Available online at www.sciencedirect.com

ScienceDirect

Thermochimica Acta 470 (2008) 18–26

thermochimica acta

www.elsevier.com/locate/tca

# Thermal solid–solid interactions and physicochemical properties of $NiO/Fe_2O_3$ system doped with $K_2O$

W.M. Shaheen

*Physical Chemistry Department, Catalysis and Surface Laboratory, National Research Center, Dokki, Cairo, Egypt*

Received 19 April 2007; received in revised form 15 January 2008; accepted 16 January 2008
Available online 21 January 2008

## Abstract

The effects of calcination temperature and doping with $K_2O$ on solid–solid interactions and physicochemical properties of $NiO/Fe_2O_3$ system were investigated using TG, DTA and XRD techniques. The amounts of potassium, expressed as mol% $K_2O$ were 0.62, 1.23, 2.44 and 4.26. The pure and variously doped mixed solids were thermally treated at 300, 500, 750, 900 and 1000 °C. The catalytic activity was determined for each solid in $H_2O_2$ decomposition reaction at 30–50 °C. The results obtained showed that the doping process much affected the degree of crystallinity of both NiO and $Fe_2O_3$ phases detected for all solids calcined at 300 and 500 °C. $Fe_2O_3$ interacted readily with NiO at temperature starting from 700 °C producing crystalline $NiFe_2O_4$ phase. The degree of reaction propagation increased with increasing calcination temperature. The completion of this reaction required a prolonged heating at temperature >900 °C. $K_2O$-doping stimulates the ferrite formation to an extent proportional to its amount added. The stimulation effect of potassium was evidenced by following up the change in the peak height of certain diffraction lines characteristic NiO, $Fe_2O_3$, $NiFe_2O_4$ phases located at "d" spacing 2.08, 2.69 and 2.95 Å, respectively. The change of peak height of the diffraction lines at 2.95 Å as a function of firing temperature of pure and doped mixed solids enabled the calculation of the activation energy ($\Delta E$) of the ferrite formation. The computed $\Delta E$ values were 120, 80, 49, 36 and 25 kJ mol$^{-1}$ for pure and variously doped solids, respectively. The decrease in $\Delta E$ value of $NiFe_2O_4$ formation as a function of dopant added was not only attributed to an effective increase in the mobility of reacting cations but also to the formation of potassium ferrite. The calcination temperature and doping with $K_2O$ much affected the catalytic activity of the system under investigation.

*Keywords:* TG–DTA; XRD; $NiO/Fe_2O_3$; $NiFe_2O_4$; Catalytic activity

## 1. Introduction

A great deal of fundamental research has been done on mixed catalysts in the field of heterogeneous catalysis [1–3]. These mixed systems may be more active than their individual components [4,5]. The so-called mixed catalysts are often produced by thermal decomposition of mixed components of transition metals [6]. The thermal treatment of mixed solid components may lead to the formation of new compounds as a result of solid–solid interactions between thermal products [7,8].

Most of divalent metal oxides (MO) interact with $Fe_2O_3$ yielding the corresponding ferrite with the formula $MFe_2O_4$. These ferrites are important materials that found wide uses in many industrial applications. Cobalt, nickel, copper, zinc and manganese ferrite were normally employed as active catalysts in a big variety of catalytic reactions. These reactions include oxidation, decomposition of alcohols and decarboxylation of some organic acids. Therefore, preparation of ferrite composites with certain specific properties as well as the mechanism of their formation became the object of several investigations [9–13]. On the other hand, ferrites crystallize in three crystal types, namely, spinel, garnet and magnetoplumbite [14]. These spinel ferrites can be obtained by solid–solid interactions between ferric and transition metal oxides or carbonates. The produced ferrites are much influenced by the prehistory of parent solids, their ratio and also by addition of small amount of certain foreign oxides [15–17].

The present work reports the results of a study on the effects of calcination temperature and doping with different amounts of $K_2O$ on solid–solid interactions and physicochemical properties of $NiO/Fe_2O_3$ system. Pure and variously doped mixed

---

*E-mail address:* waleed_shaheen@hotmail.com.

0040-6031/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2008.01.012

solids were calcined at 300, 500, 750, 900 and 1000 °C. The thermal products obtained at various treatment temperatures were characterized using thermal analyses (TG–DTA) and X-ray diffraction (XRD) techniques. The catalytic activity of all solids was measured by using catalytic decomposition of hydrogen peroxide at 30, 40 and 50 °C.

## 2. Experimental

### 2.1. Materials

The starting materials used in this investigation were solids of basic nickel carbonate [$NiCO_3 \cdot 2Ni(OH)_3 \cdot 4H_2O$], basic iron carbonate, $FeCO_3 \cdot Fe(OH)_3$ and potassium nitrate, $KNO_3$. The chemicals employed were of analytical grade and were supplied by Prolabo Company.

A series of mixed oxide catalysts of $NiO/Fe_2O_3$ system having equal molar ratio were prepared by mechanical mixing of their corresponding salts. The mixed oxides were obtained by firing the mixed solids in air at 300, 500, 750, 900 and 1000 °C for 4 h.

Samples of the doped mixed solids were prepared by impregnation method by treating a given mass of the prepared mixed solids of nickel and iron carbonates with solutions containing different proportions of potassium nitrate dissolved in the least amount of distilled water. The extents of doping expressed in mol% $K_2O$ were 0.62, 1.23, 2.44 and 4.26. The pure and doped solids were dried at 100 °C then calcined in air at 300, 500, 750, 900 and 1000 °C for 4 h.

### 2.2. Techniques

Thermal analyses, i.e., thermogravimetry (TG) and differential thermal analysis (DTA) were carried out using a Shimadzu Dt-40 thermal analyzer. The sample was placed in platinum crucible (0.1 $cm^3$). The samples were studied under air atmosphere with flowing rate of 30 ml/min. Constant weights of sample (62–69 mg) were used in order to avoid the effect of variation in sample weight on peak shape and temperature. Alpha alumina was used as a reference material in this technique. The rate of heating was fixed at 10 °C $min^{-1}$.

An X-ray investigation of pure and variously doped solids preheated in air at 300, 500, 750, 900 and 1000 °C was conducted using a Philips diffractometer (Goniometer PW 1390), employing iron Ka radiation as the X-ray source. The X-ray tube was operated at 36 kV and 16 mA. The samples were finely grounded and packed in plastic holder. The diffraction angle $2\theta$ was scanned at a rate of 2° $min^{-1}$.

