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EFFECT OF Li_2O-DOPING ON THE THERMAL STABILITY OF COBALTIC OXIDE

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ABSTRACT

The influence of lithium oxide-doping on the thermal stability of Co_3O_4 was studied using DTA, TG, DTG and X-ray diffraction techniques Pure and doped cobaltic oxide specimens were prepared by thermal decomposition of pure basic cobalt carbonate and the basic carbonate mixed with different proportions of LiOH, in air, at different temperatures between 500 and 1100°C

Pure Co_3O_4 was found to start partial decomposition when heated in air at 830°C yielding the CoO phase The complete decomposition was effected by heating at 1000°C

Doping of Co_3O_4 with different proportions of Li_2O was found to much increase its thermal stability The temperatures at which the doped oxide samples started to undergo decomposition were increased to 865, 910 and 1050°C for 0 375, 0 75 and 3% Li_2O-doped solids, respectively The DTA revealed that the 1 5% Li_2O-doped cobaltic oxide did not undergo any thermal decomposition till 1080°C The X-ray investigation showed that the prolonged heating of 1 5 and 3% Li_2O-doped solids at 1100°C for 36 h effected only a partial decomposition of Co_3O_4 into CoO Heating of these solids at temperatures varying between 900 and 1100°C led also to the formation of a new lithium oxide cobaltic oxide phase, the composition of which has not yet been identified

The role of Li_2O in increasing the thermal stability of Co_3O_4 was attributed to the substitution of some of its cobalt ions by Li^+ ions, according to Verwey and De Boer's mechanism leading to the transformation of some of the Co^{2+} into Co^{3+} ions thus increasing the oxidation state of the cobaltic oxide lattice

1 INTRODUCTION

Cobaltic oxide belongs to a *p*-type semiconductor group [1,2]. It is known to be a double-oxide solid $2\,CoO \cdot CoO_2$, containing cobalt ions in the $4+$ and $2+$ valence states [3] and has a spinel structure [4]. Introduction of foreign ions, having a different valency from those of cobalt ions, into the Co_3O_4 lattice may affect its semiconducting, surface and catalytic properties and also its thermal stability [5–8]. The modifications in these properties depend upon the nature of the foreign ions and the calcination conditions of the solid.

In a previous investigation [9], we have studied the effect of the dissolution of monovalent Li^+ ions, at 500 and 700°C, in Co_3O_4 on its catalytic properties in carbon monoxide oxidation at various temperatures between 95 and 250°C. In the present work we investigated the role of dissolution of Li_2O in the Co_3O_4 lattice on its thermal stability by heating in air over a temperature range of 500–1100°C using DTA, TG, DTG and X-ray investigation techniques.

2 EXPERIMENTAL

2.1 Materials

Pure cobaltic oxide specimens were obtained by thermal dissociation of basic cobalt carbonate in air at various temperatures between 500 and 1000°C. The basic cobalt carbonate was prepared by precipitation from hydrated cobalt nitrate using potassium bicarbonate at room temperature in a carbon dioxide atmosphere. Details of the method of preparation have been given elsewhere [10].

Different Li_2O-doped specimens were prepared by heating the basic cobalt carbonate treated with different proportions of LiOH in air at 500–1100°C for 4 h. A concentrated solution of lithium hydroxide was added to a given weight of basic cobalt carbonate making a paste. After drying at a reduced pressure at room temperature, the paste was dried at 100°C to constant weight. Four Li_2O-doped Co_3O_4 solids were prepared. These solids contained 0.375, 0.75, 1.5 and 3 mole% Li_2O.

2 1 Techniques

Differential thermal analysis (DTA) thermogravimetry (TG) and differential thermogravimetry (DTG) of basic cobalt carbonate were carried out using a Du Pont 900 thermal analyzer with a differential scanning calorimeter cell. The rate of heating was 10°C min^{-1} and the sensitivity was 1 mv in^{-1}.

An X-ray investigation of the thermal products of pure and Li-treated basic cobalt carbonate was carried out using a Philips diffractometer type PW 1050. The patterns were run with iron-filtered cobalt radiation, $\lambda = 1.7889$ Å, at 30 kV and 10 mA with a scanning speed of 2° in 2θ per minute.

The specific surface areas of various oxides were determined from nitrogen adsorption isotherms at 77 K using a conventional volumetric apparatus.

