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THERMAL BEHAVIOUR OF COBALTIC AND COBALTOUS OXIDES AS INFLUENCED BY DOPING WITH SOME ALKALI METAL OXIDES

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ABSTRACT

The role of Na_2O- and Li_2O-doping on the thermal decomposition of Co_3O_4 to CoO and the re-oxidation of cobaltous to cobaltic oxide has been investigated using DTA, with controlled rates of heating and cooling, IR and X-ray diffraction spectrometry techniques.

The DTA investigation revealed that both Li_2O and Na_2O increased the thermal stability of Co_3O_4. However, the effect was much more pronounced in the case of lithium oxide. Doping Co_3O_4 with 1.5 mole% Li_2O was found to prevent any thermal decomposition of cobaltic oxide even by heating at 1100°C. The maximum thermal stabilization effect induced by doping with sodium oxide (4.5 mole%) was 30%. The sodium oxide- and lithium oxide-doping enhanced the reactivity of the produced CoO towards the re-oxidation by O_2 yielding Co_3O_4.

The X-ray diffraction and IR spectrometric investigations showed that part of Li_2O and Na_2O was effectively incorporated in the Co_3O_4 lattice, affecting the thermal stabilization of the solid, and another part of the dopant oxide interacted with the produced CoO and also with Co_3O_4 giving a new sodium cobalt compound, and with Co_3O_4 producing, also, a new lithium cobalt oxide phase. However, the amount of Li_2O dissolved in the Co_3O_4 lattice was greater than that of Na_2O. The sudden cooling of doped solids, from 1000°C to room temperature, favoured the formation of the new sodium cobalt oxide compound, and exerted no effect on the production of the new lithium cobalt oxide phase. The characteristic *d* spacings and IR absorption bands of these new compounds have been determined.

The possible mechanisms of dissolution of Li_2O and Na_2O in cobaltic oxide lattice are discussed.

INTRODUCTION

Physico-chemical, electrical, surface, catalytic and thermal properties of cobalt oxides have been the subject of several investigations [1–19]. These properties have been found to be greatly influenced by the pre-history of parent materials [1–3], method of preparation, calcination conditions [4–9] and dissolution of foreign oxide(s) in the lattice of cobalt oxide solids [10–19].

In previous investigations we have studied the effects of dissolution of each of Li_2O, V_2O_5, MoO_3, MgO and Al_2O_3 in cobalt oxides on their

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catalytic, surface [10,12–17], and thermal properties [11,18,19]. The most probable mechanisms of dissolution of different dopant oxides in cobalt oxides were suggested. The ionic radii of the cations of these dopant oxides are equal to or smaller than those of cobalt cations in cobalt oxides [11,20,21]. Most of these dopant oxides being dissolved in cobaltic oxide increased its thermal stability to different extents depending on the nature of the oxide dissolved. The increase in the thermal stability of doped Co_3O_4 has been attributed to the increase in the oxidation character of cobaltic oxide which acts as an energy barrier opposing the reduction of Co_3O_4 to CoO.

In the present investigation, the effect of doping with Li_2O and Na_2O on the thermal decomposition of cobaltic oxide and on the reactivity of the produced cobaltous oxide for oxidation by O_2 to Co_3O_4 is studied. The techniques employed in this work are DTA, X-ray diffraction and IR absorption spectrometry.

EXPERIMENTAL

Materials

Pure and doped cobalt oxide solids were obtained by the thermal decomposition of pure basic cobalt carbonate [5,11] and basic cobalt carbonate treated with different proportions of LiOH and NaOH. The roasting was carried out at 1000°C for 4 h. Pure and doped oxide specimens were subjected to both sudden and slow cooling from 1000°C to room temperature. Four Na_2O-doped Co_3O_4 solids were prepared which contained 0.75, 1.5, 3 and 4.5 mole% Na_2O. Three Li_2O-doped Co_3O_4 specimens containing 0.75, 1.5 and 3 mole% Li_2O were also prepared.