The catalytic activity of pure and doped solids was determined using $H_2O_2$ decomposition in aqueous solution, as a model reaction, at 30, 40 and 50 °C, using 0.5 ml volume of $H_2O_2$ of known concentration diluted to 20 ml with distilled water. The mass of catalyst sample taken in each kinetic experimental was fixed at 10 mg for all samples. The reaction was followed up throughout a gasmetric measurment of oxygen liberated at different time interval. Details of experimental method have been given elsewhere [18].

## 3. Results and discussion

### 3.1. Thermal behavior of pure and variously doped mixed solids

Fig. 1a shows the (TG–DTA) curves of pure mixed solids having the formula $1/3NiCO_3 \cdot 2Ni(OH)_3 \cdot 4H_2O/FeCO_3 \cdot Fe(OH)_2$. The thermograms obtained from the mixed solids treated with small percentage of $K_2O$ were similar to each other and that of pure mixed solids. The DTA curve of pure mixed solids shows three endothermic peaks with their minima located at 56, 228 and 302 °C. In addition, an exothermic peak its maximum located at 800 °C was detected. The TG curve consisted of three weight loss processes at temperature ranged between 55 and 110 °C, 180 and 250 °C, and 280 and 400 °C. These processes were accompanied by total weight losses of 7.5, 22.5 and 29.5%. The first process corresponds to the departure of physisorbed water from both salts and the removal of water of crystallization of basic nickel carbonate [17]. The second process represents the simultaneous thermal decomposition of the $NiCO_3$ and $Ni(OH)_2$ of the anhydrous basic nickel carbonate and formation of Fe(OOH). The last process indicates the complete thermal decomposition

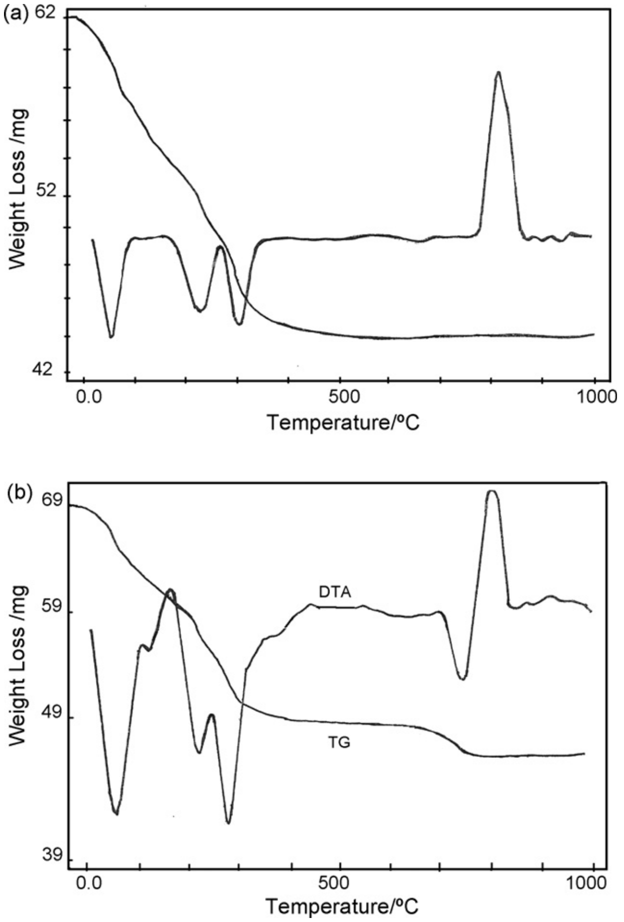

Fig. 1. (a) Thermal analysis of pure mixed solids with the formula [$1/3NiCO_3 \cdot 2Ni(OH)_3 \cdot 4H_2O/FeCO_3 \cdot Fe(OH)_2$]. (b) Thermal analysis of treated solids with the formula [$1/3NiCO_3 \cdot 2Ni(OH)_3 \cdot 4H_2O/0.4KNO_3/FeCO_3 \cdot Fe(OH)_2$].

of both salts into NiO and $Fe_2O_3$ [17,19]. The weight of this sample did not undergo any change on heating at ≥500 °C with the detection of an exothermic peak with its maxima located at 800 °C. This might reflect a probability of solid–solid interaction between the produced oxides to form nickel ferrite according to the following equation [17,20]:

$$NiO + Fe_2O_3 \rightarrow NiFe_2O_4$$

The TGA and DTA curves of the heavily $K_2O$ treated sample having the formula [$1/3NiCO_3 \cdot 2Ni(OH)_3 \cdot 4H_2O/0 \cdot 4KNO_3/FeCO_3 \cdot Fe(OH)_2$] are illustrated in Fig. 1b. The TGA curve of this sample showed four weight loss processes at temperature ranged between 50 and 110 °C, 190 and 250 °C, 260 and 300 °C, and 670 and 750 °C. These processes were accompanied by total weight losses of 7, 20, 32 and 33%. These processes were accompanied with the detection of three endothermic peaks whose minima were located at 70, 225, 283 and 750 °C. In addition, an exothermic peak with its maxima located at 799 °C.

The comparison of DTA curves of pure and doped solids revealed that potassium-doping enhanced the thermal decomposition of both basic nickel and iron carbonates into their corresponding oxides. The endothermic peak relative to this process shifted from 300 to 280 °C. Furthermore, the complete conversion of basic nickel carbonate, potassium nitrate and basic iron carbonate solids into the corresponding NiO, $K_2O$ and $Fe_2O_3$ takes place at about 280 °C with a total weight loss of 32% which is very close to the value found theoretically. The endothermic peak located at 750 °C and the exothermic peak located at 799 °C may correspond to the formation of potassium and nickel ferrite compounds, $KFe_{11}O_{17}$ and $NiFe_2O_4$, respectively. The identification of these compounds will be discussed later in the XRD section of the present work.

