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THERMAL STABILITY OF COBALT OXIDES DOPED WITH MgO AND Al_2O_3

G.A. EL-SHOBAKY, N.M. GHONEIM and I.M. MORSI

National Research Centre, Dokki, Cairo (Egypt)

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ABSTRACT

The influence of MgO and Al_2O_3 doping on the thermal decomposition of cobaltic oxide to cobaltous oxide and the re-oxidation of CoO to Co_3O_4 was studied using DTA, with controlled rate of heating and cooling, and infrared and X-ray diffraction techniques. X-ray diffraction and infrared absorption spectra were obtained for different solids subjected to both sudden and slow cooling.

The DTA investigation revealed that MgO slightly decreased both the thermal stability of Co_3O_4 and the susceptibility of CoO to oxidation by O_2 to form Co_3O_4. By contrast, Al_2O_3 considerably increased the thermal stability of cobaltic oxide to an extent proportional to the amount of dopant oxide, attaining a maximum stability of 58% for the 4.5% Al_2O_3-doped solid. Furthermore, Al_2O_3 effectively enhanced the reactivity of CoO for oxidation to Co_3O_4.

The marked thermal stability of Co_3O_4, induced by doping with Al_2O_3, was confirmed by both X-ray diffraction and infrared absorption spectrometry investigations. The sudden cooling of MgO and Al_2O_3-doped cobalt oxide specimens from 1000°C to room temperature, was accompanied by the appearance of a strong absorption band at 1380 cm^{-1}. The intensity of this band, which was more pronounced in the case of Al_2O_3-doped solids, decreased considerably with slow cooling of the doped oxide specimens.

The possible mechanisms of MgO and Al_2O_3-doping of cobalt oxides were discussed.

INTRODUCTION

Cobaltic oxide is a double oxide solid consisting of $CoO_2 \cdot 2\ CoO$ [1–5]. The host lattice cations exist in the form Co^{4+} and Co^{2+}. Co_3O_4 is stable at temperatures below 800°C above which it may decompose forming CoO [6–8]. Its thermal stability could, however, be modified by doping [8,9].

Co_3O_4 exhibits well-known surface and catalytic properties [7,10–15]. These properties have been found to be much influenced by doping [12–15]. CoO may also interact with O_2 giving solid cobaltic oxide.

In our preceding investigations, the effects of doping by Li_2O [8], V_2O_5 and MoO_3 [9] on the thermal stability, surface [14] and catalytic properties [12] of cobaltic oxide have been investigated.

In the present work, we studied the effect of doping with MgO and Al_2O_3

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on the thermal stability of cobaltic oxide and on the reactivity of the resultant cobaltous oxide for oxidation by O_2 to Co_3O_4. The techniques used in this investigation were DTA, X-ray diffraction and infrared absorption spectrometry.

EXPERIMENTAL

Materials

Pure and doped cobalt oxide specimens were prepared by thermal decomposition of pure basic cobalt carbonate, $5\ CoCO_3 \cdot Co(OH)_2$ [7,8], and basic carbonate mixed with different proportions of magnesium or aluminium nitrates. The calcination was carried out in air at 1000°C for 4 h. Two sets of specimens were obtained, the first was produced by subjecting the solids to rapid cooling from 1000°C to room temperature and the solids of the second set were allowed to cool slowly. Six Al_2O_3-doped Co_3O_4 samples were prepared. These solids contained 0.375, 0.75, 1.5, 3.0, 4.5 and 6 mole% Al_2O_3. Three MgO-doped Co_3O_4 specimens were also prepared. The magnesium oxide contents were 1.5, 3 and 6 mole%.

Techniques

Differential thermal analysis (DTA) of pure and doped basic cobalt carbonate was carried out using a DuPont 990 thermal analyser with a differential scanning calorimeter cell. The rate of both heating and cooling was kept at 20°C min^{-1} and the sensitivity was 1 mV in^{-1}. A 30 mg sample of each solid was employed in each run.

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 iron-filtered cobalt radiation (1.7889 Å) at 30 kV and 10 mA with a scanning speed of 2° in 2θ per minute.

