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Investigation of solid–solid interactions between pure and Li_2O-doped cobalt and ferric oxides

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Abstract

The solid–solid interactions between pure and lithium-doped cobalt and ferric oxides have been investigated using TG, DTG, DTA and XRD techniques. The catalytic activity, in CO oxidation by O_2 at 400°C, was determined for each solid preheated in air at 700–1000°C. The amounts of lithium, expressed as mol% Li_2O were 1.5 and 3.

The results obtained showed that Fe_2O_3 interacted readily with Co_3O_4 at temperatures starting from 700°C to produce $CoFe_2O_4$ phase in well crystallized form. The degree of propagation of this reaction increased by increasing the heating temperature. However, a small portion of unreacted free oxides was found in the case of pure-mixed solids heated at 1000°C. Lithium oxide-doping stimulates the ferrite formation to an extent proportional to its amount present. The stimulation effect of lithium was evidenced by following up the change in the peak heights of certain diffraction lines characteristic of Fe_2O_3, Co_3O_4 and $CoFe_2O_4$ phases located at '*d*' spacing of 2.69, 2.44 and 2.08 Å, respectively. The change of peak height of the diffraction line at 2.08 Å as a function of firing temperature of pure- and doped-mixed solids enabled the calculation of the activation energy of the ferrite formation (ΔE). The computed ΔE values were 57.3, 38.4 and 28.8 kJ mol^{-1} for pure-mixed solids specimen and those treated with 1.5 and 3 mol% Li_2O, respectively. The catalytic activity was found to decrease by increasing the calcination temperature and also by increasing the amount of Li_2O due to the enhanced formation of $CoFe_2O_4$ phase which is less reactive than the free oxides, Co_3O_4 and Fe_2O_3. The promotion effect of lithium in the cobalt ferrite formation was attributed to an effective increase in the mobility of diffusion of reacting cations.

Keywords: Catalysis; $CoFe_2O_4$; Doping; Mobility

1. Introduction

Cobalt ferrite can be obtained by a variety of methods [1–8]. The choice of the appropriate method depends mainly upon the specific use of the produced ferrite. This compound finds several applications as catalyst, microwave resistor, ultrasonic vibrator and electrophotographic toner [7,9,10]. $CoFe_2O_4$ can be prepared by heating a mixture of ferric oxide and cobalt salt or oxide at temperature starting from 700°C [1]. Other methods of preparation have been cited in the literature. Finely divided hexagonal cobalt ferrite powder was obtained by autoclave treatment of an aqueous alkaline suspension containing the metal cations forming the ferrite at 250–330°C, then heating the resulting materials at ≤900°C [11]. Mixed ferrites

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are usually employed due to their remarkable magnetic and semiconducting properties [1,3,12,13]. These properties depend, mainly on chemical composition, calcination conditions, structure and surface properties of the Fe_2O_3 used and the addition of small amounts of certain foreign oxides [5,14]. The mechanisms of ferrite formation have been the object of several investigations [1,13,15]. The solid–solid interaction 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 [5,14].

The solid–solid interaction between Fe_2O_3 and NiO as influenced by doping with Li_2O and Al_2O_3 has been discussed in our previous papers [5,14]. It has been shown that Li- or Al-doping enhances the $NiFe_2O_4$ formation by increasing the mobility of thermal diffusion of reacting cations through the early-formed ferrite film.

The present work reports the results of a study on the effect of addition of small amounts of Li_2O on cobalt ferrite formation, at different temperatures. The techniques employed were TG, DTG, DTA, XRD and catalysis of CO oxidation by O_2 at 400°C over the various investigated solids preheated at different temperatures.

2. Experimental

2.1. Materials

Equimolar mixtures of α-Fe_2O_3 and basic cobalt carbonate (equal moles of CoO and Fe_2O_3) were well-mixed to ensure the homogeneity of the powdered solids. The obtained specimen was heated in air at temperatures between 600 and 1000°C for 6 h. Two doped mixed solids samples were obtained by treating a known mass of mixed solids with calculated amount of lithium nitrate dissolved in the minimum amount of distilled water, dried overnight at 100°C, then calcined in air at 600–1000°C. The concentrations of lithium expressed as mol% Li_2O were 1.5 and 3. All the chemicals used were of analytical grade supplied by Prolabo. The formula of basic cobalt carbonate is $CoCO_3$ 0.5 $Co(OH)_2$.

2.2. Techniques

TG, DTG and DTA were carried out using Perkin–Elmer, seven series thermal analysis system. The rate of heating was kept at 10°C min^{-1} and the mass of solid specimen was 9 and 40 mg in the case of TG and DTA runs, respectively. The measurements were carried out in a current of N_2 flowing at a rate of 50 cm^3 min^{-1}.

An X-ray investigation of pure- and doped-mixed solids preheated in air at 600, 700, 800, 900 and 1000°C was conducted using a Philips diffractometer (type PW 1390). The patterns were run with iron-filtered cobalt radiation (λ=1.7889 Å) at 30 kV and 10 mA with a scanning speed of 2° per minute.