### 3.2. XRD investigation of pure and doped mixed solids precalcined at different temperatures

Figs. 2–6 represent the X-ray diffractograms of pure and various $K_2O$-doped $NiO/Fe_2O_3$ system calcined at 300, 500, 750, 900 and 1000 °C. In addition, Table 1 shows the effect of $K_2O$-doping and calcination temperature of $NiO/Fe_2O_3$ system on the peak height of main diffraction lines of detected phases. The examination of these figures and Table 1 shows that: (i) pure and doped solids calcined at 300 and 500 °C consisted only of the diffraction lines of NiO and $Fe_2O_3$ phases. (ii) The peak heights and the degree of crystallinity of both NiO and $Fe_2O_3$ phases progressively increased with increasing the calcination temperature. (iii) The addition of increasing amounts of $K_2O$ followed by calcination at 300 and 500 °C resulted in a progressive decrease in the peak heights and the degree of crystallinity of the detected phases with the absence of any diffraction lines of potassium oxide as a separate phase. Furthermore, the diffraction lines of NiO completely disappeared in the heavily $K_2O$-doped sample calcined at 300 °C. (iv) The X-ray diffractograms of pure and variously doped solids calcined at 750 and 900 °C consisted of the diffraction lines of free oxides as major phase together with the appearance of new diffraction peaks characteristic of nickel ferrite ($NiFe_2O_4$) phase. (v) The peak height of the main diffraction lines of nickel ferrite increased by increasing the amount of dopant up to certain extent as well as with increasing the calcination temperature to 1000 °C. (vi) The X-ray diffractograms of pure solids heavily doped with $K_2O$ and calcined at 750, 900 and 1000 °C show the detection of new diffraction lines ($d$ = 5.94, 2.97, 2.83, 2.57 and 2.54) characteristic to potassium ferrite ($KFe_{11}O_{17}$) phase beside NiO and $NiFe_2O_4$ phases with the disappearance of all diffraction lines of $Fe_2O_3$ for the solids heavily doped with $K_2O$. (vii) Furthermore, increasing the calcination temperature of all solids to 1000 °C was resulted in decreasing of the peak height of NiO and $Fe_2O_3$ phases. In contrast, the degree of crystallinity of both nickel and potassium ferrite phases increased.

Inspection of the above results indicates that: (i) no solid–solid interaction between NiO and $Fe_2O_3$ takes place at calcination temperature below 700 °C. (ii) The presence of diffraction lines of free oxides in the case of pure mixed solids preheated at 1000 °C showed that the complete conversion of these oxides into $NiFe_2O_4$ requires a prolonged heating at temperature >1000 °C [21]. It seems that the ferrite produced at 750 °C covers the surfaces of grains of the free oxides hindering their further diffusion. So, the nickel ferrite formed initially acts as an energy barrier against the completion of the solid–solid

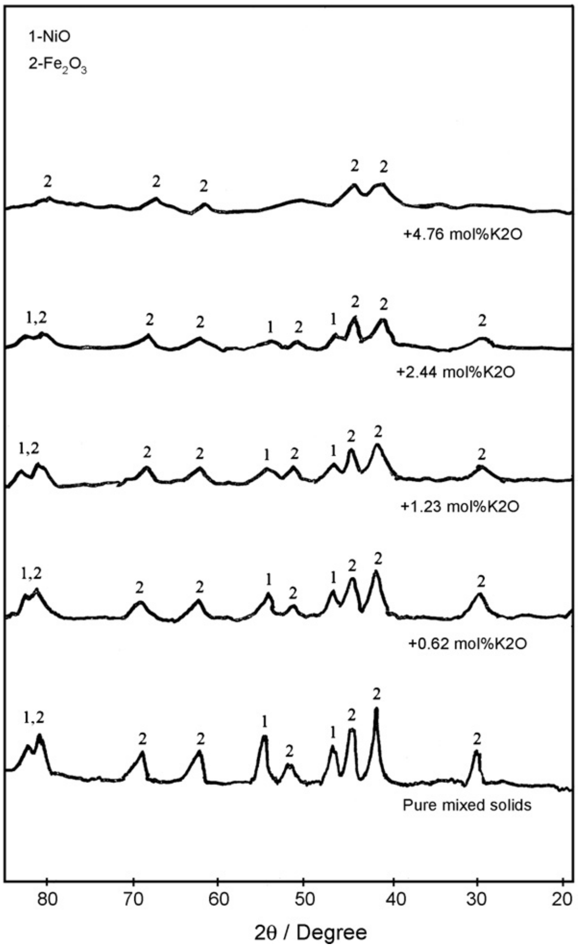

Fig. 2. X-ray diffractograms of pure mixed solids and that doped with different amounts of $K_2O$ followed by calcination at 300 °C.

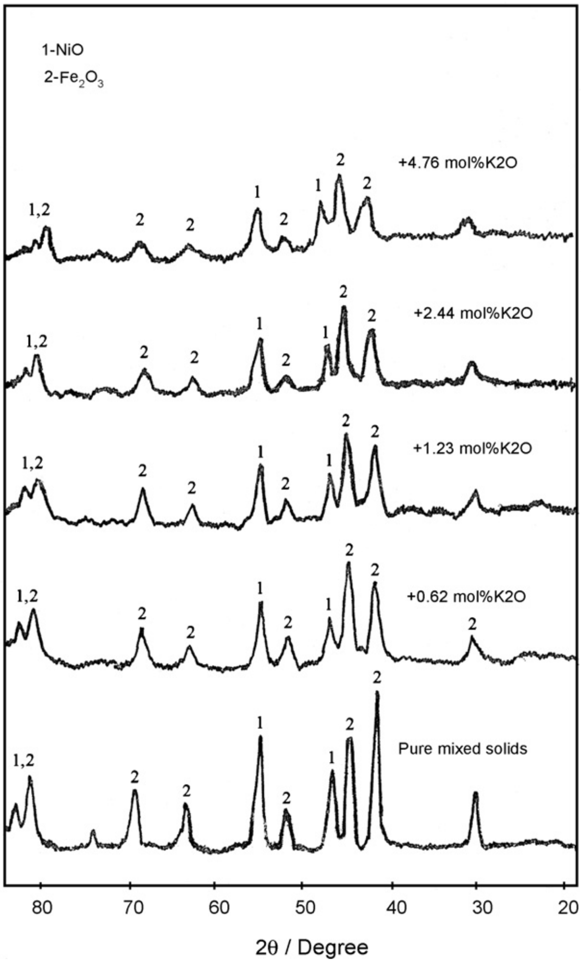

Fig. 3. X-ray diffractograms of pure mixed solids and that doped with different amounts of $K_2O$ followed by calcination at 500 °C.

interaction between NiO and $Fe_2O_3$. It has been reported by El-Shobaky et al. [16,17] that this energy barrier could be overcome by doping the reacting mixed solids with certain foreign oxides as $Li_2O$, $Al_2O_3$ or ZnO.