An infrared absorption spectrum was determined for each solid using a Beckman Spectrometer IR 4250. The IR spectra were determined from 4000 to 300 cm^{-1} but the portions between 1700 and 300 cm^{-1} were considered in this investigation. 2 mg of each solid sample were mixed with 200 mg of vacuum-dried IR-grade KBr. The mixture was dispersed by grinding for three minutes in a vibratory ball mill and placed in a steel die 13 mm in diameter and subjected to a pressure of 12 tons. The sample disks were placed in the holder of a double-grating IR spectrometer.

RESULTS

The DTA of pure basic cobalt carbonate and cobalt carbonate treated with magnesium and aluminium nitrates was carried out.

Figures 1 and 2 represent the DTA of pure basic cobalt carbonate and cobalt carbonate treated with different proportions of magnesium and aluminium nitrates. Four endothermic peaks are observed in the case of pure basic cobalt carbonate, the first is broad, extending between 50 and 200°C, while the other three peaks are sharp and strong, especially the last one. The second and third peaks, with their maxima located at 295 and 365°C correspond to the loss of water of crystallization and decomposition of $CoCO_3$ to Co_3O_4 [8,16]. The last peak, having its maximum at 910°C, indicates the decomposition of Co_3O_4 to CoO. A strong exothermic peak was detected during cooling of the thermal products of the pure solid heated at 1000°C. The maximum of the recorded exothermic peak was located at 770°C and it indicates the oxidation of CoO to Co_3O_4. These results will be confirmed later in the present investigation.

Treating the basic cobalt carbonate with magnesium or aluminium nitrates affects the area of the endothermic and exothermic peaks corresponding to

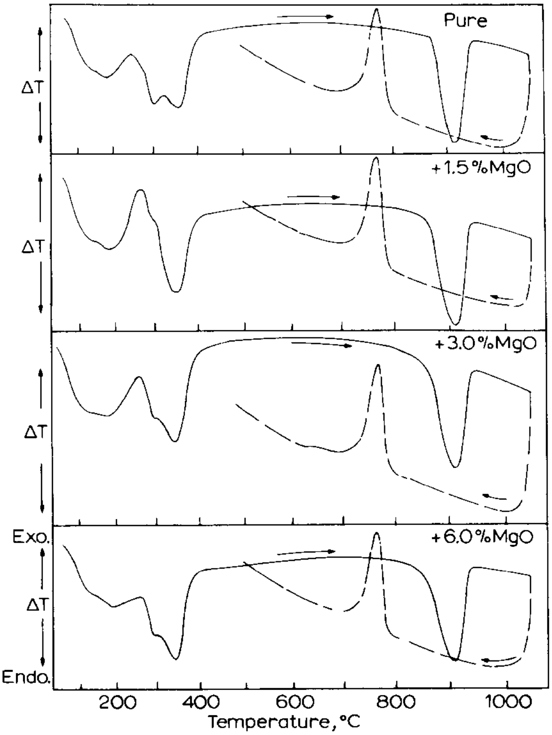

Fig. 1. DTA heating (————) and cooling (— — —) curves of pure and magnesium-nitrate-treated specimens of basic cobalt carbonate.

the decomposition of Co_3O_4 to CoO and the re-oxidation of cobaltous to cobaltic oxide. However, the maximum of the exothermic peak indicating the oxidation of CoO to give Co_3O_4 was not changed by doping with MgO and shifted to higher temperatures for the specimens doped with Al_2O_3. The magnitudes of this maximum were 770, 800, 825, 840, 840, 850 and 850°C for the pure solid and those containing 0.375, 0.75, 1.5, 3, 4.5 and 6 mole% Al_2O_3, respectively. These results may indicate that doping of cobalt oxide with Al_2O_3 increases the reactivity of CoO towards oxidation with O_2 yielding Co_3O_4, to an extent proportional to the concentration of the dopant oxide. This conclusion will be confirmed later by considering the area of the exothermic peaks.

