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Effect of La_2O_3-treatment on textural and solid–solid interactions in ferric/cobaltic oxides system

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ABSTRACT

Pure and La_2O_3-containing (0.75–3.0 mol%) Fe_2O_3/Co_3O_4 solids were prepared by thermal treatment of their carbonates at 500–700 °C. The produced solids were characterized using XRD, HRTEM, EDX and nitrogen adsorption at −196 °C. The results revealed that pure solids calcined at 600 and 700 °C consisted of nanosized $CoFe_2O_4$ phase, while pure mixed solids calcined at 500 °C consisted of trace amount of $CoFe_2O_4$ and unreacted Fe_2O_3, Co_3O_4 phases. The presence of 0.75 mol% La_2O_3 enhanced solid–solid interaction between Fe_2O_3 and Co_3O_4 at 500 °C yielding $CoFe_2O_4$. The ferrite phase existed also in all mixed oxides upon treated with La_2O_3 besides $LaCoO_3$ phase. $LaCoO_3$ existed as a major phase in all mixed oxides treated with 3 mol% La_2O_3. La_2O_3-treatment modified the crystallite size of all phases present to an extent dependent on calcination temperature and amount of La_2O_3 content. This treatment decreased effectively the S_{BET} of all mixed solids.

1. Introduction

Metal oxides play a very important role in many areas of chemistry, physics, and materials science [1–5]. The metal elements are able to form a large diversity of oxide compounds. These can adopt a vast number of structural geometries with an electronic structure that can exhibit metallic, semiconductor, or insulator characteristics. In technological applications, oxides are used in fabrications of microelectronic circuits, sensors, piezoelectric devices, fuel cells, coatings for the passivation of surfaces against corrosion, and as catalyst [6–8].

Transition metal ferrites are the most widely used magnetic materials [9–13] that exhibit chemical stability, low electric loss, high coercivity and thus interesting magnetic properties. In addition to their application in microwave devices, computer memories and magnetic storage [14], these materials of type $M^{II}Fe_2^{III}O_4$ have been recently used in heterogeneous catalysis. The activity and selectivity of transition metal ferrites could be modified by treating with small amounts of other transition metal cations [15–20]. The mechanisms of ferrite formation have been the object of several investigations [21–23]. The solid–solid interactions between Fe_2O_3 and the transition metal oxide to produce the corresponding ferrite is normally controlled by the thermal diffusion of the reacting cations through the whole mass of each solid as well as the initially formed ferrite film covering the surfaces of the grains of each oxide [24–26].

The present work reports the results of a study on the effects of La_2O_3-treatment and calcination temperature on the physicochemical and surface properties of cobalt ferrites prepared by thermal treatment of their mixed carbonates at 500–700 °C. The mixed carbonates were prepared by coprecipitation from their nitrates solutions using 1 M Na_2CO_3 solution.

2. Experimental

2.1. Materials

All chemicals employed were of analytical grade and supplied by BDH company. Cobalt ferrites $CoFe_2O_4$ were prepared using wet chemical coprecipitation route. The nitrates of cobalt and iron were dissolved in distilled water at the designated molar ratio (Fe/Co=3). Aqueous solution of 1 M Na_2CO_3 was used as the precipitating agent. The metal nitrate solutions and the Na_2CO_3 solution were added dropwise from three separate burets into a reaction vessels containing 1 l of distilled water under mechanical stirring. The mode of coprecipitation was carried out by taking 25 ml of ferric nitrate followed by dropwise addition of Na_2CO_3 till complete coprecipitation of the ferric carbonate. This process was followed by dropwise addition of 50 ml of cobalt nitrate and 25 ml of ferric nitrate with vigorous stirring till complete coprecipitation of all mixed carbonates. The rate of addition was controlled in order to maintain a constant

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pH=8 during the co-precipitation process. Coprecipitation was thermostated at the desired temperature 70 °C. The precipitate was washed till free from NO_3^- and Na^+ ions. It was then filtered, dried at 100 °C overnight then calcined at 500, 600 and 700 °C for 5 h to achieve transformation into spinel phase.

Samples treated with lanthanum were obtained by treating a known mass of finely powdered mixed carbonates prepared by coprecipitation with a calculated amount of lanthanum nitrate dissolved in the least amounts of distilled water necessary to make a paste. The paste was dried at 100 °C to constant weight and then calcined at 500, 600 and 700 °C for 5 h. The nominal concentration of lanthanum in the doped samples expressed as mol% La_2O_3 was 1.5, 3 and 4.5, respectively.

2.2. Techniques

X-ray powder diffractograms of various investigated samples calcined at 400, 500 and 600 °C were determined using a Bruker diffractometer (Bruker D 8 advance target). The patterns were run with copper Kα with secondly monochromator ($\lambda=1.5405$ Å) at 40 kV and 40 mA. The scanning rate was 8° and 0.8° in 2θ min^{-1} for phase identification and line broadening profile analysis, respectively. The crystallite size of the phases present in pure and variously La_2O_3-treated solids determined using the Scherrer equation [27]:

$$d = K\lambda/\beta_{1/2}\cos\theta$$

where d is the mean crystalline diameter, λ is the X-ray wave length, K is the Scherrer constant (0.89), $\beta_{1/2}$ is the full width at half maximum (FWHM) of the main diffraction peaks of the investigated phases, in radian and θ is the diffraction angle.

The nano-structure of the samples was examined using very dilute suspensions in water by the aid of JEOL-2100 high resolution transmission electron microscope (HRTEM) with accelerating voltage up to 200 kV. The microscopy probes of the sample was prepared by adding a small drop of the water dispersions onto a lacey carbon film-coated copper grid and allowed to dry initially in air then by applying high vacuum.

