly localised triboplasma is formed giving energy for chemical reactions to occur.

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