The catalytic activity of the various pure- and doped-mixed solids preheated at 700–1000°C was conducted via following the kinetics of CO oxidation by O_2 at 400°C over each solid using a static method and a stoichiometric mixture of CO and O_2 at a pressure of 2 torr. The product of the catalytic oxidation (CO_2) was removed from the reaction mixture by freezing in a liquid-nitrogen trap. A fresh catalyst sample of 400 mg mass was always employed for each catalytic experiment. The CO and O_2 reactants were produced by the dehydration of formic acid by concentrated H_2SO_4 and thermal decomposition of $KMnO_4$, respectively and were purified by passing them through KOH solution and over P_2O_5.

3. Results

3.1. Thermal behaviour of pure- and doped-mixed solids

Figs. 1 and 2 show TG and DTG curves of pure and doped equimolar proportions of α-Fe_2O_3 and basic cobalt carbonate. It is seen from Fig. 1 that the heating of pure-mixed solids is accompanied by four distinct mass loss processes at 227.9, 254.5, 289.9 and 811°C. The total mass loss corresponding to the first three processes is 10.86% and that corresponding to the last process at 811°C is 1.78%. The first three thermal processes are consistent with thermal decomposition of basic cobalt carbonate to produce $CoCO_3$ which decomposed to give Co_3O_4 [16,17]. In fact, the the-

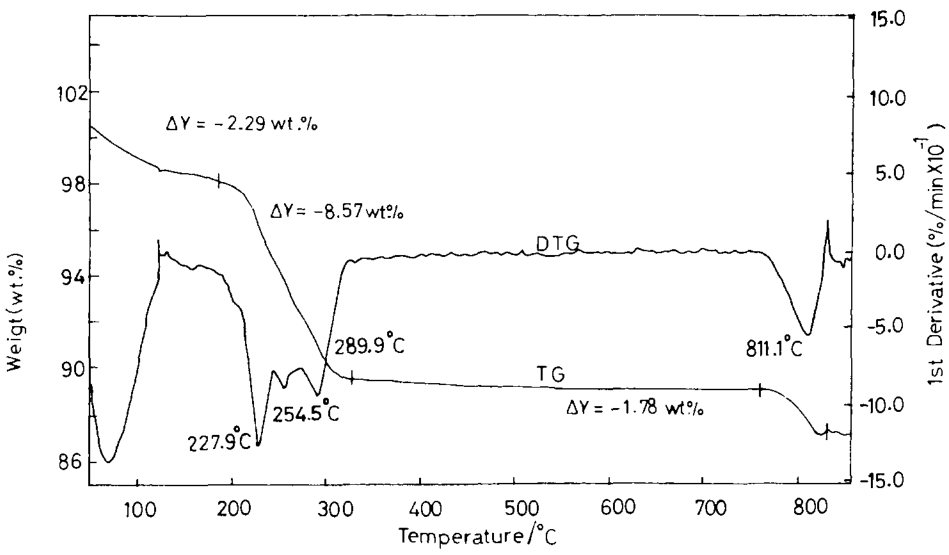

Fig. 1. TG and DTG curves of pure basic cobalt carbonate and α-Fe_2O_3 mixed solids.

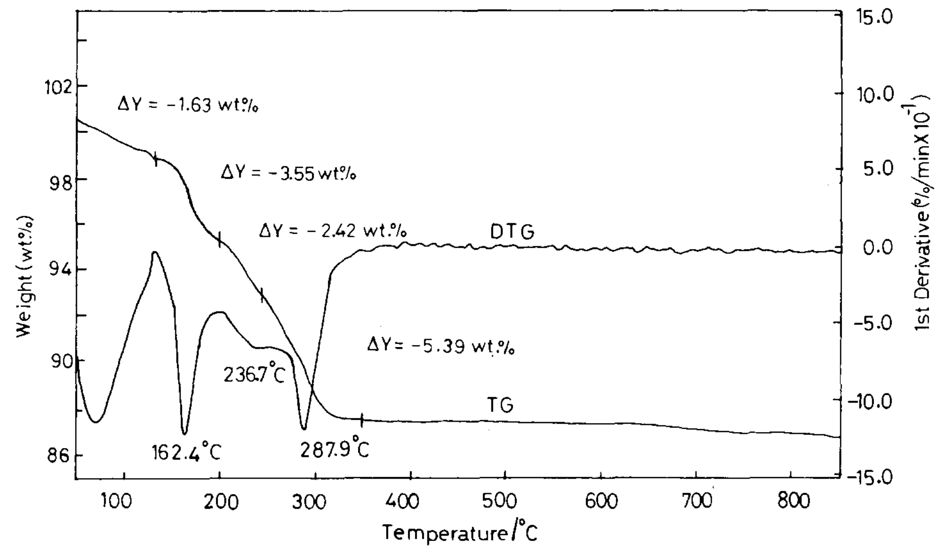

Fig. 2. TG and DTG curves of pure and lithium-doped basic cobalt carbonate and α-Fe_2O_3 mixed solids.