Techniques

Differential thermal analysis (DTA) of pure and doped basic cobalt carbonate was done using a Du Pont 990 thermal analyzer with a differential scanning calorimeter cell. The rate of heating and cooling was kept constant at 20° min^{-1} and the sensitivity was 1 mV in^{-1}. Thirty mg of each solid sample was employed in each case.

An X-ray investigation of the thermal products of pure and doped basic cobalt carbonate was carried out using a Philips diffractometer type PW 1050. The patterns were run with a scanning speed of 2° in 2θ per minute.

An infrared absorption spectrum was determined for each solid using Beckman Spectrometer IR 4250. The IR spectra were determined from 4000 to 300 cm^{-1} but the portion between 1400 and 300 cm^{-1} were considered in the present investigation. Two mg of each solid sample were mixed with 200 mg of vacuum-dried IR-grade KBr. The mixture was dispersed by grinding for 3 min in a vibratory ball mill and placed in a steel die 13 mm in diameter and subjected to a pressure of 12 tons.

Results

Figures 1 and 2 represent the DTA (heating and cooling) of pure basic cobalt carbonate and cobalt carbonate treated with different proportions of sodium and lithium hydroxide. Four endothermic peaks are observed in the case of pure basic cobalt carbonate and the cobalt carbonate treated with different proportions of NaOH. The first peak is broad, extending between 50 and 220°C, while the other three peaks are sharp and strong, especially the last one. The second and third peaks, having their maxima located at 295 and 365°C, indicate the loss of water of crystallization and decomposition of

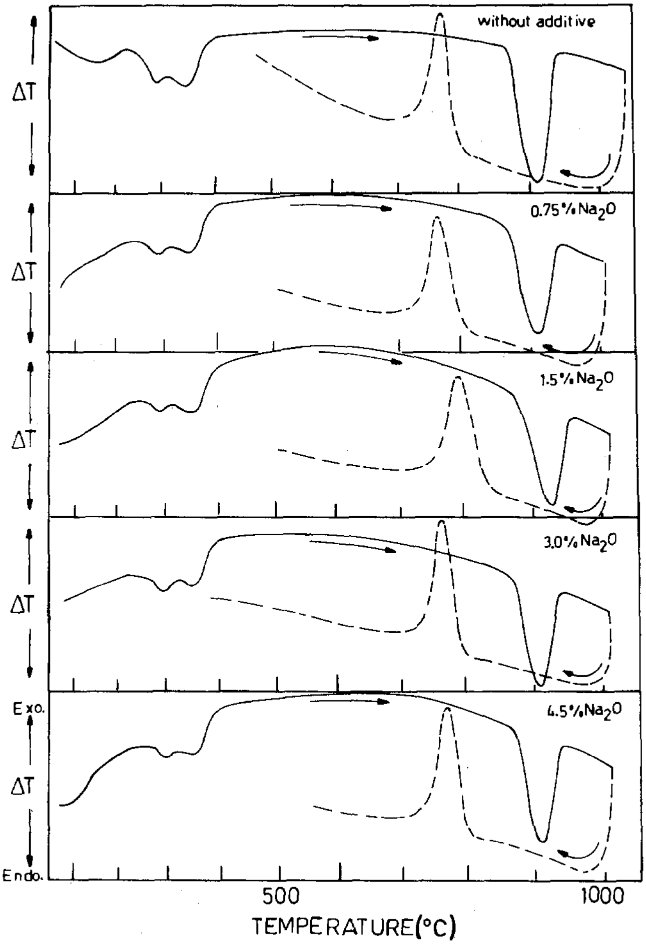

Fig. 1. DTA heating and cooling curves of pure and sodium hydroxide-treated specimens of basic cobalt carbonate.