3 RESULTS

3.1. Thermal behaviour of pure basic cobalt carbonate

Figure 1a represents the DTA of pure basic cobalt carbonate. Four endothermic peaks are observed, the first is broad extending between 50 and 220°C, whilst the other three peaks are sharp and strong, especially the last one. The second and third peaks are successive and represent two overlapped endothermic reactions. These peaks are followed by a state of thermal stability extending between 400 and 820°C. The maxima of these peaks are located at 275, 320 and 830°C. The first two peaks, in Fig. 1a, correspond to the departure of physisorbed water and water of crystallisation thus converting the basic cobalt carbonate into $CoCO_3$ [11]. The third peak indicates the decomposition of cobalt carbonate to cobaltic oxide. The Co_3O_4 produced suffers no thermal decomposition till a temperature of 820°C, above which it undergoes decomposition into CoO. These results will be confirmed by TG, DTG and X-ray diffraction in the next parts of the present investigation.

The pure basic cobalt carbonate loses about 7 wt.% by heating over a temperature range of 50–220°C, as has been shown from the plots of TG and DTG in Figs. 1b and 1c. The departure of water of constitution and carbon dioxide from the basic cobalt carbonate which occurred successively over a temperature range of 275–350°C represents a weight-loss of 30% (c.f. Figs. 1b and 1c). This value corresponds to the following reaction

$$5\,CoCO_3 \cdot Co(OH)_2 + O_2(g) \xrightarrow{275-350^\circ C} 2\,Co_3O_4 + 5\,CO_2(g) + H_2O(g)$$

The cobaltic oxide formed which remains stable till 820°C loses 6% of its weight by heating over a temperature range of 830–890°C indicating its decomposition into CoO according to the following reaction

$$Co_3O_4 \xrightarrow{830-890^\circ C} 3\,CoO + \tfrac{1}{2}\,O_2(g)$$

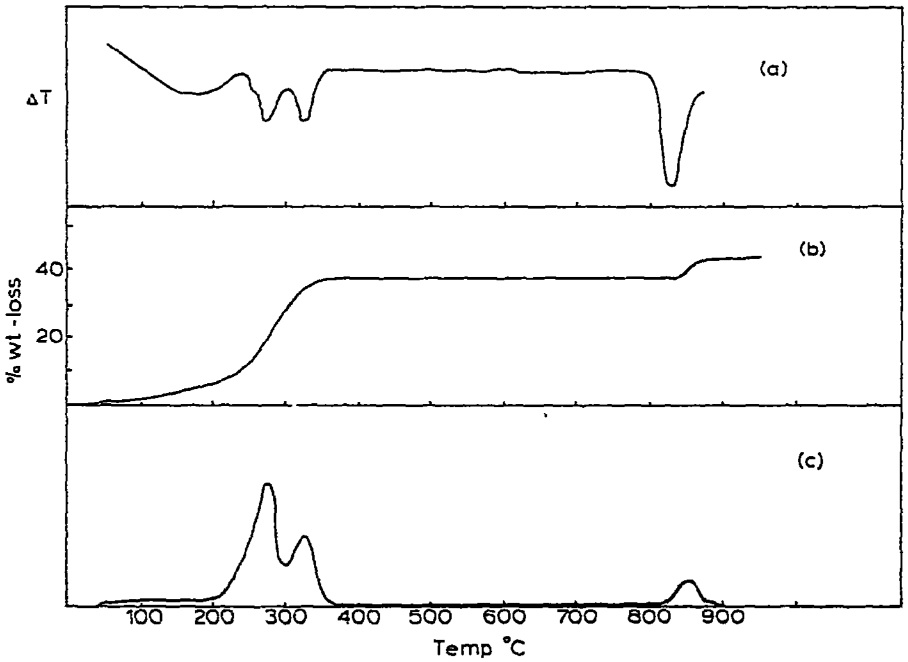

Fig. 1. (a) DTA curve, (b) TG plot, and (c) DTG plot, of pure basic cobalt carbonate

3.2. Differential thermal analysis of lithium hydroxide-treated basic cobalt carbonate

The DTA curves of various LiOH-treated basic cobalt carbonate are given in Fig. 2. This figure also includes the DTA curve of pure basic cobalt carbonate for the sake of comparison. It can be seen that the endothermic peaks corresponding to the departure of physisorbed water, water of crystallisation and CO_2 of the basic cobalt carbonate are almost the same for pure and doped solids, indicating the absence of any influence of the dopant ions on the thermal decomposition of basic cobalt carbonate.