oretical percentage mass loss following the thermal decomposition of basic cobalt carbonate, mixed with an equimolar amount of α-Fe_2O_3, yielding cobaltic oxide is 11% which is very close to the value found experimentally (10.86%). The thermal process at 811°C might correspond to decomposition of the unreacted portion of Co_3O_4 [17]. This will be confirmed later by DTA and XRD measurements given in the present work. Fig. 2 shows that the TG and DTG curves of lithium-doped mixed solids consist of three steps: the first step extends between room temperature and 133.7°C; the second between 133.7 and 243.7°C;

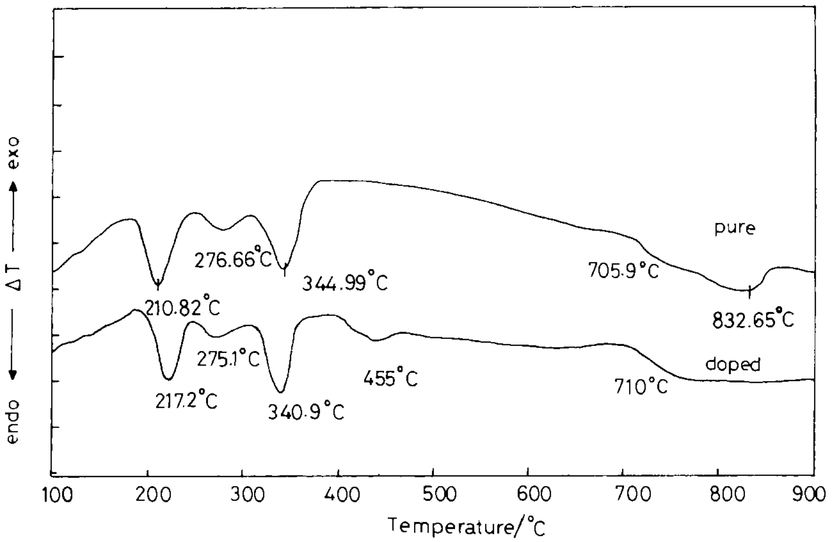

Fig. 3. DTG curves of pure and lithium-doped basic cobalt carbonate and α-Fe_2O_3.

and the last between 243.7 and 348.9°C. These steps are followed by mass losses of 1.63, 5.96 and 5.39%, respectively. The first step corresponds to desorption of physisorbed water and the second and third steps are indicative of thermal decomposition of basic cobalt carbonate to yield Co_3O_4. The comparison between Figs. 1 and 2, reveals the absence of the thermal process at 811°C in the case of lithium-doped mixed solids.

Fig. 3 shows DTA curves of pure- and doped-mixed solids. It is seen from this figure that the DTA curve of the pure-mixed solids consists of four endothermic and one exothermic peaks; the maxima of endothermic peaks are located at 210.8, 276.7, 344.3 and 832.7°C, the maximum of exothermic peak is found at 705.9°C. The first three peaks correspond to the thermal decomposition of $CoCO_3$ 0.5 $Co(OH)_2$ to $CoCO_3$ then to Co_3O_4 [17]. The last endothermic peak at 832.7°C might correspond to thermal decomposition of unreacted Co_3O_4. In fact, it has been reported that heating of cobaltic oxide at temperature $\geq$ 800°C resulted in its thermal decomposition into CoO [16,17]. However, the produced CoO can readily be oxidized by interacting with atmospheric oxygen during the cooling process, the decomposition process is normally followed by an endothermic peak [16]. The exothermic peak at 705.9°C might be indicative to solid–solid interaction between Co_3O_4 and Fe_2O_3 to produce $CoFe_2O_4$. The formation of ferrite phase will be confirmed by XRD measurements given in the next section of the present work. The DTA curve of lithium treated mixed solids consists of four endothermic and one exothermic peaks. The maxima of endothermic peaks are found at 217.2, 276.1, 340.9 and 455°C. The exothermic peak was located 710°C. The first three endothermic peaks, similar to the case of pure-mixed solids, corresponds to thermal decomposition of basic cobalt carbonate producing $CoCO_3$ then Co_3O_4. The peak at 455°C, not present in the DTA curve of pure-mixed solids, indicates the thermal decomposition of $LiNO_3$ to give Li_2O. The DTA curve of doped solids did not include the endothermic peak at 832.7°C relative to decomposition of Co_3O_4. This might indicate that Li_2O-doping resulted in a complete conversion of Co_3O_4 into $CoFe_2O_4$ via interaction with Fe_2O_3 and/or stabilized a portion of cobaltic oxide phase preventing its decomposition into CoO. It has been shown by one of the authors that Li_2O-doping of Co_3O_4 increased its thermal stability to an extent proportional to its existing amount; the presence of 3 mol% Li_2O was found sufficient to prevent completely the thermal decomposition of Co_3O_4 even by heating at 1000°C [17,18].

It can thus be concluded from TG and DTA results that lithium-doping of cobalt and ferric oxides might enhance the solid–solid interactions yielding cobalt ferrite. This conclusion comes from the absence of any thermal peak, characterizing the presence of unreacted Co_3O_4 liable to undergoing thermal decomposition. The promotion effect of lithium-doping is better investigated by XRD measurements for pure- and doped-mixed solids calcined at different temperatures between 600 and 1000°C.