In this work, it can be seen that the doping of the system under investigation with $K_2O$ resulted in stimulation of nickel ferrite formation. The observed enhancement of nickel ferrite formation as a result of doping with $K_2O$ and consequent increase in the mobility of the diffusion of nickel ions through the growing $NiFe_2O_4$ phase can be investigated by determining the activation energy of nickel ferrite formation ($\Delta E$) for pure and $K_2O$-doped mixed solids. This has been achieved from the results given in Table 1 by assuming that the height of the characterized diffraction line at 2.95 Å is a measure of the amount of $NiFe_2O_4$ present in given mixed solids at definite temperature ($T$). By plotting the peak height of the diffraction line at 2.95 Å versus $1/T$, a straight line is obtained whose slope determines ($\Delta E$) value by direct application of the Arrhenius equation (see Fig. 7). The computed ($\Delta E$) values 120, 80, 49, 36 and 25 kJ mol$^{-1}$ for pure and those solids doped with 0.62, 1.23, 2.44 and 4.26 mol% $K_2O$, respectively. The decrease in ($\Delta E$) values, due to potassium-doping to an extent proportional to the amount of $K_2O$ present, reflects an effective increase in the mobility of thermal diffusion of the reacting oxides and consequent easily solid-state reaction process. It can also be seen from Table 1 that the presence of $K_2O$ brought about a regular decrease in the peak heights of the diffraction lines at 2.08 and 2.69 Å characteristic to NiO and $Fe_2O_3$ with a subsequent increase in the peak height of the line at 2.95 Å characteristic to $NiFe_2O_4$ phase. These results showed clearly that $K_2O$-doping enhances the ferrite formation to an extent, proportional to its amount present.

### 3.3. Catalytic activity measurements of pure and doped mixed solids precalcined at different temperatures

The experimental results obtained revealed that the decomposition of $H_2O_2$ over pure and variously $K_2O$-doped NiO/$Fe_2O_3$ system calcined at 300 and 500 °C followed first-order kinetics. The kinetics of the catalyzed reaction being monitored for reactions carried out at 30, 40 and 50 °C by measuring the volume liberated oxygen at different time intervals until no further $O_2$ was liberated. Table 2 depicts the values of reaction rate constant $k$ (min$^{-1}$) measured at different reaction temperatures. The val-

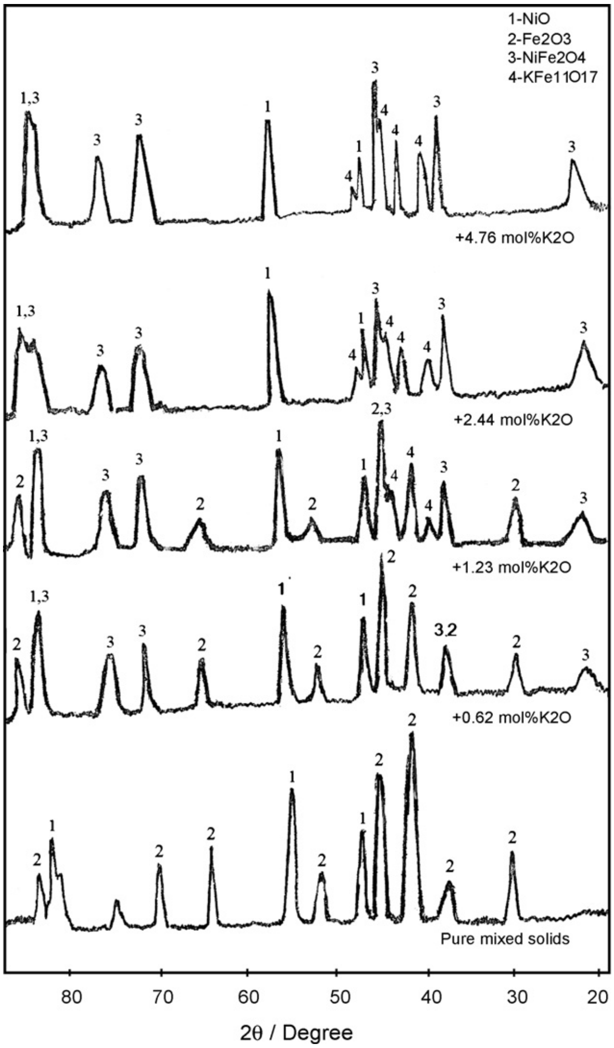

Fig. 4. X-ray diffractograms of pure mixed solids and that doped with different amounts of $K_2O$ followed by calcination at 750 °C.

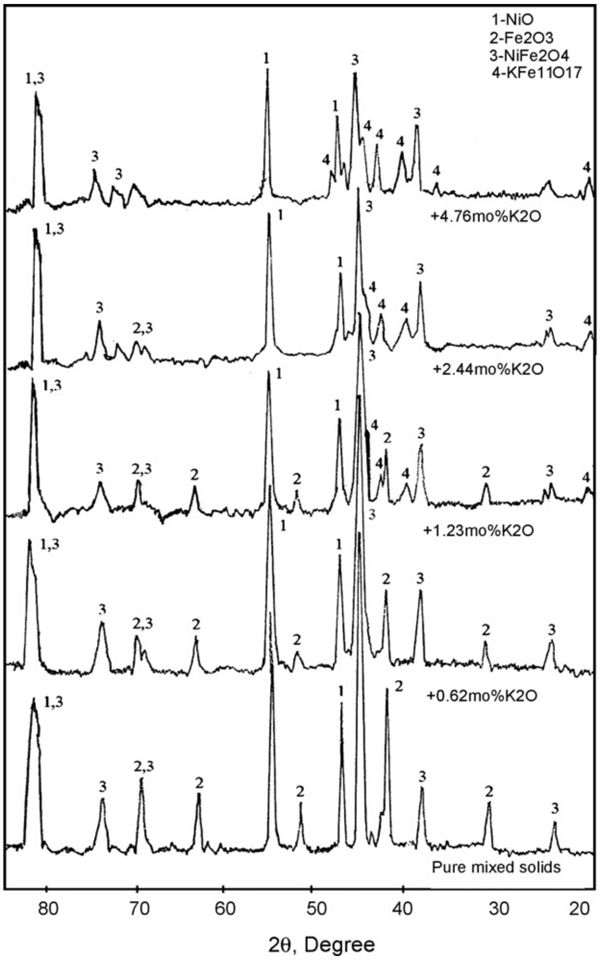

Fig. 5. X-ray diffractograms of pure mixed solids and that doped with different amounts of $K_2O$ followed by calcination at 900 °C.

ues of rate constants were obtained from the plots of $\ln(a/a-x)$ against time, where $a$ is the initial concentration of $H_2O_2$ and $x$ is the amount of evolved oxygen (see Fig. 8a and b). In addition, the effect of doping process and calcination temperature on the catalytic activity of $NiO/Fe_2O_3$ system under investigation is represented in Fig. 9a and b.