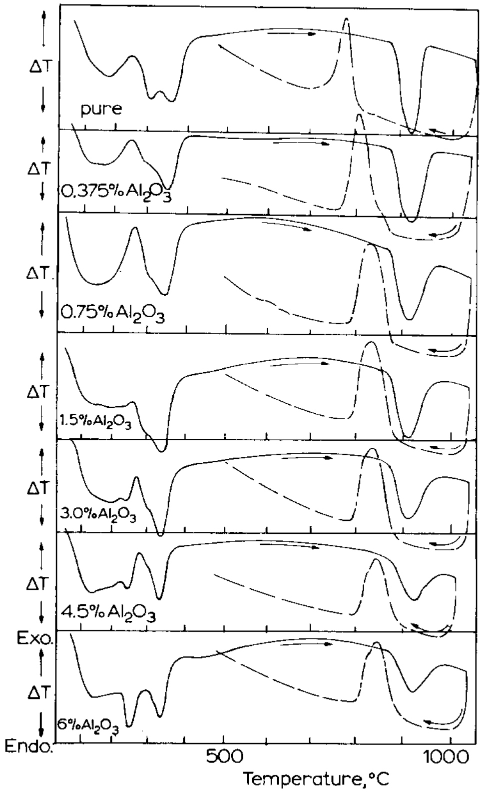

Fig. 2. DTA heating (————) and cooling (— — —) curves of pure and aluminium-nitrate-treated specimens of basic cobalt carbonate.

Since a constant weight of pure and treated basic cobalt carbonate was taken in each DTA run, the area of the endothermic and exothermic peaks for each solid could be regarded as a measure of the amount of solid that undergoes a chemical change (decomposition, $Co_3O_4 \rightarrow CoO$, and oxidation $CoO \rightarrow Co_3O_4$). The data of the endothermic and exothermic peaks, indicat-

TABLE 1

Effect of MgO and Al_2O_3-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)		% Change in the area of endothermic	Ratio between the area of exothermic and endothermic peaks
	Endothermic peak	Exothermic peak		
Pure basic cobalt carbonate	23.92	18.12	0.0	0.76
Basic carbonate+				
1.5% MgO	25.68	17.64	−7.36	0.69
3.0% MgO	26.08	17.40	−9.03	0.67
6.0% MgO	26.08	16.16	−9.03	0.62
0.375% Al_2O_3	20.40	23.40	+14.72	1.15
0.750% Al_2O_3	19.40	25.20	+20.40	1.32
1.500% Al_2O_3	17.72	25.32	+25.92	1.43
3.000% Al_2O_3	14.84	26.12	+38.00	1.76
4.500% Al_2O_3	10.00	18.28	+58.20	1.83
6.000% Al_2O_3	9.90	16.08	+58.62	1.62

[a] The data in this column were obtained by subtracting the area of the endothermic peak for each solid from 23.92 (the value for the pure solid). The negative sign indicates a decrease in the thermal stability of Co_3O_4, while the positive sign indicates an increase in this stability.

ing the decomposition of cobaltic to cobaltous oxide and oxidation of cobaltous to cobaltic oxide, are given in Table 1 for pure and doped solids. This table also includes the percentage change in the area of the endothermic peak due to doping with MgO and Al_2O_3 and the ratio between the area of the exothermic and endothermic peaks. It can be seen from Table 1 that doping of cobalt oxide with MgO effected a slight increase in the area of the endothermic peak and a slight decrease in the area of the exothermic peak proportional to the amount of dopant oxide added. In other words, incorporation of MgO in cobalt oxide slightly decreased both the thermal stability of Co_3O_4 and the reactivity of CoO for oxidation to Co_3O_4. By contrast, Al_2O_3 effected a considerable decrease in the area of the endothermic peak and an important increase in the area of the exothermic peak proportional to the amount of Al_2O_3 added. However, the increase in the area of the exothermic peak attained a maximum value for the cobalt oxide sample doped with 3% Al_2O_3. These data clearly indicate that the Al_2O_3 dissolved in the Co_3O_4 lattice increased its thermal stability. Furthermore, incorporation of trivalent Al^{3+} ions in the CoO lattice increased its reactivity towards oxidation with O_2 to give Co_3O_4. The enhanced reactivity of cobaltous oxide for oxidation to cobaltic oxide due to Al_2O_3-doping was also deduced from the shift in the maximum of the exothermic peaks towards higher temperatures, which was observed for Al_2O_3-doped solids (see Fig. 2).

Table 1 also shows that the ratio between the area of the exothermic and endothermic peaks is smaller than unity in the case of pure and MgO-doped solids and greater than unity in the case of all Al_2O_3-doped solids. These results may indicate that during the cooling of pure and doped oxides, in air from 1000 to 500°C (see Figs. 1 and 2), at a rate of 20°C min^{-1}, a partial oxidation of pure and MgO-doped solids took place. A complete oxidation of CoO occurred in the case of Al_2O_3-treated solids. The fact that the ratio between the area of the exothermic and endothermic peaks is greater than unity in the case of cobalt oxide doped with Al_2O_3 might indicate an enhanced chemisorption of O_2 on the surface of Co_3O_4. The enhanced activity of aluminium-doped Co_3O_4 towards O_2 chemisorption could be attributed to modifications in the electronic structure [24] of the solid which behaves as a *p*-type semiconductor [1,2].