3.2. XRD measurements on pure- and doped-mixed solids preheated at different temperatures

X-ray diffractograms of pure- and doped-mixed solids precalcined in air at different temperatures were determined. The results obtained showed that pure-mixed solids preheated at 500 and 600°C, consist entirely of α-Fe_2O_3 and Co_3O_4 phases that have an excellent degree of crystallinity. Raising the calcination temperature to 700°C resulted in the appearance of new diffraction lines characterizing $CoFe_2O_4$ phase together with all diffraction lines of free α-Fe_2O_3 and Co_3O_4. The rise in calcination temperature in the 700–1000°C range brought about a progressive increase in the peak height of the lines relative to $CoFe_2O_4$ phase with subsequent decrease in the peak heights of free Co_3O_4 and α-Fe_2O_3.

Figs. 4–6 represent X-ray diffractograms of pure- and doped-mixed solids preheated at 700, 800 and 900°C. It is clearly shown from these figures that solid–solid interactions take place between α-Fe_2O_3 and Co_3O_4 to produce $CoFe_2O_4$ at temperatures starting from 700°C. The rise in heating temperature above 700°C stimulates the ferrite formation. Therefore, the exothermic peaks found at 705.9 and 710°C in the

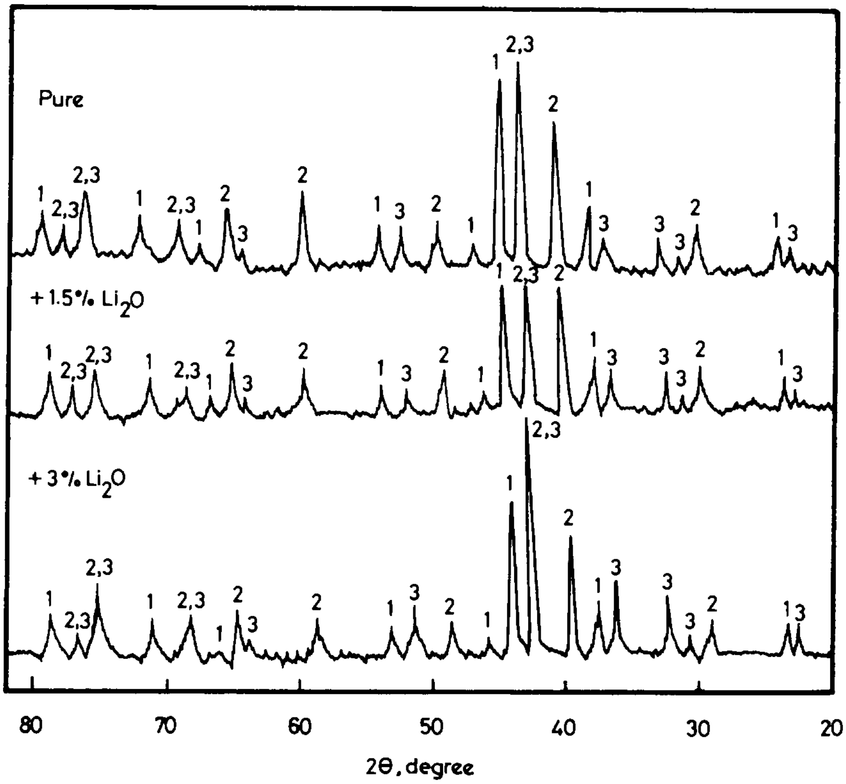

Fig. 4. XRD patterns of pure and doped mixed solids preheated in air at 700°C; lines 1 refer to Co_3O_4; lines 2 refer to α-Fe_2O_3; lines 3 refer to $CoFe_2O_4$.