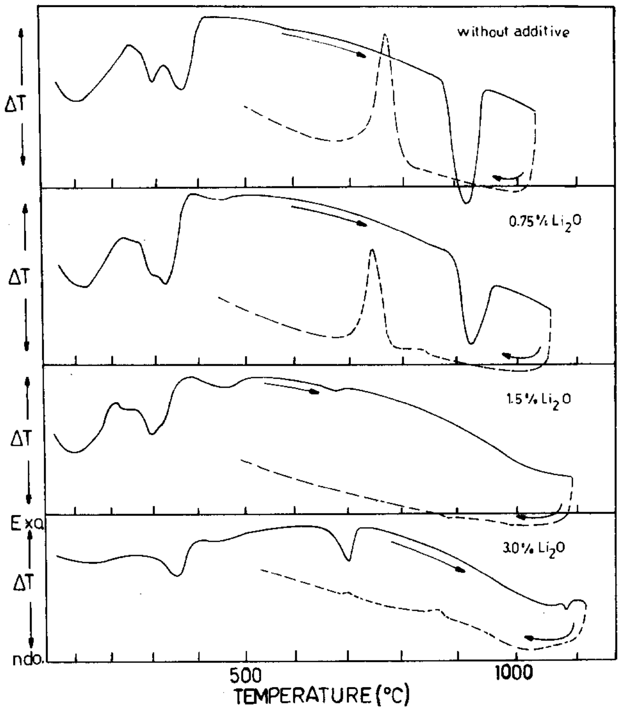

Fig. 2. DTA heating and cooling curves of pure and lithium hydroxide-treated specimens of basic cobalt carbonate.

$CoCO_3$ to Co_3O_4 [11,18]. The last peak, with its maximum at 910°C (925°C in the case of the solid treated with 1.5% Na_2O), corresponds to the decomposition of Co_3O_4 to CoO [11,18]. A strong exothermic peak was observed during the cooling of pure and sodium hydroxide-treated solid. The maximum of this peak is located at 770°C in the case of pure and sodium-treated solids except the solid containing 1.5% Na_2O, its maximum was found at 790°C. This shift in temperature indicates an early oxidation of the produced CoO phase in the 1.5% Na-doped solid.

Treating the basic cobalt carbonate with a small amount of lithium hydroxide (1.5 mole%) or sodium hydroxide affects the area of endothermic and exothermic peaks corresponding to the decomposition of Co_3O_4 to CoO and the oxidation of cobaltous to cobaltic oxide. Increasing the amount of LiOH to 3 mole% was accompanied by disappearance of both endothermic and exothermic peaks corresponding to the decomposition of Co_3O_4 to CoO and the reoxidation of cobaltous to cobaltic oxide. In other words, doping of Co_3O_4 with 1.5 mole% Li_2O caused its complete thermal stabilization till a temperature as high as 1100°C. When the amount of Li_2O attained 3 mole%, a very small endothermic peak at 1080°C and a very small exothermic peak at 865°C were observed. These peaks indicate that a very small portion of

TABLE 1

The effect of Na_2O- and Li_2O-doping on the peak area of the DTA curves of the thermal decomposition of Co_3O_4 and oxidation of CoO

Solid	Peak area (arbitrary unit)		%Decrease in the area of endothermic peak[a]	Ratio between the area of exothermic and endothermic peaks
	Endothermic peak	Exothermic peak		
Pure basic cobalt carbonate	19.74	15.47	0.0	0.78
Basic cobalt carbonate +				
0.75% Na_2O	15.64	14.64	20.77	0.94
1.5% Na_2O	15.32	15.64	22.39	1.02
3.0% Na_2O	14.88	14.52	24.62	0.98
4.5% Na_2O	13.80	14.72	30.01	1.07
0.75% Li_2O	7.45	8.94	62.25	1.20
1.5% Li_2O	nil	nil	100.00	
3.0% Li_2O	0.10	0.10	99.50	1.00

[a] The data of this column were obtained by subtracting the area of the endothermic peak for each solid from 19.74 (that for the pure solid).

Co_3O_4 underwent decomposition yielding CoO which interacted with O_2, during cooling, to reproduce cobaltic oxide. A new endothermic peak, with its maximum at 695°C, was observed in the case of the 3% lithium oxide-doped solid. This peak corresponds to decomposition of LiOH giving Li_2O [11,22] and not to an earlier decomposition of Co_3O_4 to CoO. This speculation is experimentally confirmed by the absence of any strong exothermic peak in the DTA curve of the solid doped with 3 mole% Li_2O (Fig. 2).

