



Nanosized copper ferrite materials: Mechanochemical synthesis and characterization

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ABSTRACT

Nanodimensional powders of cubic copper ferrite are synthesized by two-steps procedure of co-precipitation of copper and iron hydroxide carbonates, followed by mechanochemical treatment. X-ray powder diffraction, Mössbauer spectroscopy and temperature-programmed reduction are used for the characterization of the obtained materials. Their catalytic behavior is tested in methanol decomposition to hydrogen and CO and total oxidation of toluene. Formation of nanosized ferrite material is registered even after one hour of milling time. It is established that the prolonging of treatment procedure decreases the dispersion of the obtained product with the appearance of Fe₂O₃. It is demonstrated that the catalytic behavior of the samples depends not only on their initial phase composition, but on the concomitant ferrite phase transformations by the influence of the reaction medium.

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1. Introduction

Transition metal spinel oxides are technologically important as magnetic materials, semiconductors, pigments and as effective catalysts for number of industrial processes, such as aluminum production [1–4], oxidative dehydrogenation of butane to butadiene, two step thermochemical methane reforming [5], hydrodesulphurization of petroleum, photo-catalytic reactions [6], CO oxidation [7], treatment of automotive exhausted gases [8], hydrogen production by steam reforming of DME [9–11], etc. Copper ferrite is an inverse ferromagnetic spinel, which could be described as a cubic closed packed arrangement of oxygen ions with Cu²⁺ and Fe³⁺ cations in tetrahedral (A) and octahedral (B) coordination. The cations distribution in this structure can be represented by (Cu_xFe_{1-x})_A(Cu_{1-x}Fe_{1+x})_BO₄, where x is the inversion parameter and $x=0$ and 1 stands for the inverse and normal cases, respectively [12,13]. The crystal symmetry and the properties of these ferrites are highly sensitive to the cations distribution, which in turn depends on the method of preparation. It was established that depending on the preparation method, CuFe₂O₄ can crystallize either in tetragonal or cubic symmetry [14,15]. Although the stable low temperature ferrite phase is tetragonal, a deficit of Cu²⁺ cations in the B-sublattice leads to the absence of cooperative Jan-Teller distortion and transformation of crystal phase to cubic one [1,13–19]. Nedkov et al. [19] considered the formation of cubic structure of CuFe₂O₄ at temperatures below

600 K and tetragonal one above 700 K. Jiang et al. [12] demonstrated the predominant formation of CuFe₂O₄ with tetragonal unit cell symmetry if the sample is slowly cooled from high temperatures.

Nanosized spinel ferrites show unusual properties in comparison with their bulk analogs and receive enormous attention during last decade because of their potential applications [20–22]. They can be obtained by variety of methods such as solid state reaction [23,24], sol-gel [25], co-precipitation [23,25–27] and combustion synthesis [28]. The use of ball-milling [1,12,13] is alternative synthesis route with the preparation of material with particles in nanometer scale, with high vacancy densities and variations in the site population.

The aim of the present work is to investigate the possibility of CuFe₂O₄ nanodimensional powders synthesizing by co-precipitation of the corresponding hydroxide carbonate followed by mechanochemical treatment. The relationship between synthesis parameters, phase composition, structural and catalytic properties of the obtained materials is studied. Methanol decomposition to CO and hydrogen as well as total oxidation of toluene were used as test reactions in order to follow the effect of the reduction and oxidation reaction atmosphere, respectively, on the phase transformations of the obtained spinel materials.

2. Experimental

2.1. Materials

The synthesis of copper ferrites was performed by two step procedure, including (1) co-precipitation and (2) mechanical milling of the co-precipitation precursors as it was described in

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[29]. Co-precipitated hydroxide carbonates, which were used as precursors were prepared from aqueous solution of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ by dropwise addition of 1 M sodium carbonate up to pH 9 at continuous stirring. After washing (until the absence of nitrates) and drying at RT, brown substances are formed, denoted as $\text{CuFe}(\text{HC})$. The as-obtained precursor powders were milled using a Fritsch Planetary miller in a hardened steel vial together with grinding balls having different diameters (from 3 to 10 mm). The precursors were mechanically milled for 1, 2, 3 and 5 h. Samples were denoted as $\text{CuFe}(x)$, where x corresponds to the duration of milling treatment in hours.

2.2. Methods of investigation

The powder XRD patterns were recorded by use of a TUR M62 diffractometer with $\text{Co } K\alpha$ radiation. The observed patterns were cross-matched with those in the JCPDS database. The room temperature (RT) and liquid nitrogen temperature (LNT) Mössbauer spectra were obtained with a Wissel (Wissenschaftliche Elektronik GmbH, Germany) electromechanical spectrometer working in a constant acceleration mode. A $^{57}\text{Co}/\text{Cr}$ (activity $\cong 10 \text{ mCi}$) source and a $\alpha\text{-Fe}$ standard were used. The experimentally obtained spectra were fitted to mathematical processing according to the least squares method. The parameters of hyperfine interaction such as isomer shift (δ), quadrupole splitting (Δ), effective internal magnetic field (B), line widths (Γ_{exp}) and relative weight (G) of the partial components in the spectra were determined. Temperature-programmed reduction (TPR) of the samples was carried out in the measurement cell of a differential scanning calorimeter (DSC-111, SETARAM) directly connected to a gas chromatograph (GC). Measurements were made in the 300–973 K range at 10 K/min heating rate in a flow of $\text{Ar}:\text{H}_2=9:1$, the total flow rate being 20 ml/min. A cooling trap between DSC and GC removes the water obtained during the reduction.