X-Ray investigation of the thermal products of pure basic cobalt carbonate and cobalt carbonate treated with magnesium or aluminium nitrates

The X-ray diffraction patterns of the thermal products of pure basic cobalt carbonate heated in air at 1000°C for 4 h and subjected to sudden cooling revealed that these solids consisted of a very crystalline CoO phase, indicating a complete decomposition of Co_3O_4. By contrast, all diffraction lines of the Co_3O_4 phase were detected only in the X-ray diffraction patterns of pure cobalt oxide heated in air and allowed to cool slowly from 1000°C to room temperature. These results indicate that the CoO phase produced was completely oxidized to Co_3O_4.

The X-ray diffraction patterns of the thermal products of basic cobalt carbonate treated with magnesium nitrate and heated in air at 1000°C for 4 h followed by sudden cooling, revealed that the MgO-doped solid consisted entirely of a very crystalline CoO phase. The diffraction lines of free magnesium oxide were not detected in the diffraction patterns of the doped oxides. These results might indicate that all the amounts of MgO added were completely dissolved in the cobalt oxide lattice. The diffraction lines of both the Co_3O_4 and CoO phases were detected in the patterns of MgO-doped solids heated in air at 1000°C and allowed to cool slowly to room temperature. These results indicate that the MgO dissolved in the CoO lattice decreased its reactivity for oxidation with O_2 to give Co_3O_4.

The X-ray diffraction patterns of the thermal products of basic cobalt carbonate treated with aluminium nitrate and heated in air at 1000°C followed by sudden cooling to room temperature indicated that the Al_2O_3-doped solids were composed of both Co_3O_4 and CoO phases. The relative intensities of the CoO lines were, however, greater than those of the Co_3O_4 phase. These results clearly indicate that the aluminium oxide in the Co_3O_4 lattice effects an important increase in its thermal stability thus preventing a portion of the Co_3O_4 from decomposing to CoO even by heating at 1000°C for 4 h. The role of Al_2O_3 in increasing the thermal stability of Co_3O_4 is, thus, confirmed by both DTA and X-ray diffraction techniques. All the characteristic lines of the Co_3O_4 phase were detected only in the case of Al_2O_3-doped solids heated in air at 1000°C and cooled slowly to room temperature.

Infrared spectrometric investigation of the thermal products of pure basic cobalt carbonate and cobalt carbonate mixed with magnesium nitrate

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, 3, and 6 mole% MgO and subjected to both slow and sudden cooling, respectively. It is clear from Fig. 3 that pure and doped oxides when cooled slowly exhibited almost the same IR spectra; however, a weak absorption band located at 1380 cm^{-1} was found in the case of magnesium-oxide-doped solids. Five strong absorption bands were detected in the IR spectra of pure and MgO-doped solids heated at 1000°C and cooled slowly. These bands were located at 660, 645, 560, 420, and 390 cm^{-1} and correspond to a cobalt oxide structure in the form of Co_3O_4 [17–19]. The sudden cooling of pure and doped solids was accompanied by the disappearance of all the absorption bands corresponding to Co_3O_4, except the band at 660 cm^{-1} which persisted but with a very small intensity (see Fig. 4). The