Once a constant weight of pure and treated cobalt carbonate was taken in each DTA run, the area of endothermic ane exothermic peaks for each solid could be considered as a measure of the extent of the solid that suffers a chemical change (decomposition, $Co_3O_4 \rightarrow CoO$, and oxidation, $CoO \rightarrow Co_3O_4$). The data of the endothermic and exothermic peaks corresponding to the decomposition of cobaltic to cobaltous oxide and oxidation of cobaltous to cobaltic oxide for pure and doped oxide specimens are given in Table 1. This table also includes the percentage decrease in the area of the endothermic peak due to doping with Na_2O and Li_2O and the ratio between the area of the exothermic and endothermic peaks. It can be deduced from Table 1 that doping of Co_3O_4 with Na_2O effected a decrease in the area of the endothermic peak proportional to the amount of the dopant oxide added, a 30% decrease was attained by doping with 4.5 mole% Na_2O. In the case of Li_2O-doping, the addition of 0.75 mole% Li_2O to Co_3O_4 effected an important decrease of 62.2% in the area of the endothermic peak indicating much more thermal stabilization of Co_3O_4 than that induced by doping with Na_2O. The addition of 1.5 mole% Li_2O to Co_3O_4 prevented any thermal decomposition of the solid.

The ratio between the area of exothermic and endothermic peaks (Table 1, the last column), gives a measure of the reactivity of the produced CoO towards re-oxidation by O_2 during the cooling process from 1000 to 500°C. It can be seen that doping of cobalt oxide with Na_2O or Li_2O increases the reactivity of the produced cobaltous oxide for re-oxidation. The fact that this ratio is smaller than unity (0.78) in case of pure solid and tends to unity for most of doped solids, indicates that the produced CoO was not completely oxidized to Co_3O_4 in case of pure solid and was almost entirely oxidized to cobaltic oxide in case of doped solids.

It can be concluded that doping of cobalt oxide by Li_2O or Na_2O affected the thermal stabilization of Co_3O_4. However, the thermal stabilization effect is much more pronounced in the case of Li_2O-doping. Moreover, the addition of an alkali metal oxide to cobalt oxide increases the reactivity of the produced cobaltous oxide for re-oxidation yielding Co_3O_4. These results will be confirmed by an X-ray investigation of pure and doped solids.

X-Ray investigation of pure and doped cobalt oxides

The X-ray diffraction patterns of the thermal products of pure basic cobalt carbonate heated in air at 1000°C and subjected to sudden cooling to room temperature revealed that the solid produced was composed entirely of the very crystalline CoO phase. The pure solid heated at 1000°C and allowed to cool slowly to room temperature was composed of a mixture of Co_3O_4 and CoO phases, indicating that the produced cobaltous oxide underwent partial oxidation giving cobaltic oxide. These results are in good agreement with those of DTA (Table 1, last column).

The X-ray diffraction patterns of sodium oxide-doped cobalt oxide, containing 3 and 4.5 mole% Na_2O, and calcined at 1000°C followed by sudden cooling to room temperature, revealed that the solids were composed of CoO together with a new phase. The 2θ and d spacings of this new phase were calculated and their data are

d	14.66	1.285	1.498
2θ	6.4	88.2	73.3

These data which did not correspond to the characteristic diffraction lines of free Na_2O, NaOH or Na_2CO_3 [23] may belong to a sodium cobalt oxide compound. The known sodium cobalt oxide compounds are $NaCo_2O_4$ and Na_4CoO_4 [23]. The newly detected lines in the X-ray diffraction patterns of Na_2O-doped solids are different from those of the known sodium cobalt oxide solids. It can be concluded that a portion of sodium oxide was effectively dissolved in the cobalt oxide lattice giving a solid solution and the other portion underwent a chemical interaction with cobalt oxide, in the solid state, to produce a new sodium cobalt oxide compound. The absence of free sodium oxide in the doped solid may indicate that most of the dopant oxide added was involved in the formation of both solid solution and the new sodium cobalt oxide compound.