The essential differences between the DTA curves of pure and doped solids are the position and the area of the endothermic peak indicating the decomposition of Co_3O_4. It is observed that Li_2O-doping shifted the decomposition temperature of cobaltic oxide towards a higher range. These temperatures are 860, 910 and 1050°C for 0.375, 0.75 and 3% Li_2O-doped Co_3O_4 specimens, respectively. In the case of the 3% Li_2O-doped solid an additional endothermic peak at 670–700°C was observed. This peak indicates the dehydration of LiOH yielding Li_2O [12,13]. It is also observed from Fig. 2 that doping of Co_3O_4 with 1.5% Li_2O prevented its thermal decomposition in air till 1080°C as indicated by the absence of any endothermic peak in the DTA curve of this solid over a temperature range of 400–1080°C. Figure 2 also shows that the area of the endothermic peak corresponding to the decomposition of cobaltic oxide decreases by increasing the amount of Li_2O dissolved in the Co_3O_4 lattice. This indicates that Li_2O-doping not only retarded the decomposition of cobaltic oxide but also decreased the amount of the solid that undergoes the thermal decomposition.

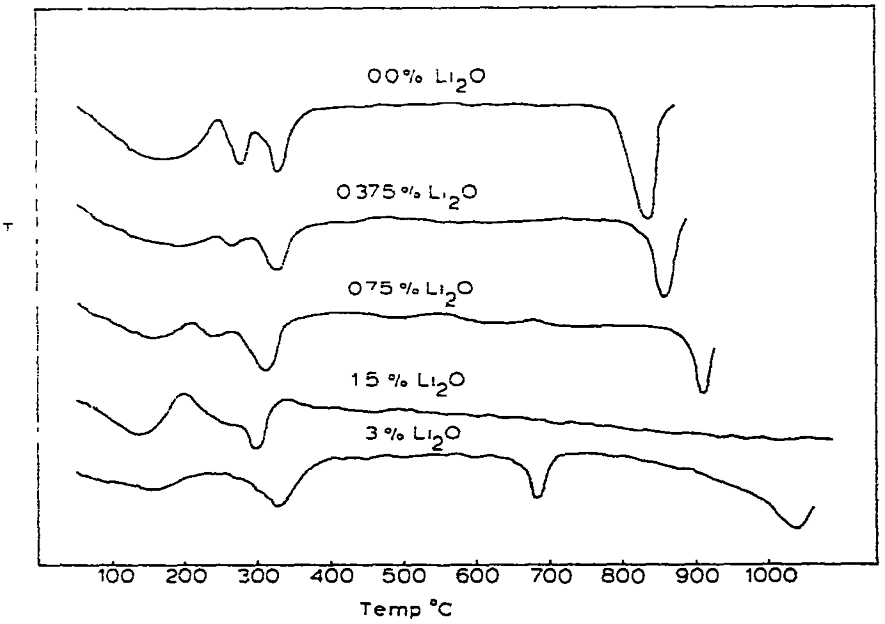

Fig 2 DTA curves of pure and different specimens of LiOH-treated, basic cobalt carbonate

It can be concluded that doping of cobaltic oxide with lithium oxide much increases its thermal stability i.e. stabilizes the Co_3O_4 lattice and the extent of stabilization is directly proportional to the amount of Li_2O added to the cobaltic oxide.

3.3. X-Ray investigation of thermal products of pure basic cobalt carbonate

The X-ray diffraction patterns of thermal products of pure basic cobalt carbonate in air at different temperatures varying between 500 and 1000°C revealed that the solids produced at 500–700°C (Fig. 3) were composed entirely of the very crystalline Co_3O_4 phase. These results agree well with those of DTA, TG and DTG previously presented. The X-ray diffraction patterns of pure solids obtained at 900 and 1000°C are schematically represented in Fig. 3. It is observed that cobaltic oxide decomposes entirely at 1000°C yielding cobaltous oxide, whilst at 900°C the decomposition process is not complete as indicated by the presence of the characteristic lines of both the Co_3O_4 and CoO phase. It was observed from the TG plot (Fig. 1b) that the pure oxide loses 6% of its weight by heating at 830–890°C while the percentage weight-loss corresponding to the complete decomposition must attain 6.5% thus indicating an incomplete decomposition of Co_3O_4. It is to be concluded that prolonged heating of cobaltic oxide at 900°C is necessary to effect its total conversion into CoO.