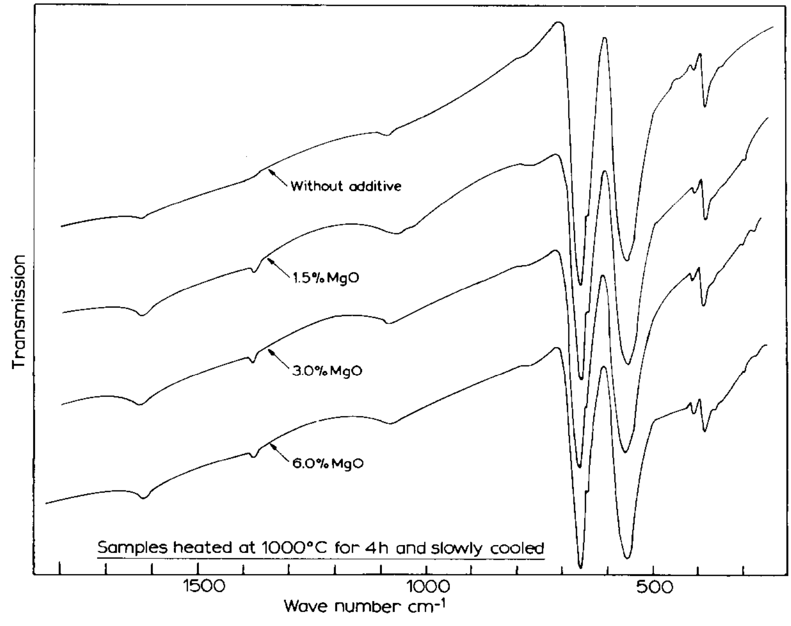

Fig. 3. Infrared absorption spectra of pure and magnesium-nitrate-treated samples of basic cobalt carbonate heated in air at 1000°C (4 h), then cooled slowly to room temperature.

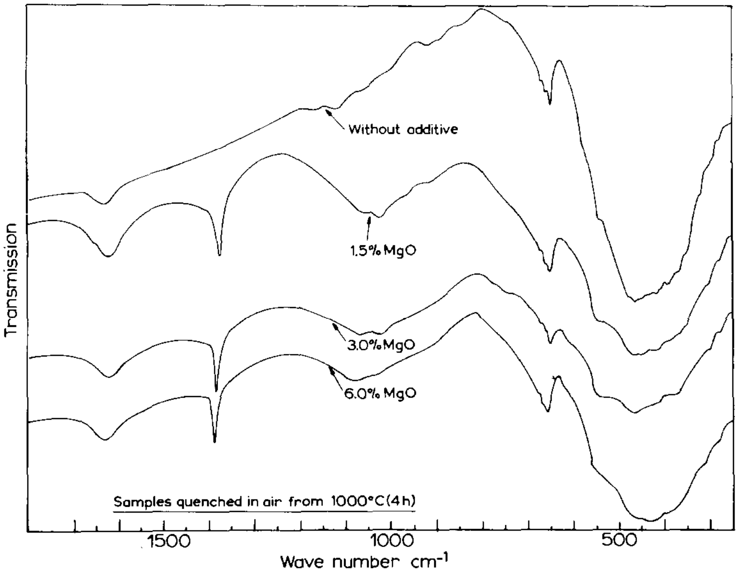

Fig. 4. Infrared absorption spectra of pure and magneisum-nitrate-treated samples of basic cobalt carbonate heated in air at 1000°C (4 h), then subjected to sudden cooling to room temperature.

intensity of the band at 1380 cm^{-1} was greatly increased by subjecting the MgO-doped solids to sudden cooling from 1000°C to room temperature. A broad band extending between 600 and 300 cm^{-1} was detected in the spectra of all solids subjected to sudden cooling. This extended broad band may characterize a cobalt oxide structure different from that of Co_3O_4. The only possible stable structure of the solid produced from the thermal decomposition of $CoCO_3$ at elevated temperatures is CoO. The presence of a weak band at 660 cm^{-1} in the IR spectra of the solids heated at 1000°C and allowed to cool suddenly may indicate the presence of a minute amount of Co_3O_4 which is undetectable by X-ray diffraction technique. It can be concluded from the IR spectrometric investigation that the pure and magnesium-doped solids heated in air at 1000°C were constituted entirely of CoO, a trace of which, upon sudden cooling, was oxidized by O_2 to give Co_3O_4. The band found at 1380 cm^{-1} could not correspond to a MgO structure [20]. In other words, all the MgO added was effectively dissolved in the cobalt oxide lattice. The band might characterize a cobalt oxide structure different from those of Co_3O_4 and CoO and the sudden cooling of doped cobalt oxide is in favour of such a structure. The identification of this structure needs further investigations.