The diffraction patterns of cobalt oxide doped with Na_2O (3 and 4.5 mole%), heated in air at 1000°C and allowed to cool slowly to room temperature indicated that the solids produced were composed of Co_3O_4 together with the newly formed sodium cobalt oxide. However, the intensity of the diffraction lines of the new compound decreases by subjecting the doped solid to slow cooling. These results which show that all the CoO produced was entirely oxidized by O_2 to Co_3O_4 are in agreement with the results of DTA (Table 1, last column). The fact that the slow cooling of sodium-doped cobalt oxide from 1000°C to room temperature effected a decrease in the intensity of the newly detected diffraction lines may indicate that Na_2O interacted with both Co_3O_4 and CoO to produce the newly formed compound. In the course of slow cooling, from 1000°C, the produced CoO interacted more easily with O_2 than with Na_2O.

The X-ray investigation of Li_2O-doped solids has been presented previously [11]. The results obtained could be summarized as follows: (1) Li_2O-doped cobalt oxides containing 1.5 and 3 mole% heated at 900 and 1000°C, then allowed to cool suddenly, were composed entirely of Co_3O_4 phase together with a new lithium cobalt oxide compound; (2) the lithium-doped solid calcined at 1100°C was composed of a mixture of Co_3O_4, CoO and the new compound; (3) the 2θ and d spacings of the newly formed compound 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 [23], may characterize the formation of a new compound resulting from the interaction between lithium oxide and cobalt oxide in the solid state [11].

It can be concluded that Li_2O-doping of cobalt oxide caused a pronounced thermal stabilization of Co_3O_4 phase which is clearly shown by DTA, heating and cooling, and confirmed by X-ray investigation of the doped solids. In order to obtain more details about the characteristics of the newly formed sodium and lithium cobalt oxide compounds, the IR absorption spectra of sodium and lithium-oxide doped cobalt oxides were measured.

IR spectrometric investigation of the thermal products of pure basic cobalt carbonate and cobalt carbonate mixed with sodium hydroxide

The IR absorption spectra were measured for pure and doped solids heated in air at 1000°C for 4 h and subjected to both sudden and slow cooling. Figures 3 and 4 represent the absorption spectra of pure and doped solids containing 1.5 and 4.5 mole% Na_2O and subjected to both sudden and slow cooling, respectively. It is observed from Fig. 3 that pure and doped oxides suddenly cooled from 1000°C to room temperature exhibit a very strong broad band extending between 300 and 600 cm^{-1} which characterizes a CoO structure [18]. A second band at 660 cm^{-1} was also observed in the IR of pure and doped oxides, the percentage transmission of this band increases by increasing the amount of dopant oxide. The doped oxides also exhibit other bands at 570 cm^{-1}, 780 cm^{-1}, 800 cm^{-1} and a strong band at 1090 cm^{-1} (in the case of the solid treated with 4.5 mole% Na_2O). The bands located at 570 cm^{-1} and 660 cm^{-1} characterize a Co_3O_4 structure [10,25]. The bands at 780, 800 and 1090 cm^{-1} did not belong to either free NaOH, Na_2O or Na_2CO_3 [24,25]. They may characterize a sodium oxide–cobalt oxide compound. The small % transmission of the band at 660 cm^{-1} in the pure solid indicates that the extent of Co_3O_4 present is very small, so it was not detected by X-ray diffraction as mentioned previously in this investigation. The increase in the % transmission of the band at 660 cm^{-1} and the appearance of the band at 570 cm^{-1} in the IR spectra of