Methanol decomposition experiments were carried out in a flow reactor using argon as a carrier gas, at methanol partial pressure of 1.57 kPa and $\text{WHSV}=1.5 \text{ h}^{-1}$. On-line gas chromatographic analysis were performed on HP 5890 on PLOT Q column, with simultaneous using of detector of thermo conductivity and flame ionization detector and an absolute calibration method. Toluene oxidation was studied at atmospheric pressure using a fixed-bed flow reactor, air as carrier gas and 30 mg sample (particle size 0.2–0.8 mm) diluted with 60 mg glass beads of the same diameter previously checked to be inactive. The air stream passed through a saturator filled with toluene and equilibrated at 273 K ($p_{\text{toluene}}=0.9 \text{ kPa}$). The activity was determined in the temperature interval of 623–723 K at $\text{WHSV}=1.2 \text{ h}^{-1}$. On-line analysis of the reaction products were performed using HP-GC with a 25 m PLOT Q capillary column.

3. Results and discussion

3.1. Physicochemical characterization

XRD patterns of the obtained pair copper and iron materials are presented in Fig. 1. Before the milling procedure only broad reflections of hydroxide carbonate precursor, $\text{CuFe}(\text{HC})$, could be distinguished. Well defined reflections of CuFe_2O_4 ($a=8.39 \text{ \AA}$, PDF 25-283) appear after 1 h of milling and a tendency of copper ferrite crystallization during the prolonging of milling procedure is observed. This assumption is well illustrated by the average particles size and microstrain degree, determined from the experimental XRD profiles by using the Williamson–Hall equation

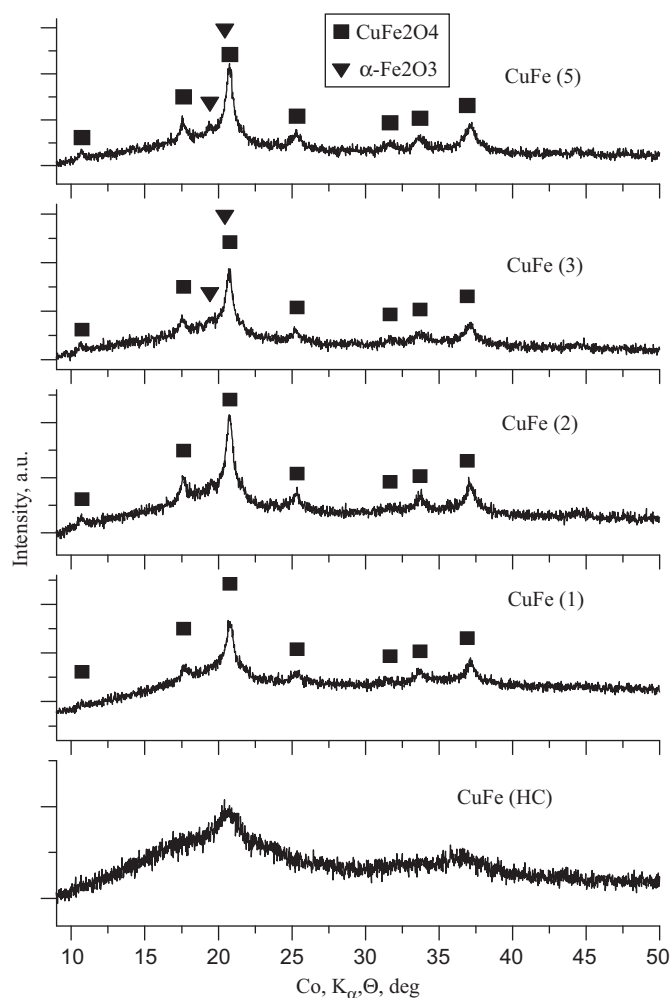


Fig. 1. XRD patterns of hydroxide carbonate precursor and the materials obtained after various milling duration.

Table 1

Average crystallites size (D), degree of microstrain (e) and lattice parameters (a) determined from the experimental XRD profiles.

Sample	Phase	D (nm)	$e \times 10^3$ (a.u.)	a (\AA)
CuFe(1)	CuFe_2O_4 -cubic	7.4	10.31	8.39
CuFe(2)	CuFe_2O_4 -cubic	9.2	9.87	8.39
CuFe(3)	CuFe_2O_4 -cubic	8.0	9.62	8.39
CuFe(5)	CuFe_2O_4 -cubic	9.9	5.64	8.38

[30] (Table 1). The obtained data indicate the increase of ferrite crystal size in the range of 7–10 nm with about two fold decrease of microstrain degree with increasing of treatment duration from 1 to 5 h. We should stress on the formation of impurities of crystalline $\alpha\text{-Fe}_2\text{O}_3$ phase (PDF 79-1741) in the case of the samples prepared after 3 and 5 h of milling.

In order to describe the state of iron containing phases more precisely, Mössbauer spectra of the studied materials were obtained (Fig. 2, Table 2). RT spectrum of $\text{CuFe}(\text{HC})$ sample exhibits a quadruple doublet with $\delta=0.36 \text{ mm/s}$, $\Delta=0.68 \text{ mm/s}$, indicating that the precursor is paramagnetic and the iron ions are in trivalent oxidized state. RT Mössbauer spectra of all materials after mechanochemical treatment represent doublets and sextets. The parameters of the doublet components of the spectra are typical of high spin Fe^{3+} ions in octahedral

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