Energy dispersive X-ray analysis (EDX) was carried out on a Hitachi S-800 electron microscope with a Kevex Delta system attached. The parameters were as follows: −15 kV accelerating voltage, 100 s accumulation time, 8 μm window width. The surface molar composition was determined by the Asa method (Zaf-correction, Gaussian approximation).

Different surface characteristics namely; specific surface area (S_{BET}), total pore volume (V_p) and mean pore radius (r^-) of various solids were determined from nitrogen adsorption–desorption isotherms measured at −196 °C using conventional volumetric apparatus. Before undertaking such measurements, each sample was degassed under a reduced pressure of 10^{-5} Torr for 3 h at 200 °C. The values of V_p were computed from the relation:

$$V_p = 15.45 \times 10^{-4} \times V_{st}\ cm^3/g$$

where V_{st} is the volume of nitrogen adsorbed at P/P^0 tends to unity. The values of r^- were determined from the equation:

$$r^- = \frac{2V_p}{S_{BET}} \times 10^4 Å.$$

3. Results and discussion

3.1. X-ray investigation of various solids

X-ray diffractograms of pure and variously La_2O_3-treated solids being calcined at 500–700 °C were determined. The diffractograms of the investigated solids are given in Figs. 1–3

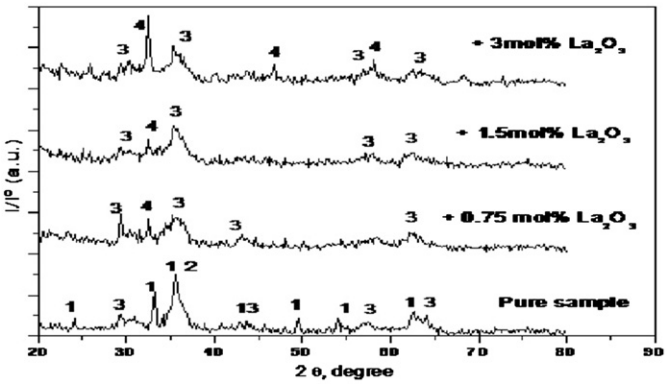

Fig. 1. X-ray diffractograms of pure and treated solids calcined at 500 °C, Lines 1 refer to Fe_2O_3, Lines 2 refers to Co_3O_4, Lines 3 refers to $CoFe_2O_4$ and Lines 4 refers to $LaCoO_3$.

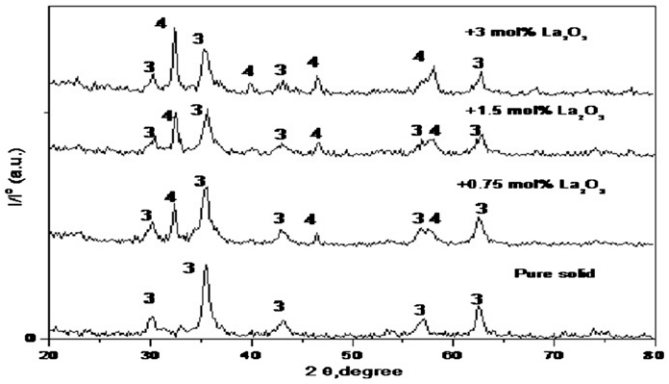

Fig. 2. X-ray diffractograms of pure and treated solids calcined at 600 °C, Lines 1 refer to Fe_2O_3, Lines 2 refers to Co_3O_4, Lines 3 refers to $CoFe_2O_4$ and Lines 4 refers to $LaCoO_3$.

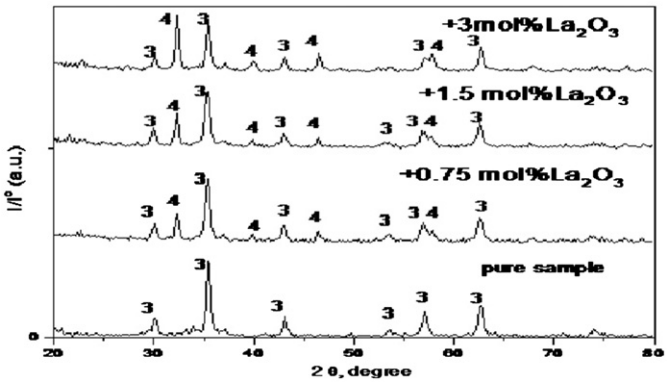

Fig. 3. X-ray diffractograms of pure and treated solids calcined at 700 °C, Lines 1 refer to Fe_2O_3, Lines 2 refers to Co_3O_4, Lines 3 refers to $CoFe_2O_4$ and Lines 4 refers to $LaCoO_3$.

corresponding to the solids calcined at 500, 600 and 700 °C, respectively. It is clear from these figures that the diffractograms of pure Fe_2O_3/Co_3O_4 calcined at 500 °C consisted of the diffraction peaks of $CoFe_2O_4$ as a major phase together with all diffraction peaks of unreacted α-Fe_2O_3 and Co_3O_4 phases. This finding shows clearly that heating a mixture of pure Fe_2O_3 and Co_3O_4 at 500 °C for 5 h. was not sufficient for their complete conversion into the ferrite phase. It can also be seen from Fig. 1 that the presence of the smallest amount of La_2O_3 (0.75 mol%) in mixed solids calcined at 500 °C led to the complete disappearance of Fe_2O_3 and Co_3O_4 as