Infrared spectrometric investigation of the thermal products of basic cobalt carbonate mixed with aluminium nitrate

The IR absorption spectra were measured for doped solids heated in air at 1000°C and subjected to both slow and sudden cooling. Figures 5 and 6 represent the IR spectra of Al_2O_3-doped solids heated at 1000°C and allowed to cool slowly and suddenly, respectively. These figures also include the IR spectra of pure solids for the sake of comparison. Figure 5 shows that both pure and aluminium oxide-doped solids, heated in air at 1000°C and cooled slowly to room temperature, exhibited almost the same spectra. However, similar to the case of MgO-doping, a weak absorption band at 1380 cm^{-1} was detected in the spectra of all oxides containing different amounts of Al_2O_3. The spectra of these solids are typical of that of Co_3O_4. The band detected at 1380 cm^{-1}, which is not characteristic of the aluminium oxide structure [20], indicates that all the amounts of dopant oxide were effectively dissolved in the cobalt oxide lattice. The aluminium-doped solids heated at 1000°C and subjected to sudden cooling exhibited IR spectra different from that of the pure solid. The weak band at 660 cm^{-1}, detected in the spectra of the pure solid, had a higher intensity in the case of doped oxide samples. The intensity of this band was found to be proportional to the amount of Al_2O_3 added. Furthermore, other characteristic bands corresponding to Co_3O_4, at 645 and 560 cm^{-1}, were observed in the IR spectra of

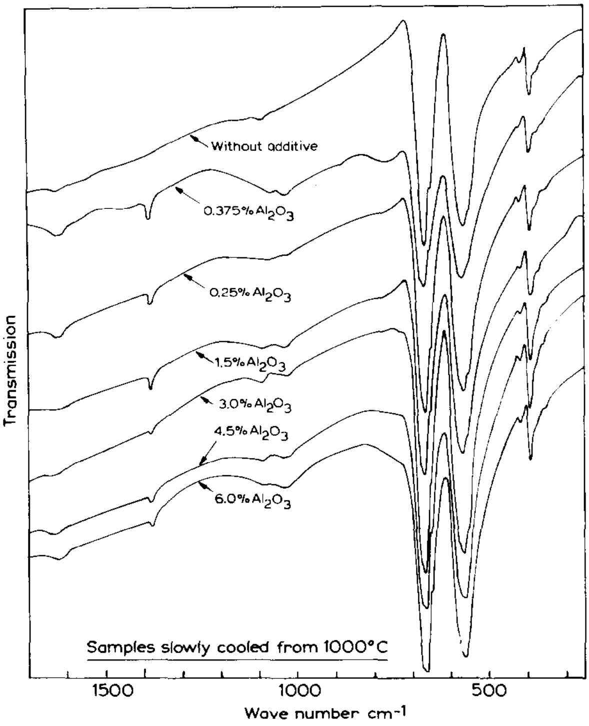

Fig. 5. Infrared absorption spectra of pure and aluminium-nitrate-treated samples of basic cobalt carbonate heated in air at 1000°C (4 h), then cooled slowly to room temperature.

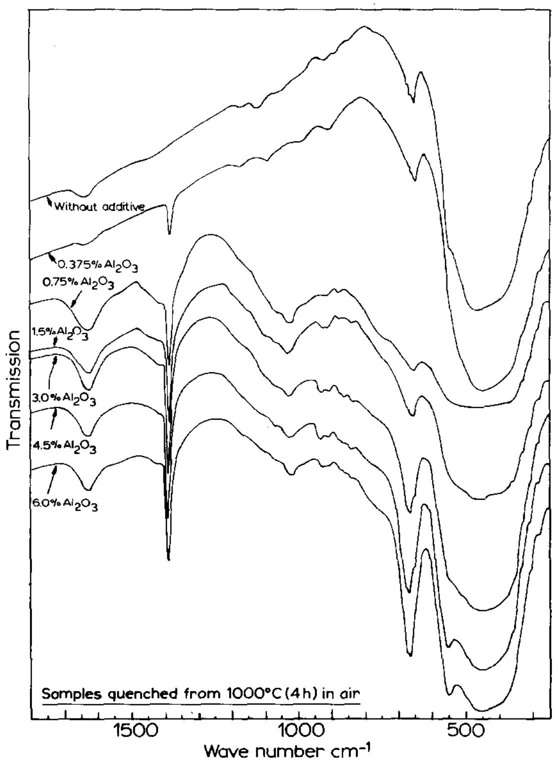

Fig. 6. Infrared absorption spectra of pure and aluminium-nitrate-treated samples of basic cobalt carbonate heated in air at 1000°C (4 h), then subjected to sudden cooling to room temperature.