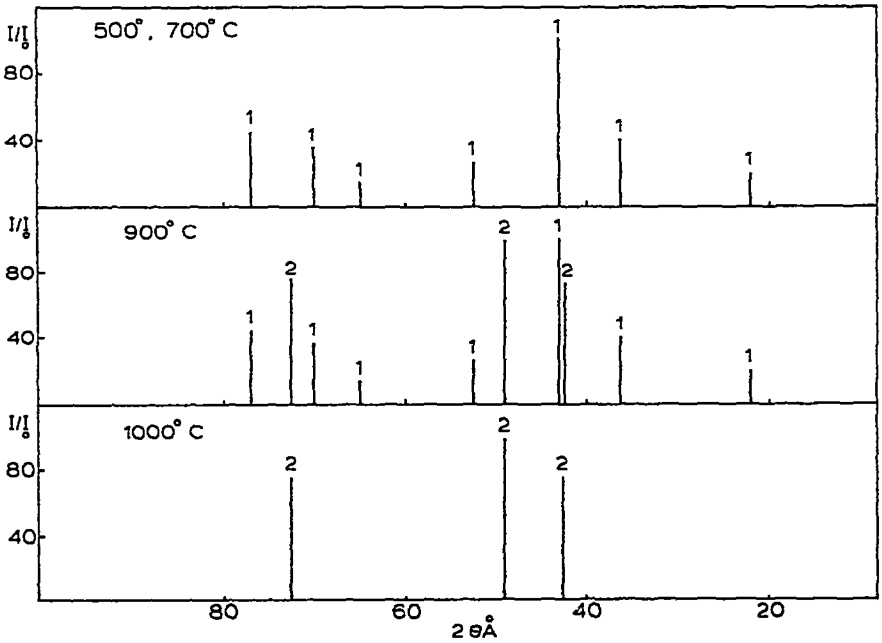

Fig 3. X-Ray diffraction patterns of the solids produced from thermal decomposition of pure basic cobalt carbonate in air at 500, 700, 900 and 1000°C. 1, the Co_3O_4 phase; 2, the CoO phase.

3.4. X-Ray investigation of thermal products of lithium hydroxide-treated basic cobalt carbonate

The X-ray diffraction patterns (not presented here) for all doped solids prepared at 500–700°C are similar to those found for pure solids. In contrast, in the case of 1.5 and 3% Li_2O-doped solids heated in air at 900 and 1000°C the characteristic lines of CoO phase were not detected in their diffraction patterns (c.f. Fig. 4). The cobaltous oxide phase together with the Co_3O_4 phase were present in the 0.375% and 0.75% Li_2O-doped solids heated in air at 1000°C (c.f. Fig. 5) indicating that the addition of these small amounts of lithium oxide to cobaltic oxide retarded its decomposition from 900 to 1000°C and even at 1000°C the decomposition was not complete. These results are in good agreement with those of DTA given before. And for effecting the decomposition of 1.5 and 3% Li_2O-doped Co_3O_4 a thermal treatment at higher temperatures is needed. In fact, the X-ray diffraction of these solids heated at 1100°C (4 h) revealed the presence of CoO together with the Co_3O_4 phase (c.f. Fig. 4). The prolonged heating of these oxide specimens at 1100°C (36 h) could not effect the complete decomposition of cobaltic into cobaltous oxide, as indicated by the appearance of the characteristic lines of both Co_3O_4 and CoO phases in their diffraction patterns.

The progressive increase in the decomposition temperature of Co_3O_4 with increase in the concentration of dopant ions indicates that lithium oxide dissolved in cobaltic oxide increases its thermal stability to an extent proportional to the amount of foreign ions dissolved in its lattice.

Figure 4 also showed the appearance of new lines in the diffraction patterns of 1.5 and 3% Li_2O-doped solids heated in air at 900, 1000 and 1100°C. The *d* spacings