Inspection of the data given in Table 1 and Figs. 8–9 shows that: (i) individual NiO or $Fe_2O_3$ obtained by thermal treatment of their salts at 300 and 500 °C exhibit a very small catalytic activity in $H_2O_2$ decomposition. (ii) The catalytic activity of mixed $NiO–Fe_2O_3$ obtained by thermal treatment of mixed solids at the same calcination temperatures was found to be greater than those of single oxides. This can be interpreted in terms of the concept of bivalent catalytic centers [6,22]. In other words, the higher catalytic activity of two component oxides may be attributed to the fact that besides the one-component sites $Ni^{+2}$ or $Fe^{+3}$ there will also be the mixed sites ($Ni^{+2}$–$Fe^{+3}$). (iii) The catalytic activities of pure and variously doped solids progressively increased with increasing the reaction temperature from 30 to 50 °C. In addition, it decreased on increasing their calcination temperatures from 300 to 500 °C. (iv) Treating the system investigated with an increasing amount of $K_2O$ followed by calcination at 300 resulted in a progressive increase in the ($k$) values reaching to a maximum limit in the presence of 1.23 mol% $K_2O$ then decreased by increasing the amount of $K_2O$ added above this limit. The maximum increase in the catalytic activity measured at 30 °C attained 41%. The XRD investigation of pure and variously $K_2O$-doped solids calcined at 300 and 500 °C showed clearly that this treatment decreased the crystallite size of both NiO and $Fe_2O_3$ phases. This finding might lead to an effective increase in the external surface area of both NiO and $Fe_2O_3$ with subsequent increases in the concentration of active sites taking part in $H_2O_2$ decomposition.

On the other hand, it was found by many authors that alkali-doping of transition metal oxide catalysts is normally accompanied by an increase in its catalytic activity [22–24]. This expectation comes from the fact that the alkalinity treatment of solid catalysts increases the (pH) value of the solution. The results of this work show that $K_2O$ treatment of the investigated system was thought to increase its catalytic activity towards $H_2O_2$ decomposition due to a possibly induced increase in the pH value of $H_2O_2$ solution. Preliminary experiments showed that the pH value of the solution resulting from treating a given

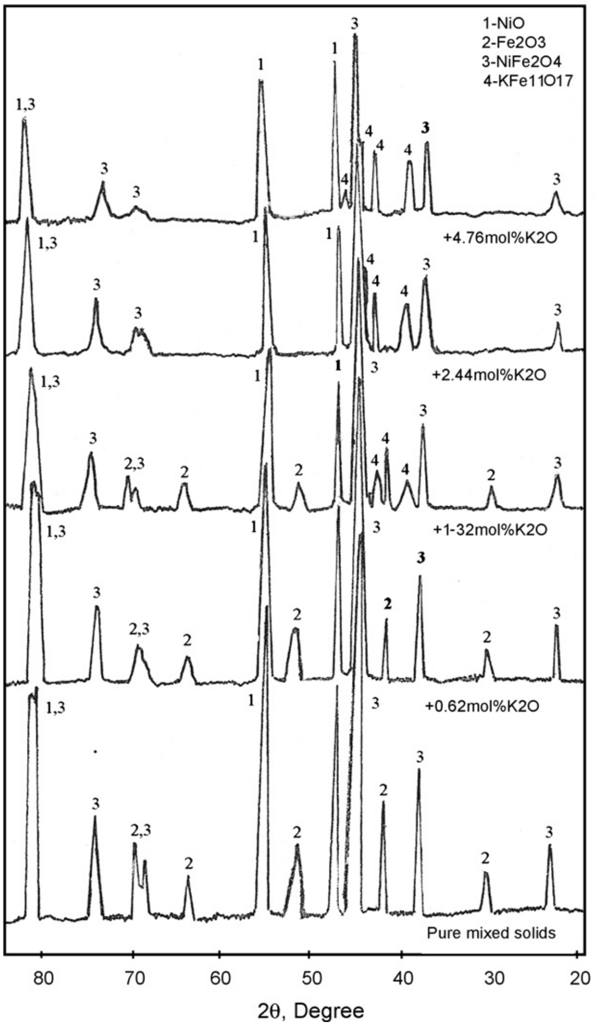

Fig. 6. X-ray diffractograms of pure mixed solids and that doped with different amounts of $K_2O$ followed by calcination at 1000 °C.

Table 1
Effect of calcination temperature and $K_2O$-doping of $NiO/Fe_2O_3$ system on the peak height of main diffraction lines of NiO ($d = 2.08$, 100%), $Fe_2O_3$ ($d = 2.69$, 100%), $NiFe_2O_4$ ($d = 2.95$, 28%) and $KFe_{11}O_{17}$ ($d = 2.65$, 71%)

| Pure and variously doped solids | Calcination temperature (°C) | NiO (a.u.) ($d = 2.08$) (100%) | $Fe_2O_3$ (a.u.) ($d = 2.69$) (100%) | $NiFe_2O_4$ (a.u.) ($d = 2.95$) (28%) | $KFe_{11}O_{17}$ (a.u.) ($d = 2.65$) (71%) |
|---|---|---|---|---|---|
| $NiO/Fe_2O_3$ | 300 | 45 | 63 | – | – |
| +0.62 mol% $K_2$ | | 39 | 56 | – | – |
| +1.23 mol% $K_2O$ | | 32 | 46 | – | – |
| +2.44 mol% $K_2O$ | | 22 | 42 | – | – |
| +4.76 mol% $K_2O$ | | – | 22 | – | – |
| $NiO/Fe_2O_3$ | 500 | 77 | 105 | – | – |
| +0.62 mol% $K_2O$ | | 51 | 60 | – | – |
| +1.23 mol% $K_2O$ | | 49 | 54 | – | – |
| +2.44 mol% $K_2O$ | | 48 | 49 | – | – |
| +4.76 mol% $K_2O$ | | 47 | 46 | – | – |
| $NiO/Fe_2O_3$ | 750 | 122 | 168 | 24 | – |
| +0.62 mol% $K_2O$ | | 88 | 72 | 33 | – |
| +1.23 mol% $K_2O$ | | 81 | 63 | 41 | 20 |
| +2.44 mol% $K_2O$ | | 80 | – | 42 | 29 |
| +4.76 mol% $K_2O$ | | 61 | – | 44 | 32 |
| $NiO/Fe_2O_3$ | 900 | 124 | 106 | 47 | – |
| +0.62 mol% $K_2O$ | | 122 | 59 | 52 | – |
| +1.23 mol% $K_2O$ | | 97 | 48 | 53 | 24 |
| +2.44 mol% $K_2O$ | | 95 | – | 52 | 31 |
| +4.76 mol% $K_2O$ | | 84 | – | 50 | 33 |
| $NiO/Fe_2O_3$ | 1000 | 124 | 85 | 80 | – |
| +0.62 mol% $K_2O$ | | 112 | 56 | 74 | – |
| +1.23 mol% $K_2O$ | | 95 | 43 | 67 | 27 |
| +2.44 mol% $K_2O$ | | 92 | – | 60 | 33 |
| +4.76 mol% $K_2O$ | | 90 | – | 56 | 35 |