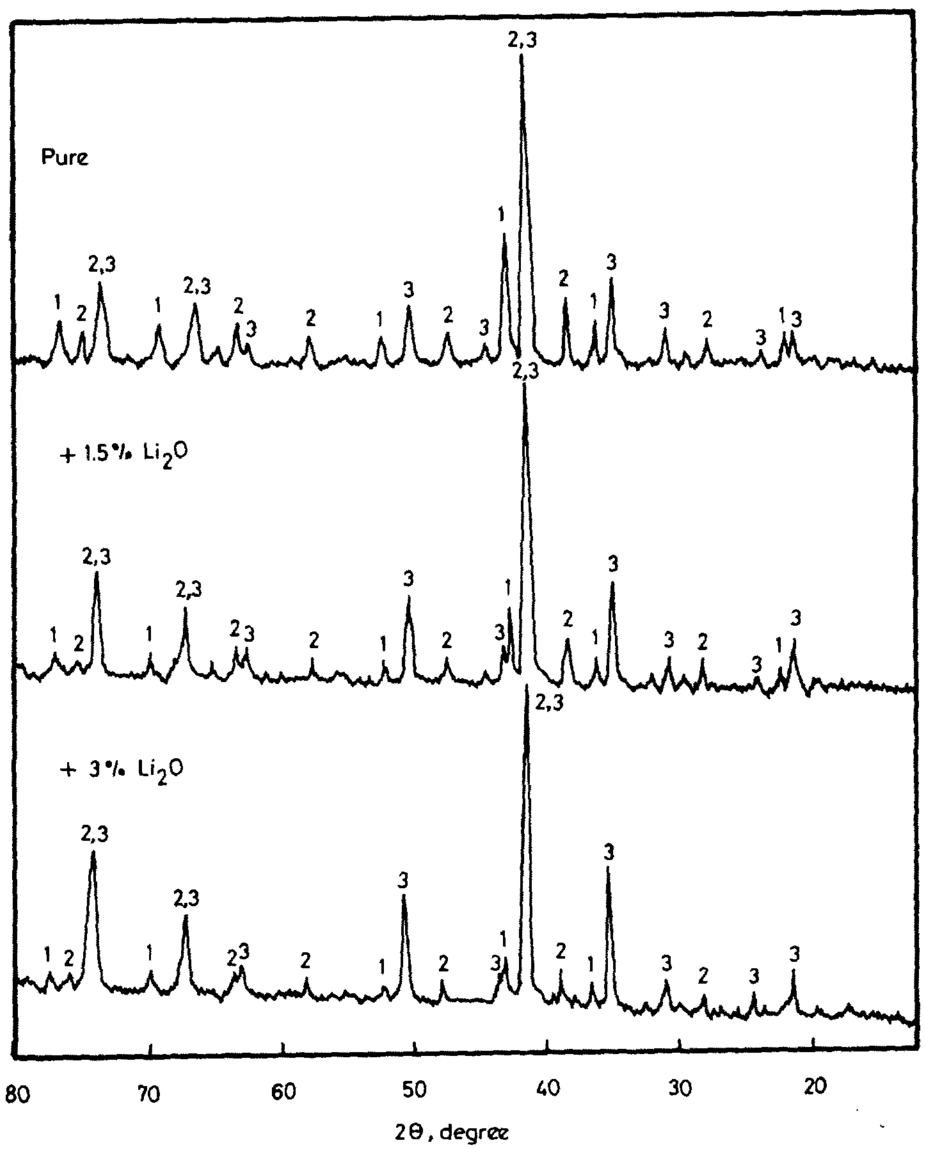

Fig. 5. XRD patterns of pure and doped mixed solids preheated in air at 800°C; lines 1 refer to Co_3O_4; lines 2 refer to α-Fe_2O_3; lines 3 refer to $CoFe_2O_4$.

DTA curves of pure and doped solids correspond to the reaction

$$3Fe_2O_3 + Co_3O_4 \xrightarrow{700-900C} 3CoFe_2O_4 + 1/2O_2.$$

This reaction is followed by a mass loss of about 1%. Although the reaction of ferrite formation starts at 700°C its completion requires a prolonged heating at temperature > 900°C. However, the XRD measurements, not given here, for pure- and doped-mixed solids showed the presence of very small portions of unreacted free oxides in the case of pure solids, on the other hand, doped solids prefired at 1000°C consist entirely of the $CoFe_2O_4$ phase.

Inspection of Figs. 4–6 also show that the presence of Li_2O enhances the ferrite formation to an extent,

