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Structural; magnetic and catalytic properties of nanocrystalline $Cu_{0.5}Zn_{0.5}Fe_2O_4$ synthesized by microwave combustion and ball milling methods

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ABSTRACT

Effects of high energy ball-milling on nanosized $Cu_{0.5}Zn_{0.5}Fe_2O_4$ powders were studied at 30 and 330 min of milling. The powders were initially synthesized from its stoichiometric metal nitrates and urea mixtures, using a microwave assisted combustion method. Ball-milling induced electromechanical reaction was examined by XRD, TEM, Mössbauer spectroscopy, magnetization, and catalytic performance by exploring potential changes in size, phases and chemical structure. Before Milling, the as-prepared powders were comprised of small grains of poor spinel crystallinity and very small crystallite size, and a minor α-Fe_2O_3 phase. Progressive milling significantly reduced the grain size, increased chemical disorder, and reduced the hematite phase. These changes are also manifested in the magnetization measurements. The Catalytic activity performance was carried out using dehydrogenation of isopropyl alcohol. The observed activity was correlated to the presence of Cu^{2+} and Fe^{3+} catalysts at octahedral sites before and after milling.

1. Introduction

Nanocrystalline Spinel ferrites have been investigated intensively in recent years due to their promising technological applications in microwave devices, magnetic recording, and as an absorbent material [1–4]. Finite-size and surface effects, in addition to changes in the degree of inversion, cause nano ferrites to display novel magnetic behaviors. Small particles structurally differ from bulk solids, in that a large fraction of atoms resides at the surface. Therefore, surface-to-volume ratios in particles play a predominant role in influencing the material properties [5–7]. Physical and catalytic properties of the spinel oxides could be influenced not only by the nature and the oxidative state of the transition metal ions but also by their distribution in the spinel structure. The preparation method plays a very important role with regard to the chemical and structural properties of the spinel ferrite. Of particular interest is the low-temperature processing techniques, such as combustion synthesis (CS) and room-temperature ball-milling [8–13]. Microwave Combustion synthesis is an effective, low-cost method for the production of various nano-sized industrially useful materials. With this method, the heating and evaporation of desired nitrate solution employing an organic compound (usually glycine, urea, or citric acid, etc.) can result in self-firing to generate heat by exothermic reaction. This liberated heat is used to synthesize the ceramic oxide powders. This method has advantages of applying inexpensive raw materials, maintaining a relatively simple, quick and straight forward preparation process, and achieving a fine powder with high homogeneity. High-energy ball milling (HEBM) is a suitable solid-state processing technique to obtain nanostructures ferrites from the material in its bulk state. During the ball-milling, materials in powder form suffer severe high-energy impacts in the process of ball-to-ball and ball-to-vial wall collisions of the grinding media.

The ferrite is a promising material in chemical reactions as catalyst and it is well known that its activity is strongly dependent on the conditions of the synthesis route [14,15]. To our knowledge there is no systematic investigation on the catalytic dehydrogenation of isopropyl alcohol to acetone of $Cu_{0.5}Zn_{0.5}Fe_2O_4$ nanoparticles prepared by microwave combustion method as a catalyst

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using nitrogen as a carrier gas has not been reported yet.

The objectives of the present study are synthesis of $Cu_{0.5}Zn_{0.5}Fe_2O_4$ nanoparticles by the combination of microwave combustion and high-energy ball milling, and study the effects of preparation conditions and ball milling on the structural and magnetic properties. Also the effects of the preparation conditions and ball milling on their catalytic performance in the dehydrogenation of isopropyl alcohol were investigated.

2. Experimental

2.1. Materials and methods

The starting materials used were Fe $(NO_3)_3.9H_2O$, Cu $(NO_3)_2.3H_2O$, Zn $(NO_3)_2.6H_2O$ and $(CO\ (NH_{2)2})$. Cu–Zn ferrite powders $(Cu_{0.5}Zn_{0.5}F_2O_4)$ were prepared in two steps: (1) microwave combustion method, and (2) mechanical milling of the precursor. The appropriate amount of metal nitrates and urea $(CO\ (NH_{2)2})$ were dissolved in a minimum quantity of distilled water. The molar ratio of nitrates to urea was 1: 1. The solution was introduced into a microwave oven operating at a maximum power of 800 W for 20 min. The solution boils and undergoes dehydration followed by decomposition with the evolution of large amount of gases. After the solution reaches the point of spontaneous combustion, it begins burning and releases lots of heat, vaporizes all the solution instantly and becomes a solid powder. The as synthesized powder were milled for periods (30, 330 min) using a SPEX 8000, with vial and balls of tungsten carbide, and a ball-to-powder weight ratio (BPR) of 10:1.