weight (10 mg) of heavily $K_2O$-doped solid samples precalcined at 300 and 500 °C with a given volume of distilled water (20 ml) at 30 °C for about 1 h increases slightly from 6.90 to 7.7. This increase in the pH value of the test solutions might suggest that most of $K_2O$ added was effectively retained in the investigated solids. If most of the dopant added remained as a separate phase, it would dissolve easily in distilled water leading to a measurable increase in its pH value, which has not been verified experimentally. The observed increase in the catalytic activity of mixed solids due to the treatment with $K_2O$ might reflect an effective increase in the concentration of catalytically active constituents of the system under investigation. (v) Increasing the amount of dopant above 1.23 mol% resulted in a measurable decrease in the ($k$) value. The addition of 4.76 mol% $K_2O$ per mol catalyst followed by calcination at 300 °C led to a maximum decrease of 57% in ($k$) value measured at 30 °C. (vi) $K_2O$-doping of the

Table 2
Effect of $K_2O$-doping of $NiO/Fe_2O_3$ system precalcined at 300, 500 °C on the reaction rate constant ($k$), activation energies ($\Delta E_a$, $\Delta E_a^*$) and frequency factor ($\log A$) for $H_2O_2$ decomposition conducted at 30, 40 and 50 °C

| Dopant concentration (mol%) | Calcination temperature (°C) | 30 °C $k \times 10$ (min$^{-1}$) | 40 °C $k \times 10$ (min$^{-1}$) | 50 °C $k \times 10$ (min$^{-1}$) | ($\Delta E_a$) kJ mol$^{-1}$ | $\log A$ | ($\Delta E_a^*$) kJ mol$^{-1}$ |
|---|---|---|---|---|---|---|---|
| $NiO/Fe_2O_3$ | 300 | 0.81 | 1.36 | 1.84 | 34 | 12.25 | 34 |
| +0.62 mol%$K_2O$ | | 0.94 | 1.50 | 2.45 | 40 | 14.61 | 34 |
| +1.23 mol% $K_2O$ | | 1.14 | 1.83 | 3.02 | 40 | 14.70 | 34 |
| +2.44 mol% $K_2O$ | | 0.60 | 1.14 | 2.19 | 54 | 19.90 | 34 |
| +4.76 mol% $K_2O$ | | 0.35 | 0.73 | 1.55 | 61 | 22.40 | 35 |
| Fe-salt | | 0.20 | 0.36 | 0.70 | 62 | 22.40 | – |
| Ni-salt | | 0.06 | 0.15 | 0.40 | 79 | 28.67 | – |
| $NiO/Fe_2O_3$ | 500 | 0.71 | 1.20 | 2.19 | 47 | 17.22 | 47 |
| +0.62 mol%$K_2O$ | | 0.66 | 1.09 | 2.04 | 54 | 16.03 | 47 |
| +1.23 mol% $K_2O$ | | 0.54 | 0.81 | 1.60 | 45 | 16.28 | 47 |
| +2.44 mol% $K_2O$ | | 0.36 | 0.67 | 1.22 | 51 | 18.51 | 48 |
| +4.76 mol% $K_2O$ | | 0.26 | 0.51 | 0.96 | 55 | 19.94 | 48 |
| Fe-salt | | 0.08 | 0.17 | 0.36 | 62 | 22.17 | – |
| Ni-salt | | 0.03 | 0.08 | 0.22 | 82 | 29.56 | – |

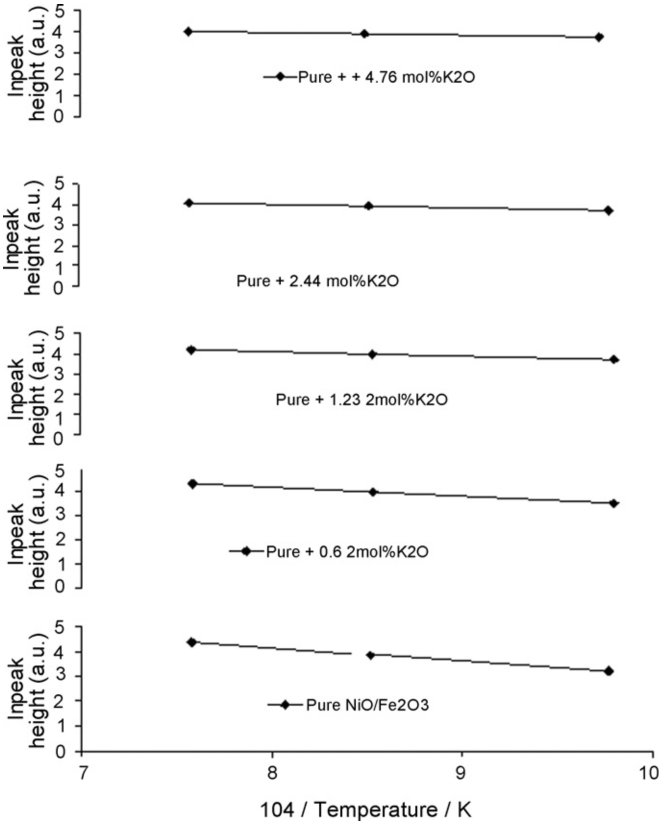

Fig. 7. Change of ln peak height of the diffraction line of $NiFe_2O_4$ (2.95 Å) as a function of precalcination temperature for pure and $K_2O$-doped mixed solids.