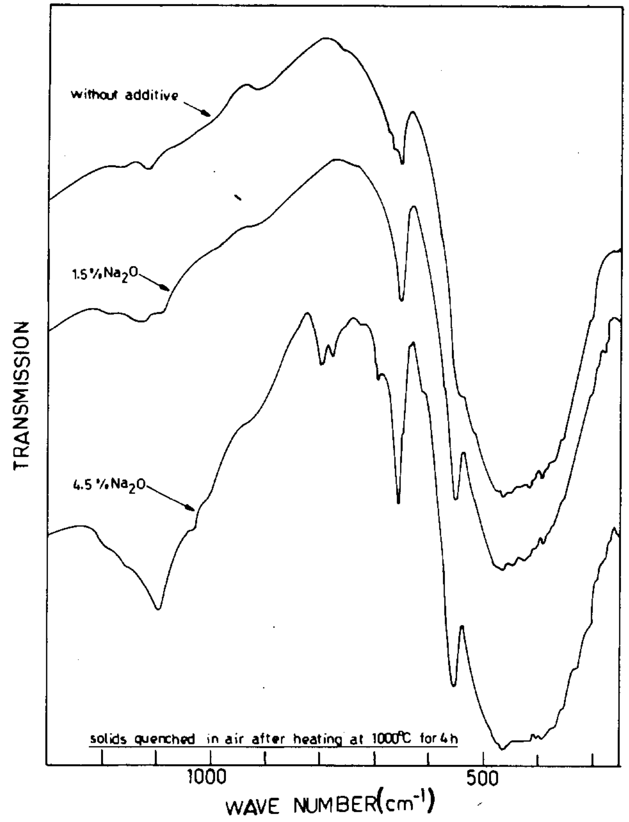

Fig. 3. IR absorption spectra of pure and sodium hydroxide-treated samples of basic cobalt carbonate heated in air at 1000°C for 4 h and subjected to sudden cooling to room temperature.

doped oxides revealed that doping of cobalt oxide by Na_2O increases the thermal stability of Co_3O_4, preventing a part of this oxide from decomposition at 1000°C. Moreover, the extent of thermal stabilization induced by Na_2O-doping is directly proportional to the amount of dopant oxide added. These results are in good agreement with those of DTA (Table 1, column 4).

The slow cooling of the pure and doped oxide from 1000°C to room temperature produced five strong bands in their IR spectra. These bands are located at 660, 645, 560, 420 and 390 cm^{-1}, and other two bands at 675 and 580 cm^{-1} were detected in the spectra of the 4.5 mole% Na_2O-doped solids. These seven bands represent all the characteristic absorption bands of Co_3O_4 [25]. The IR spectra of Co_3O_4 heated at 700°C was composed of these seven absorption bands [18]. The slow cooling of sodium-doped oxide solids was accompanied by the disappearance of the bands at 780, 800 and 1090 cm^{-1} present in the IR spectra of the suddenly cooled doped oxides. The appearance of all bands of Co_3O_4 in the spectra of doped solids subjected to

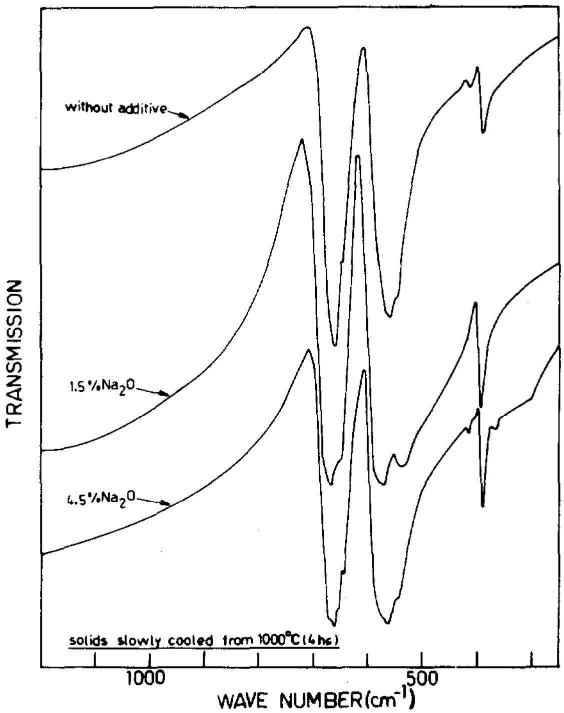

Fig. 4. IR absorption spectra of pure and sodium hydroxide-treated samples of basic cobalt carbonate heated in air at 1000°C for 4 h and allowed to cool slowly to room temperature.

slow cooling from 1000°C to room temperature indicates that the CoO produced was entirely oxidized by O_2, producing Co_3O_4. These results are in good agreement with those of DTA (Table 1, column 5) and the X-ray investigation given previously in this work. The absence of the bands at 780, 800 and 1090 cm^{-1} in the IR spectra of the slowly cooled doped solids may indicate that the sudden cooling of these oxides favoured the formation of the new sodium cobalt oxide compound. It is plausible that Na_2O interacts mainly with CoO to produce a new sodium cobalt oxide and during the slow cooling of the doped oxide cobaltous oxide is produced preferentially and interacts with O_2 to yield Co_3O_4.