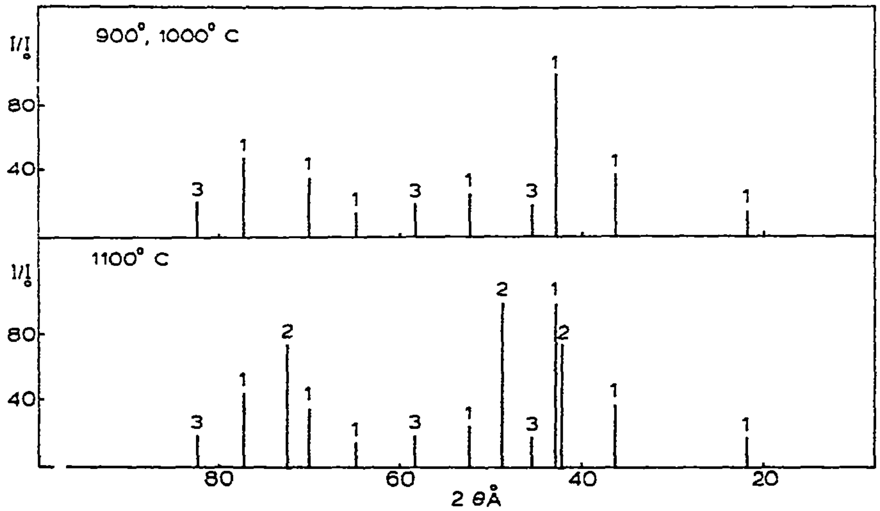

Fig 4 X-Ray diffraction patterns of 1.5% Li_2O-doped cobaltic oxide heated in air at 900, 1000 and 1100°C 1, the Co_3O_4 phase, 2, the CoO phase, 3, a new compound

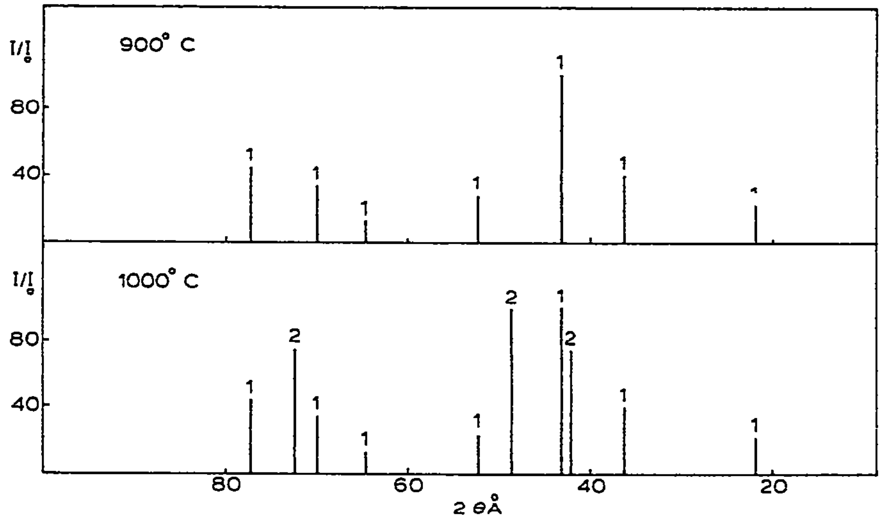

Fig 5 X-Ray diffraction patterns of 0.75% Li_2O-doped cobaltic oxide heated in air at 900 and 1000°C.

and 2θ of these lines were calculated and their data are

d:	2.299	1.836	1.347
2θ:	45.8	58.3	83.2

These data, which did not belong to either Li_2O or cobalt oxides [14], may characterize the formation of a new compound resulting from the interaction between lithium oxide and cobalt oxide in the solid state.

It can be concluded that, at temperatures equal to or higher than 900°C a portion of Li_2O was dissolved in the Co_3O_4 lattice (1.5 and 3% Li_2O-doped) increasing its thermal stability and the other portion underwent a solid–solid interaction with a fraction of Co_3O_4 yielding a new compound. This new compound remained stable at 1100°C. It was not possible, however, to determine the extent of Li_2O dissolved in the Co_3O_4 lattice or that involved in the formation of the new compound.

3.5. Specific surface areas of pure and doped oxides

The specific surface areas of pure and doped oxide specimens prepared at 700°C were determined from nitrogen adsorption isotherms at 77 K using the BET equation. The results obtained are 30, 19, 18 and 7 $m^2\ g^{-1}$ for pure, 0.375, 1.5 and 3% Li_2O-doped cobaltic oxide samples, respectively. Preliminary experiments showed that the specific surface areas of all doped oxides prepared at 900°C were too small to be measured accurately with the volumetric apparatus used. It is observed that dissolution of lithium oxide in the Co_3O_4 lattice led to an important decrease in its surface area, the decrease is, however, more pronounced in the case of the 3% Li_2O-doped specimen. Furthermore, the diminution in surface area of the doped oxides increases with an increase in the preparation temperature due to the increase in the amount of dopant ions effectively dissolved in the oxide lattice.