system investigated followed by calcination at 500 °C resulted in a significant decrease in its catalytic activity. The maximum decrease in the ($k$) value measured at 30 °C reaches 64%. The observed decrease in the catalytic activity as a result of increasing the dopant concentration above 1.23 mol% $K_2O$ might be attributed to a possible location of potassium ions on top surface layers of the treated catalyst blocking some of active sites that contribute in $H_2O_2$ decomposition. (vii) Increasing of calcination temperature from 300 to 500 °C was accompanied by a progressive decrease in the catalytic activity of pure and doped samples under investigation. This is because of increasing the degree of crystallinity of catalytically active sites of nickel of ferric oxide phases which was accompanied by increasing their crystallite size calculated by using Scherrer equation [25]. (viii) No measurable catalytic activity was observed for all pure and doped mixed solids preheated at 750, 900 and 1000 °C (not given). This behavior may be attributed to the formation of nickel and potassium ferrites ($NiFe_2O_4$ and $KFe_{11}O_{17}$). The poor performance of mixed solids preheated at 750, 900 and 1000 °C might be explained in terms of the restricted redox couple represented by ($M^n/M^{n-1}$) in the electronic composition of the catalysts and, possibly, the absence of $M^n$ on the octahedral lattice site which may initiate the cyclic electron-transfer process on the catalyst surface [23,26].

Determination of the apparent activation energy ($\Delta E$) for the catalysis of $H_2O_2$ decomposition over pure and variously doped samples shed some light on the possible change in the mechanism of the catalyzed reaction and hence gives useful information about possible changes in the concentration and nature of the catalytically active constituents. The values of $k$ measured at 30, 40 and 50 °C over pure and variously doped solids enable $\Delta E$ to be calculated by direct application of Arrhenius equation. The calculated values of $\Delta E$ are given in Table 2, which also include the values of pre-exponential factor $A$ of the Arrhenius equation. It is shown that $\log A$ changes from 12.25 to 22.40 for pure and variously doped solids preheated at 300 °C and from 16.03 to 19.94 for the catalysts investigated calcined at 500 °C. The changes in the value of $\log A$ due to doping with $K_2O$ are normally followed by corresponding changes in the magnitude of $\Delta E$. The magnitudes of $\Delta E$ were recalculated ($\Delta E^*$) for the different treated solids preheated at 300 and 500 °C. The computed ($\Delta E^*$) values are given in the last column of Table 2. The results given in Table 2 clearly show that the values of $\Delta E$ and $\Delta E^*$ are identical for the untreated solids, but $\Delta E^*$ remains virtually unchanged for pure and doped solids calcined at 300

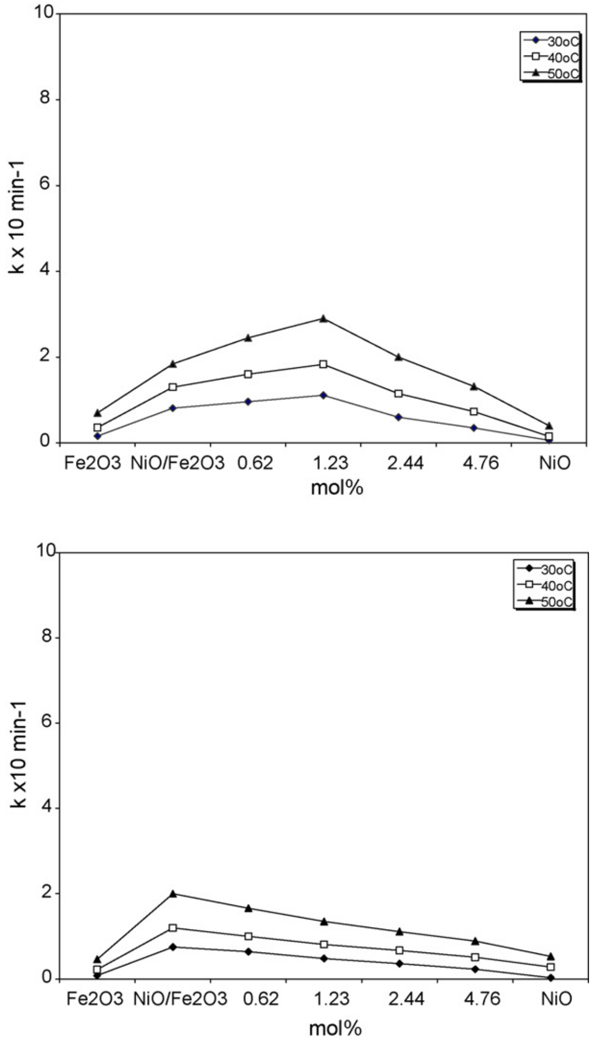

Fig. 8. (a) Effect reaction temperature and $K_2O$-doping on the reaction rate constant ($k$) of pure $NiO/Fe_2O_3$ system heated at 300 °C. (b) Effect reaction temperature and $K_2O$-doping on the reaction rate constant ($k$) of pure $NiO/Fe_2O_3$ system heated at 500 °C.

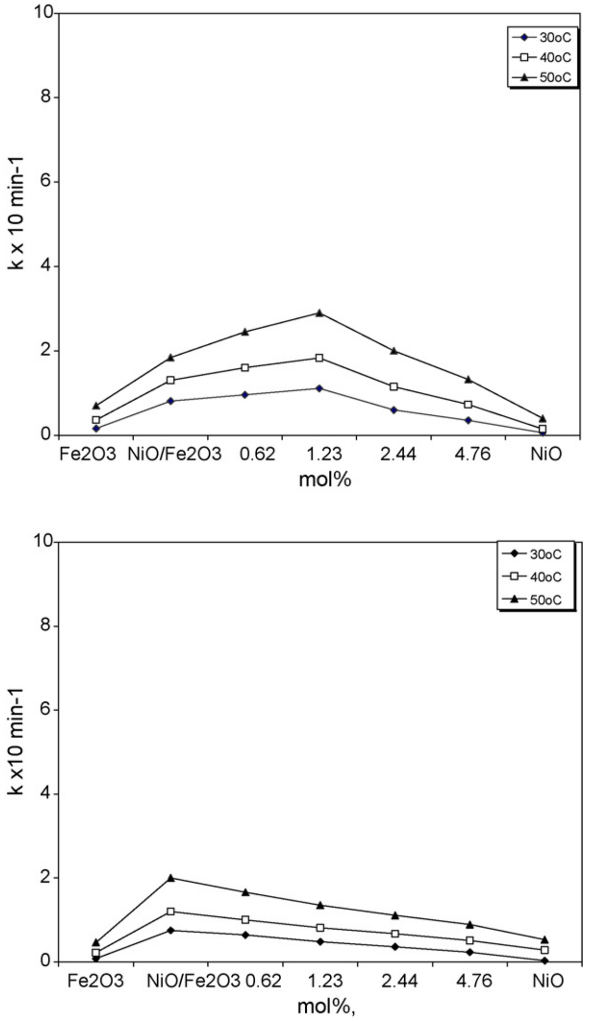

Fig. 9. (a) Effect reaction temperature and $K_2O$-doping on the reaction rate constant ($k$) of pure $NiO/Fe_2O_3$ system heated at 300 °C. (b) Effect reaction temperature and $K_2O$-doping on the reaction rate constant ($k$) of pure $NiO/Fe_2O_3$ system heated at 500 °C.