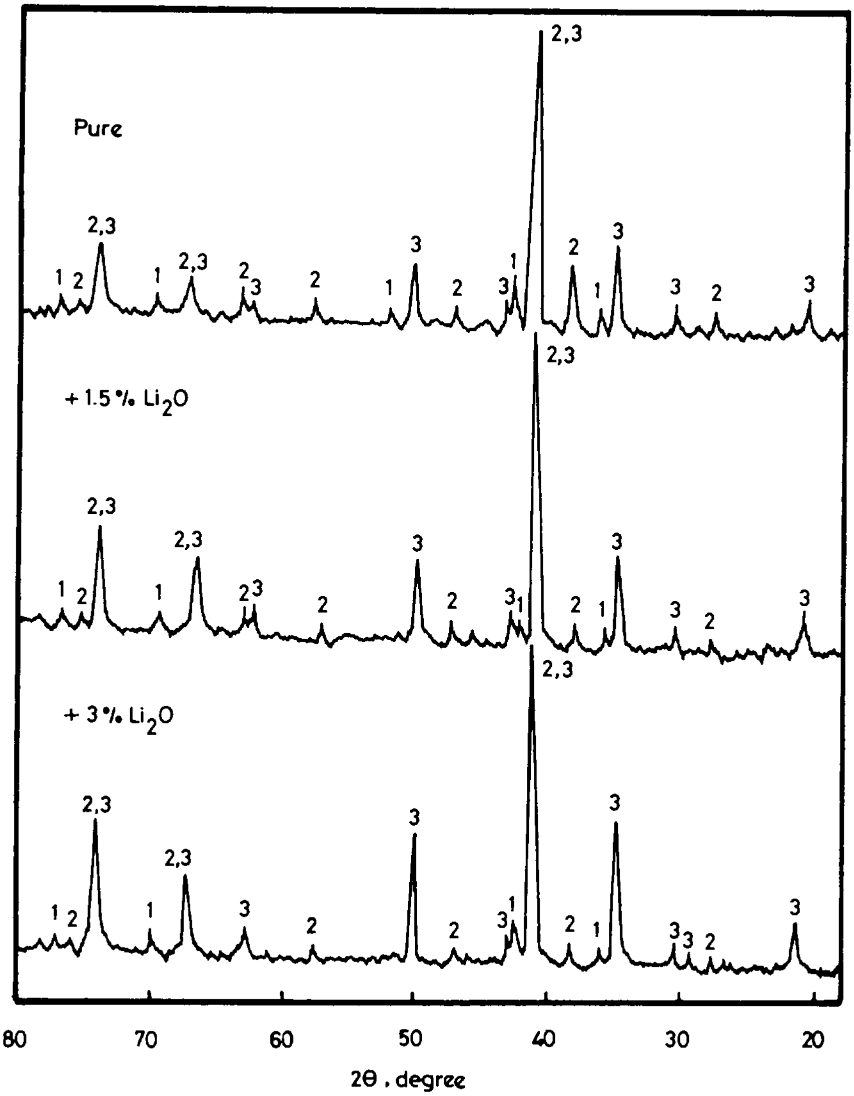

Fig. 6. XRD patterns of pure and doped mixed solids preheated in air 900°C; lines 1 refer to Co_3O_4; lines 2 refer to α-Fe_2O_3; lines 3 refer to $CoFe_2O_4$.

proportional to the amount present. This conclusion comes from the fact that Li_2O-doping brought about a regular increase in the peak height of the diffraction lines relative to $CoFe_2O_4$ phase with subsequent decrease in peak heights of the free Co_3O_4 and Fe_2O_3 solids.

The promotion effect of lithium-doping in cobalt ferrite formation is better investigated by comparing the peak heights of some diffraction lines characteristics for α-Fe_2O_3, Co_3O_4 and $CoFe_2O_4$. These lines are located at '*d*' spacings of 2.69, 2.44 and 2.08 Å for the earlier mentioned compounds, respectively. The choice of these lines is based on the fact that they are not common among the diffraction lines of α-Fe_2O_3, Co_3O_4 and $CoFe_2O_4$ phases.

Inspection of Table 1 reveals that the peak heights of free oxides decrease progressively by increasing the calcination temperature in the 700–900°C range. On the other hand, this treatment led to a progressive increase in the peak height of the produced ferrite phase. The appearance of diffraction lines of free oxides, in the case of pure-mixed solids heated at 1000°C for 6 h, showed that the complete conversion of these oxides into $CoFe_2O_4$ requires a prolonged heating at temperature > 1000°C. It seems that the ferrite produced at 700°C covers the surfaces of grains of the free oxides hindering their further diffusion. So, the $CoFe_2O_4$ formed initially acts as an energy barrier against the completion of the solid–solid interaction between Fe_2O_3 and Co_3O_4.

It can also be seen from Table 1 that the presence of Li_2O brought about a regular decrease in the peak heights of the diffraction lines at 2.69 and 2.44 Å with subsequent increase in the peak height of the lines at 2.08 Å. These results showed clearly that Li_2O-doping enhances the ferrite formation to an extent, proportional to its amount present.

3.3. *Catalytic activity of pure- and doped-mixed solids*

The catalytic activity of pure- and doped-mixed solids preheated at 700–1000°C was determined for each solid specimen using the oxidation of CO by O_2 at 400°C under a static conditions. The catalyst sample (400 mg) was activated by heating at 400°C under a reduced pressure ($P = 10^{-6}$ torr) for 2 h before carrying out the catalytic reaction. The results showed that the catalytic reaction proceeds according to a first-order law. The plots of log P/P_0 (P_0 initial pressure of reacting gases $CO + \frac{1}{2}O_2$, and P the pressure at time t) against time t enabled the calculation of the reaction rate constant (k) for each catalyst sample by calculating the slopes of the plots relating log k vs. t. The magnitude of k stands for the catalytic activity of each solid. The computed values of k for the various pure and doped solids are given in Table 2.

It is seen from Table 2 that k decreases progressively by increasing the amount of Li_2O present. The decrease was, however, more pronounced for the solids preheated at temperatures ≥800°C. Free Co_3O_4 and Fe_2O_3 are active solids for the catalysis of CO oxidation by O_2 [19,20]. These solids exhibit higher catalytic activity than cobalt ferrite [20]. So, the conversion of Fe_2O_3 and Co_3O_4 into $CoFe_2O_4$ is expected to be followed by a decrease in the catalytic activity of the mixed oxide and the observed decrease in the value of k due to doping could be taken as a measure for the propagation of the solid–solid interaction yielding $CoFe_2O_4$. On this basis, Li_2O-doping of different mixed oxides enhances the ferrite formation to an extent, proportional to its amount present. However, the decrease in the catalytic activity of the investigated solids could also be due to an effectiving sintering of the doped solids [21]. These results offer a further evidence for the role of lithium oxide-doping in stimulating the ferrite formation.