IR spectrometric investigation of the thermal products of basic cobalt carbonate treated with lithium hydroxide

The IR absorption spectra were measured for doped oxides heated in air at 1000°C for 4 h and subjected, also, to both sudden and slow cooling to room temperature. Both the suddenly and slowly cooled doped solids, containing 1.5 and 3 mole% Li_2O, exhibit all the absorption bands characterizing the Co_3O_4 structure together with a new strong band at 1140

$\mathrm{cm^{-1}}$. However, the % transmission of this band decreases by increasing the amount of $\mathrm{Li_2O}$ added from 1.5–3 mole%. This band which did not correspond to free LiOH or $\mathrm{Li_2O}$ may characterize a new lithium cobalt oxide. These results clearly indicate that lithium oxide-doping of cobalt oxide increases the thermal stability of $\mathrm{Co_3O_4}$ and interacts with a part of cobaltic oxide giving a new compound.

DISCUSSION

The DTA, X-ray diffraction and IR spectrometric investigations of pure and doped cobalt oxides revealed clearly that the addition of monovalent $\mathrm{Li^+}$ and $\mathrm{Na^+}$ ions to cobalt oxide increased the thermal stability of cobaltic oxide. However, this effect was limited in the case of $\mathrm{Na^+}$-doping and a complete thermal stabilization of the $\mathrm{Co_3O_4}$ phase was reached by dissolution of $\mathrm{Li^+}$ ions in the cobaltic oxide lattice. The observed increase in the thermal stability of $\mathrm{Co_3O_4}$ due to doping indicates an effective dissolution of the foreign ions in the cobaltic oxide lattice. The dissolution of the dopant ions in the oxide lattice may proceed via location in cationic vacancies, in interstitial positions or by substitution of some of the cobalt ions of the $\mathrm{Co_3O_4}$ lattice. The location of $\mathrm{Na^+}$ and $\mathrm{Li^+}$ in cationic vacancies or in interstitial positions in cobalt oxide solid should be accompanied by a decrease in the concentration of trivalent cobalt ions present in a non-stoichiometric $\mathrm{Co_3O_4}$ solid according to

$$\mathrm{Li_2O} + 2\,\mathrm{Co^{3+}} \rightarrow 2\,\mathrm{Li}\boxed{\triangle} + 2\,\mathrm{Co^{2+}} + 1/2\,\mathrm{O_{2(g)}} \tag{1}$$

$$\mathrm{Na_2O} + 2\,\mathrm{Co^{3+}} \rightarrow 2\,\mathrm{Na}\boxed{\triangle} + 2\,\mathrm{Co^{2+}} + 1/2\,\mathrm{O_{2(g)}} \tag{2}$$

$\mathrm{Li}\boxed{\triangle}$, $\mathrm{Na}\boxed{\triangle}$ are lithium and sodium ions located in cationic vacancies or in interstitial positions, $\mathrm{Co^{3+}}$ ions are the charge carriers in a non-stoichiometric *p*-type $\mathrm{Co_3O_4}$ solid [11,26]. The dissolution of $\mathrm{Na^+}$ and $\mathrm{Li^+}$ according to such a mechanism is accompanied by degassing of some excess $\mathrm{O_2}$ of $\mathrm{Co_3O_4}$ followed by subsequent transformation of some of $\mathrm{Co^{3+}}$ into $\mathrm{Co^{2+}}$ ions. In other words, the oxidation character of $\mathrm{Co_3O_4}$ decreases by doping and its reduction to CoO becomes energetically easier. Such a mechanism must be excluded in our case because the reduction of $\mathrm{Co_3O_4}$ to CoO became more difficult by doping with $\mathrm{Li^+}$ and $\mathrm{Na^+}$ ions.