4 DISCUSSION

The evaluation of the thermal stability of cobaltic oxide and its surface area by doping with lithium oxide revealed an effective incorporation of monovalent Li^+ ions in the Co_3O_4 lattice. The dissolution of Li_2O in Co_3O_4 occurred at temperatures equal to or higher than 700°C at which LiOH decomposed completely into Li_2O [12,13]. Cobaltic oxide is known as the double oxide solid, $2\,CoO \cdot CoO_2$. The stoichiometric Co_3O_4 contains cobalt ions in the 4+ and 2+ valence states. It behaves, similar to NiO, as a *p*-type semiconductor [1,2] due to the presence of a slight excess of oxygen with respect to the stoichiometric composition. This oxygen is accommodated in the oxide lattice as cationic vacancies with the appearance of some trivalent cobalt ions, each oxygen ion in-excess is accompanied by the transformation of two Co^{2+} into two trivalent cobalt ions [15]. The Co^{3+} ions are the charge carriers in a *p*-type Co_3O_4 semiconductor [1,2].

The dissolution of Li_2O in Co_3O_4 may follow different mechanisms depending mainly on the history and calcination conditions of the solid. These mechanisms are

a) Location of dopant ions in cationic vacancies pre-existing in the pure Co_3O_4 solid [16].

b) Introduction of foreign ions in interstitial positions [17].

c) Substitution of some of the cobalt ions of the Co_3O_4 lattice by monovalent Li^+ ions [5].

Introduction of lithium ions into cationic vacancies is restricted by the concentration of cationic vacancies in the pure Co_3O_4 solid, so it is limited by the extent that cobaltic oxide deviates from the stoichiometric composition. Incorporation of Li^+ ions in the Co_3O_4 lattice either in cationic vacancies or in interstitial positions might be accompanied by the transformation of pre-existing Co^{3+} ions into Co^{2+} ions, thus decreasing effectively the semiconducting character of the doped solid. The transition of Co^{3+} into Co^{2+} might also be accompanied by an expansion of the Co_3O_4 lattice and subsequent increase of its specific surface area. The lattice expansion resulted from the geometrical difference in the ionic radii of Co^{3+} and Co^{2+} which are 0.64 Å and 0.78 Å, respectively [8]. It has been shown, in the present investigation, that Li_2O-doping of Co_3O_4 at 700°C led to an important decrease in its surface area. On the basis of specific surface area determination, dissolution of lithium oxide in the cobaltic oxide lattice could not proceed either through location of dopant ions in the cationic vacancies or in the interstitial positions. The most probable mechanism of dissolution of Li_2O in Co_3O_4 may thus be via substitution of some of the cobalt ions of the cobaltic oxide lattice by monovalent ions. This process of substitution has been previously proposed by Verwey and De Boer and it can be simplified by the use of Kroger's notions [18] in the following manner

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

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

$Li(Co^{2+})$ 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. Equations (1) and (2) show that the doping process is accompanied by the transformation of some cobalt ions from the divalent into the trivalent state thus increasing the concentration of charge carriers and enhancing the semiconductor character and decreasing effectively the specific surface area of doped oxide resulting from contraction of its lattice.

The observed decrease in the surface area of doped Co_3O_4 could be attributed to the dissolution of Li_2O in cobaltic oxide according to the mechanism expressed in Eqns. (1) and (2). These equations indicate that the doping process is also accompanied by the fixation of atmospheric oxygen in the doped Co_3O_4 lattice. The thermal stabilization effect induced by the dissolution of Li_2O in Co_3O_4 could be attributed to the increase in the oxidation state of the doped oxide (creation of Co^{3+} ions) and to the built-in oxygen which act as a barrier resisting the reduction of Co_3O_4 into CoO. The greater the amount of Li_2O dissolved in the cobaltic oxide lattice the greater the concentration of trivalent cobalt ions created, the higher the oxidation state of the solid, the greater will be its thermal stability. However, the induced thermal stability was found to attain a certain value which was reached by adding 1.5 mole% Li_2O to Co_3O_4. The decomposition temperature of 3% doped oxide was lower than that for 1.5% doped solid. It seems that by increasing the amount of Li_2O above 1.5% an important portion of the dopant oxide preferentially underwent a solid–solid interaction with a portion of cobaltic oxide yielding a new compound (c.f. the results of X-ray investigation). Furthermore, evaporation of some of the Li_2O dissolved in Co_3O_4 at high temperatures above 1000°C may also account for the limited thermal stability of doped solids.

Dissolution of foreign ions in the Co_3O_4 solid having valencies higher than those of the lattice cobalt ions such as V^{5+} and Mo^{6+} may induce an opposite effect from that observed by the dissolution of Li^+ ions. The effect of doping cobaltic oxide with Mo^{6+} and V^{5+} ions on its thermal stability will be the subject of a forthcoming investigation.

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