Table 1
Effect of lithium-doping on the heights of some diffraction lines of α-Fe_2O_3, Co_3O_4 and $CoFe_2O_4$ for pure- and doped-mixed solids precalcined at different temperatures

Reaction solids	Reaction temperature (°C)	Peak height (arbitrary units)		
		2.69 Å α-Fe_2O_3 (100%)	2.44 Å Co_3O_4 (100%)	2.08 Å $CoFe_2O_4$ (20%)
$Co_3O_4 + Fe_2O_3$	700	112	142	15
+ 1.5% Li_2O	do	102	110	32
+ 3.0% Li_2O	do	92	108	40
$Co_3O_4 + Fe_2O_3$	800	64	95	40
+ 1.5% Li_2O	do	40	56	50
+ 3.0% Li_2O	do	26	38	68
$Co_3O_4 + Fe_2O_3$	900	35	35	50
+ 1.5% Li_2O	do	16	15	65
+ 3.0% Li_2O	do	15	15	80
$Co_3O_4 + Fe_2O_3$	1000	10	10	70
+ 1.5% Li_2O	do	—	—	75
+ 3.0% Li_2O	do	—	—	92

Table 2
Effect of Li_2O-doping on the reaction rate constant (k) of CO oxidation by O_2 at 400°C over different mixed solids preheated at various temperatures

Catalyst	Calcination temperature (°C)	$k \times 10^{-3}$ (min^{-1})
$Co_3O_4 + Fe_2O_3$	700	16
+ 1.5% Li_2O	do	12
+ 3.0% Li_2O	do	10
$Co_3O_4 + Fe_2O_3$	800	10.2
+ 1.5% Li_2O	do	6.5
+ 3.0% Li_2O	do	4.3
$Co_3O_4 + Fe_2O_3$	900	10.5
+ 1.5% Li_2O	do	3.8
+ 3.0% Li_2O	do	2.5
$Co_3O_4 + Fe_2O_3$	1000	8.7
+ 1.5% Li_2O	do	3.3
+ 3.0% Li_2O	do	1.6

4. Discussion

Fe_2O_3 and Co_3O_4 undergo solid–solid interaction to produce $CoFe_2O_4$ that appear to cover the grains of each reacting oxide [1]. The propagation of this reaction is controlled by the thermal diffusion of cobalt and iron cations through the ferrite film which acts as an energy barrier. The fact that minute amounts of free Fe_2O_3 and Co_3O_4 were detected in the pure-mixed solids heated at 1000°C, gives an indication of the energy barrier which has to be overcome. In the case of the NiO, Fe_2O_3 system, it has been reported by one of the authors [20] that heating of these oxides at temperatures as high as 1100°C, was sufficient to conduct partial conversion of the reacting oxides into $NiFe_2O_4$. This comparison sheds light about the magnitude of the energy barrier for formation in the two cases ($CoFe_2O_4$, $NiFe_2O_4$), i.e. $CoFe_2O_4$ formation is energetically more favourable than $NiFe_2O_4$.

Cobaltic oxide is known as a *p*-type electronic semiconductor and can dissolve Li_2O in its lattice [22–24]. It is known to be a double-oxide solid $2CoO{\cdot}CoO_2$ containing cobalt ions in the 4+ and 2+ valence states [23]. Lithium oxide could be incorporated into the Co_3O_4 lattice according to different mechanisms [21]. The mechanism dominating at temperature $\geq$700°C could take place via substitution of cobalt ions in the tetra and/or divalent states with subsequent uptake of atmospheric oxygen and creation of trivalent cobalt ions. This process can be simplified by the use of Kröger's mechanism [25] in the following manner:

$$Li_2O + 1/2O_2(g) \rightarrow 2Li^+(Co^{2+}) + 2Co^{3+}$$

$$Li_2O + 3/2O_2(g) \rightarrow 2Li(Co^{4+}) + 6Co^{3+}$$

$Li^+(Co^{2+})$ and $Li(Co^{4+})$ are monovalent ions located in the positions of the host cations Co^{2+} and Co^{4+} present in the Co_3O_4 lattice. Dissolution of Li^+ ions according to this mechanism is accompanied by transformation of some of cobalt ions from a divalent into a trivalent state. This process is normally accompanied by an increase in oxidation state of the treated Co_3O_4 solid. The induced increase in the oxidation state of cobaltic oxide acts as an energy barrier hindering its decomposition (reduction) into CoO [22]. The question raised could be, what is the possible effect of conversion of some cobalt ions from divalent into trivalent state in the ferrite formation? The solid–solid interaction between Fe_2O_3 and certain transition metal oxides to produce the corresponding ferrite requires that the reacting transition metal oxide is preferably existing in the divalent state. So, it is expected that Li_2O-doping might inhibit the ferrite formation.