The dissolution of monovalent dopant ions must, consequently, proceed via substitution of some cobalt ions of the $\mathrm{Co_3O_4}$ lattice, which are $\mathrm{Co^{2+}}$ and $\mathrm{Co^{4+}}$ [21], according to [11,27]

$$\mathrm{A_2O} + 1/2\,\mathrm{O_{2(g)}} \rightarrow 2\,\mathrm{A(Co^{2+})} + 2\,\mathrm{Co^{3+}} \tag{3}$$

$$\mathrm{A_2O} + 3/2\,\mathrm{O_{2(g)}} \rightarrow 2\,\mathrm{A(Co^{4+})} + 6\,\mathrm{Co^{3+}} \tag{4}$$

where $\mathrm{A_2O}$, $\mathrm{A(Co^{2+})}$ and $\mathrm{A(Co^{4+})}$ are lithium or sodium oxide, lithium or sodium ions located in the position of host cations Co^{2+} and Co^{4+} present in the cobaltic oxide lattice respectively, and Co^{3+} is the charge carrier ion created in Co_3O_4. The reactions expressed by eqns. (3) and (4) are accompanied by fixation of atmospheric oxygen and subsequent transformation of some divalent cobalt ions into trivalent cobalt ions, thus increasing the oxidation character of the solid. The increase in oxidation character of Co_3O_4 acted as an energy barrier, resisting its reduction into CoO. The amount of O_2 build in Co_3O_4 and that of created Co^{3+} ions, induced by dissolution of a given amount of foreign ions according to reaction (4), are three times greater than those caused by dissolution of the same amount of dopant ions according to reaction (3). In other words, the extent of increase in thermal stability of Co_3O_4 due to doping according to reaction (4) could be expected to be three times as high as that induced by doping according to reaction (3). Analysis of the DTA curves for the pure and doped solid revealed that the addition of 0.75 mole% Li_2O and 0.75 mole% Na_2O to cobalt oxide caused an increase of 62.2% and 20.7%, respectively, in the thermal stability of Co_3O_4 (Table 1). These results may indicate that Li^+ ions preferentially substitute some Co^{4+}, especially the addition of the small amounts (0.75 mole%), while Na^+ ions may substitute some Co^{2+} of the Co_3O_4 lattice. These results could be attributed to the similarity between the ionic radii of Li^+ and Co^{4+} ions which are 0.60 Å and 0.56 Å, respectively. The ionic radius of Na^+ (0.95 Å) [20], being much greater than that of Co^{4+} and still greater than that of divalent cobalt ion (0.78 Å), may account for the limited thermal stabilization by Na_2O-doping due to a limited solubility of Na^+ ions in the cobaltic oxide lattice.

It can be concluded that the small size of Li^+ ions enhances its dissolution in cobaltic oxide lattice by substituting some of its ions, thus considerably increasing the oxidation character of the doped solid. The increase of the oxidation character of Co_3O_4 due to dissolution of 1.5 mole% Li_2O was capable of preventing any thermal decomposition of the doped oxide. It is plausible that the main part of Li_2O added to cobalt oxide was effectively dissolved in the oxide lattice and a small part of the dopant oxide underwent a solid–solid interaction with a portion of Co_3O_4 producing a new lithium cobalt oxide phase. By contrast, the main part of Na_2O added to cobalt oxide might be involved in a solid–solid interaction with CoO and Co_3O_4 yielding a new sodium cobalt oxide phase, while a small part of Na_2O was dissolved in the Co_3O_4 lattice.

The ionic radii of the other alkali metal ions, K^+, Rb^+, Cs^+ and Fr^+ (1.33, 1.48, 1.69 and 1.76 Å, respectively) are too large to dissolve in the cobaltic oxide lattice. So, the addition of these monovalent ions to cobalt oxide would be expected to have no effect on its thermal stability.

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