and 500 °C, respectively. These results indicate that potassium oxides doping of $NiO/Fe_2O_3$ did not modify the mechanism of $H_2O_2$ decomposition affective in the concentration of the catalytically active sites present in outermost surface layers of the treated solids.

## 4. Conclusions

The following are the main conclusions that may be drawn from the obtained results:

1. Treatment of equimolar proportion of basic nickel and iron carbonate with potassium nitrate enhanced the thermal decomposition of these salts to NiO and $Fe_2O_3$.
2. $K_2O$ treatment of $NiO/Fe_2O_3$ system followed by calcination at 300 and 500 °C decreased the degree of crystallinity of nickel and ferric oxide phases.
3. Solid–solid interaction between NiO and $Fe_2O_3$ takes place at temperature starting from 700 °C forming nickel ferrite ($NiFe_2O_4$) phase whose degree of crystallinity increased by increasing the calcination temperature within 700–1000 °C.
4. Doping of the system investigated with $K_2O$ enhanced the formation of crystalline nickel ferrite phase up to certain extent of amount of the dopant added. The computed value of activation energy of formation of nickel ferrite was 120, 80, 49, 36 and 25 kJ mol$^{-1}$ for pure mixed solid samples and for those doped with 0.62, 1.23, 2.44 and 4.26 mol% $K_2O$, respectively.
5. The samples heavily doped with $K_2O$ resulted in the formation of potassium ferrite ($KFe_{11}O_{17}$) phase starting from 750 °C. The degree of crystallinity of this phase increased with increasing the amount of $K_2O$ as well as with increasing the calcination temperature up to 1000 °C.
6. The catalytic activity of mixed oxides, NiO–$Fe_2O_3$, which decreased by increasing the treatment temperature from 300 to 500 °C was found to be bigger than those of single oxides. In addition, there is no measurable catalytic activity for all the solids preheated at 750, 900 and 1000 °C.
7. The catalytic activity of $NiO/Fe_2O_3$ system preheated at 300 °C increased by doping with $K_2O$ up to a certain extent. The addition of 4.76 mol% $K_2O$ affected a decrease of 57% and 63% in the value of reaction rate constant over the doped catalysts calcined at 300 and 500 °C, respectively.
8. The doping process did not modify the mechanism of catalytic reaction, but changed the concentration of catalytically active components.

## References

[1] A. Tsyganok, P.J.E. Harlick, A. Sayari, Catalysis Communication 8 (5) (2007) 850–854.
[2] H.G. El-Shobaky, A.S. Ahmeda, N.R.E. Radwan, Colloids and Surfaces A 274 (2006) 138–144.
[3] A.A. Zahran, W.M. Shaheen, G.A. El-Shobaky, Materials Research Bulletin 40 (2005) 1065–1080.
[4] N.R.E. Radwan, H.G. El-Shobaky, S.A. El-Mola, Applied Catalysis A 297 (1) (2006) 31–39.
[5] W.M. Shaheen, Materials Science and Engineering B 135 (1) (2006) 30–37.
[6] W.M. Shaheen, Materials Science and Engineering A 445–446 (2007) 113–121.
[7] H.G. El-Shobaky, N.R.E. Radwan, Thermochmica Acta 398 (2003) 223–231.
[8] W.M. Shaheen, Materials Chemistry and Physics 101 (2007) 182–190.
[9] T.M.S. Malwadkar, S. Pai, S.C.P. Sebastain, C.V.V. Satyanarayana, V.V. Bokade, Catalysis Letters 91 (2003) 217.
[10] K.P. Tikhomolova, I.B. Dmitrieva, M.V. Ivanova, Russian Journal of Applied Chemistry 71 (1998) 550.
[11] A.M. Ghozza, H.G. El-Shobaky, Materials Science and Engineering B 127 (2006) 233–238.
[12] S. Zahi, M. Hashim, A.R. Daud, Journal of Magnetism and Magnetic Materials 308 (2007) 177–182.
[13] G.A. El-Shobaky, F.H.A. Abdalla, A.M. Ghozza, Thermochimica Acta 292 (1997) 123–133.
[14] D. Stoppels, Journal of Magnetism and Magnetic Materials 26 (1982) 306.
[15] J.L.G. Fierro, Applied Catalysis A 92 (2) (1992) 131–141.
[16] G.A. El-Shobaky, F.H.A. Abdalla, A.A.F. Zikry, Thermochimica Acta 289 (1996) 81.
[17] G.A. El-Shobaky, G.A. Fagal, A. Abd El-Aal, A.M. Ghozza, Thermochimica Acta 256 (1995) 429.
[18] W.M. Shaheen, M.M. Selim, Thermochimica Acta 322 (1998) 117–128.

[19] W.M. Shaheen, Materials Letters 52 (2002) 272–282.
[20] F. Novel, R. Valenzuela, Materials Research Bulletin 30 (3) (1995) 335–340.
[21] G.A. El-Shobaky, A.N. Al-Noaimi, A. Abd El-Aal, A.M. Ghozza, Materials Letters 22 (1995) 39–45.
[22] W.M. Shaheen, A.A. Ali, Materials Research Bulletin 36 (2001) 1703–1716.
[23] W.M. Shaheen, A.A. Ali, International Journal of Inorganic Materials 3 (2001) 1073–1081.
[24] A.M. Ghozza, Materials Letters 57 (2003) 2120–2129.
[25] W.M. Shaheen, A.A. Zahran, G.A. El-Shobaky, Colloids and Surfaces, A 231 (2003) 51–65.
[26] V. Mucka, Collection of Czechoslovak Chemical Communications 41 (8) (1988) 1836–1846.