Ferric oxide can dissolve a very small amount of Li_2O [20] due to the ability of formation of lithium ferrite [20]. On this basis, most of the dopant (Li_2O) added was dissolved in the Co_3O_4 lattice. The results obtained, opposite to the predicted effect of Li_2O-

doping, showed an effective enhancement of cobalt ferrite formation. These results may point to the role of Li-doping, in increasing the mobility of thermal diffusion of cobalt ions facilitating their diffusion through the whole mass of the doped cobalt oxide and also through the early-formed $CoFe_2O_4$ phase. It has been reported in our previous investigations that the Li-doping increases the mobility of nickel, molybdenum and vanadium ions through the whole mass of their corresponding oxides [17–21]. The observed enhancement of cobalt ferrite formation, as a result of doping with Li_2O and the consequent increase in the mobility of the diffusion of cobalt ions through the growing $CoFe_2O_4$ phase, can be investigated by determining the activation energy of cobalt ferrite (ΔE) for pure and lithium-doped mixed solids. This has been tentatively achieved from the results given in Table 1 by assuming that the heights of the characterized diffraction lines at 2.94 and 2.08 Å are a measure of the amount of $CoFe_2O_4$ present in a given mixed solid at definite temperature T. By plotting the peak height of one of these lines vs. $1/T$, a straight line is obtained whose slope determines the ΔE value by direct application of the Arhenius equation. This trial has been successfully carried out at temperatures between 700 and 1000°C, and the plots obtained are given in Fig. 7. The computed ΔE values, obtained from the diffraction line at d spacing of 2.08 Å, are 57.3, 38.4 and 28.8 kJ mol^{-1} for pure-mixed solids and those doped with 1.5 and 3 mol% Li_2O, respectively. The activation energy of nickel ferrite formation has been determined in our previous investigation, adopting the same method used in the present work [5]. The ΔE values for $NiFe_2O_4$ were 112.9, 87.8 and 75.2 kJ mol^{-1} for pure solids and those doped with 3 and 5 mol% Li_2O, respectively. The comparison between the ΔE values for nickel and cobalt ferrites reveals that $CoFe_2O_4$ formation is energetically more easier than $NiFe_2O_4$. This conclusion has been verified experimentally from the fact that the heating of cobalt and ferric oxides at 1000°C resulted in the transformation of most of them into $CoFe_2O_4$, while in the case of nickel and ferric oxides the heating at 1100°C brought about a partial conversion of these oxides into $NiFe_2O_4$ [5]. The decrease in ΔE values, due to lithium-doping to an extent proportional to the amount of Li_2O present, reflects an effective increase in the mobility of thermal diffusion of the reacting cations through the whole mass of the reacting oxides and through the early-produced $CoFe_2O_4$ film.

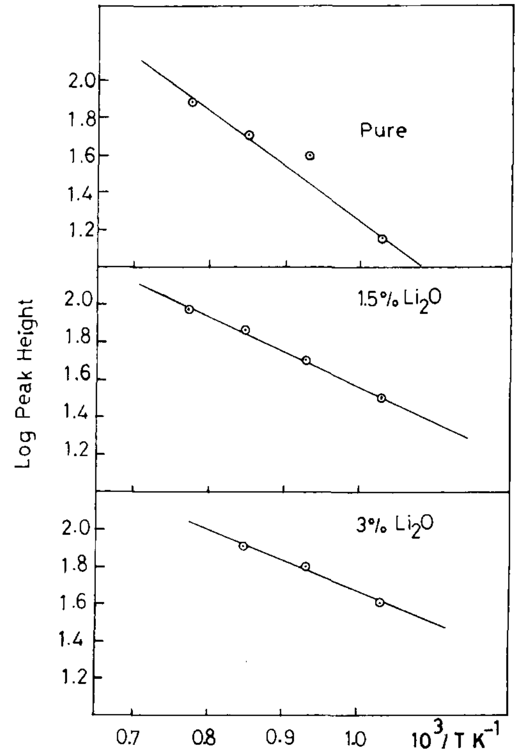

Fig. 7. Change of log peak height of the diffraction line of $CoFe_2O_4$(2.08 Å) as a function of pure and Li-doped mixed solids.

5. Conclusions

The main conclusions that can be derived from the obtained results are:

1. Solid–solid interaction between α-Fe_2O_3 and Co_3O_4 occurred at temperatures starting from 700°C to produce a cobalt ferrite phase. The extent of this reaction increased on increasing the heating temperature in the 700–1000°C range. However, minute amounts of unreacted oxides were detected in the pure-mixed solids heated at 1000°C.
2. Lithium-doping was found to stimulate the ferrite formation to an extent proportional to the amount of Li_2O present. The promotion effect of lithium-

doping has been evidenced from the observed reduced amounts of free oxides and the increased amount of $CoFe_2O_4$ present in the doped mixed solids preheated at temperatures between 700 and 1000°C, and also by the observed progressive decrease in the catalytic activity, in CO oxidation by O_2, of different doped solids preheated at different temperatures.

3. The addition of 1.5 mol% Li_2O was found sufficient to effect the complete conversion of cobalt and ferric oxides into $CoFe_2O_4$ by heating at 1000°C.
4. The activation energy of formation of $CoFe_2O_4$ was determined for pure and Li-doped solids and found to be 57.3, 38.4 and 28.8 kJ mol^{-1} for pure-mixed solids and those treated with 1.5 and 3 mol% Li_2O, respectively. These values suggest that lithium oxide-doping enhanced the ferrite formation process through an increase in the mobility of thermal diffusion of the reacting cations.

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