2.2. Characterizations and measurements

Phase identification of the samples was performed using X-ray diffractometer equipped with an automatic divergent slit (XRD; Philips PW1700 diffractometer, Netherlands). Diffraction patterns were obtained using CuKα radiation ($\lambda = 0.15418$ nm) and a graphite monochromator in the 2θ range from 15° to 70°. The patterns were fitted using pseudo Lorentzian line shapes to account for the asymmetry of the peaks, and for accurate determination of lattice parameters and apparent crystallite size. The particle size, shape, and microstructure were further observed for some representative samples using a transmission electron microscope (TEM, Tecnai G20, Super twin, double tilt) operating at an accelerating voltage of 200 kV. The Mössbauer spectra of the samples were recorded with a time mode spectrometer at room temperature and 20 K. The source was ^{57}Co in a Rh matrix with an initial activity of 30 mCi. The characterization has been over a period of time and the same results were obtained which confirmed the structure and stability of the sample. The Magnetic measurements were carried out at room temperature using vibrating sample magnetometer (VSM) Lakeshore Model 7410 equipped with 2 T magnet. The specific surface areas of the catalyst samples were determined from Nitrogen adsorption–desorption isotherms, which measured at −196 °C using Quantachrome Instrument Corporation, USA (Model Nova 3200). Test samples were thoroughly out gassed for 2 h at 150 °C to a residual pressure of 10^{-5} torr and the weight of the out gassed sample was that used in calculations. The porosity of the catalysts determined from the desorption curve using Nova enhanced data reduction software (Version 2.13). The specific surface area of these nanoparticles was calculated by the BET equation. The catalytic activities of the various solid catalyst samples were tested by the dehydrogenation–dehydration using isopropyl alcohol (IPA) at 250 C° in a conventional fixed bed flow type Pyrex glass tube reactor at atmospheric pressure. A 0.2 g catalyst was placed in the middle of the reactor tube with quartz wool. In all tests, N_2 gas was used as carrier with a total flow rate of 50 ml/min. The temperature of the isopropanol in the saturator was set at 0 °C using dry ice. The reaction temperature was controlled with a Gallenkamp temperature controller. The exit feed was analyzed by direct sampling of the gaseous products into a Unicom PROGC gas Chromatograph using a flame ionization detector (FID). A mixture of IPA and N_2 was introduced into the reactor after nitrogen was bubbled through IPA saturator. The total flow rate was fixed at 50 ml/min. The gas feed of the reaction products was analyzed chromatographically by an FID on a Unicom PROGC using 10% PEG 400 glass column (2 m). Measurements of the conversion and yield (in %) were recorded after 2 h from the initial introduction of IPA into the reactor.

3. Results and discussion

3.1. Structure and crystallite size

The XRD patterns of different $Cu_{0.5}Zn_{0.5}Fe_2O_4$ powders synthesized by the combustion technique and milled at different periods of time are depicted in Fig. 1. All the characteristic peaks of Cu–Zn cubic spinel phase are present in the investigated diffraction pattern. A weak peak between (220) and (311) is observed for the as synthesized sample using microwave assisted combustion method (sample (a)) came from the existence of a small amount of α-Fe_2O_3 (Hematite) impurity and <15 wt% of CuO. The sample b represent the sample (a) milled for 30 min, in sample b the second phase lines become less noticeable. No secondary phases were detected in the diffraction patterns of the sample c (sample c indicate to the produced powder when the as prepared sample was milled for 330 min) which suggests the phase purity of the final product. The decrease of X-ray peak amplitude with increasing milling time correlates with the increased structural disorder caused by the ballistic nature of the milling processes. It is clear even with visual inspection that the widths of the X-ray lines increase with increasing milling time, which gives an evidence of a decrease in the mean particle size of the ball-milled samples. The average crystallite sizes D of the samples were determined from the full width at half maximum (FWHM) of the XRD patterns using the well-known Scherer formula [16,17]:

$$D = \frac{k \cdot \lambda}{\beta \cos\theta}, \tag{1}$$

Where β is the observed angular width at half maximum intensity

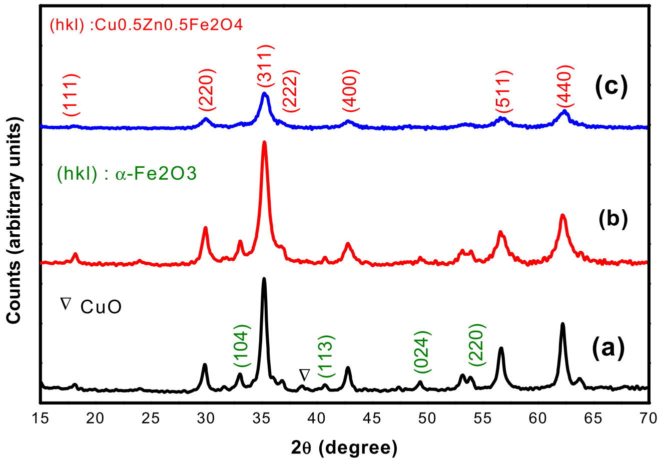

Fig. 1. XRD patterns of $Cu_{0.5}Zn_{0.5}Fe_2O_4$ samples (a) As prepared (b) milled for 30 min. (c) milled for 330 min.