the doped solids containing 4.5 and 6 mole% Al_2O_3. Finally, the sudden cooling of all Al_2O_3-doped solids, as in the case of MgO-doping, was accompanied by an important increase in the intensity of the band located at 1380 cm^{-1}. This band, which does not belong to a free aluminium oxide phase, might characterize a cobalt oxide structure different from those of CoO and Co_3O_4. Such a structure might be stabilized by Al_2O_3-doping and also by sudden cooling of the doped solid specimens. It can be concluded that Al_2O_3 dissolved in the cobalt oxide lattice effected an appreciable stabilization of the cobalt oxide phase even by heating in air at 1000°C for 4 h. Such a conclusion was reached in the preceding parts of this work through DTA and X-ray investigations of pure and doped solids.

DISCUSSION

The quantitative differential thermal analysis, X-ray diffraction and infrared absorption spectrometric investigations of pure and doped cobalt oxides revealed that for all amounts of the doped oxides, the MgO and Al_2O_3 were completely dissolved in cobalt oxide lattice. The MgO doping process was accompanied by a slight decrease in both the thermal stability of Co_3O_4 (9%) and the reactivity of CoO for oxidation by O_2 to Co_3O_4. These results might indicate a dissolution of magnesium ions in the cobaltic and cobaltous oxides lattices. Mg^{2+} could substitute some of the host cations in the lattice of Co_3O_4. These cations are Co^{2+} and Co^{4+} [2]. The dissolution of divalent magnesium ions by substituting some of the Co^{2+} ions might not be accompanied by any change in the concentration of the charge carriers in solid Co_3O_4 [21] and might not affect the oxidation character of cobaltic oxide and, consequently, would not exert any influence on the thermal stability of cobaltic oxide [8]. By contrast, the dissolution of Mg^{2+} ions via substitution of some Co^{4+} ions might increase the concentration of charge carriers of Co_3O_4 leading to an increase in its oxidation character which would effect an augmentation of its thermal stability [8]. The dissolution processes could be simplified [22] to give

$$MgO + \tfrac{1}{2}O_2(\text{gas}) \rightarrow Mg(Co^{4+}) + 2\,Co^{3+} \quad (1)$$

$$MgO \rightarrow Mg(Co^{2+}) \quad (2)$$

$Mg(Co^{4+})$ and $Mg(Co^{2+})$ are divalent magnesium ions located in the positions of host cations Co^{4+} and Co^{2+} present in the Co_3O_4 lattice; Co^{3+} is a charge-carrier ion created in cobaltic oxide. The reaction expressed by eqn. (1) is accompanied by fixation of atmospheric O_2 in the oxide lattice, thus increasing its oxidation character and, consequently, opposes, its reduction to give CoO. Magnesium oxide is known to be easily soluble in the cobaltous oxide lattice producing a homogeneous MgO–CoO solid solution [10]. The fact that for MgO-doped Co_3O_4 a slight decrease was found in the thermal stability, and not an increase, indicates that most of the MgO added underwent a solid–solid interaction with CoO. It is plausible to suppose that the MgO–CoO solid exhibited a very small affinity towards oxidation with O_2 giving Co_3O_4. This was confirmed by the X-ray investigation, given previously in this paper, which revealed the presence of CoO and Co_3O_4 in the magnesium-oxide-doped solids, heated at 1000°C and allowed to cool slowly to room temperature. In the case of the pure solid, also cooled slowly, all the CoO formed was oxidized to Co_3O_4. Incorporation of Mg^{2+} ions in the Co_3O_4 lattice according to the mechanism represented by eqn. (2) might not affect the thermal stability of Co_3O_4. The formation of a MgO–CoO solid solution and incorporation of Mg^{2+} in Co_3O_4 according to reaction (2) might account for the small change observed in the thermal stability of MgO-doped Co_3O_4.

Al_2O_3 which also was completely dissolved in the cobaltic oxide effected a marked increase in the thermal stability of Co_3O_4 to an extent proportional to the amount of dopant oxide dissolved, reaching a constant value of 58%

(see Table 1) when the amount of Al_2O_3 added was equal to or greater than 4.5 mole%. The thermal stability of cobaltic oxide due to Al_2O_3 doping could be attributed to incorporation of trivalent aluminium ions in the Co_3O_4 lattice via substitution of some tetravalent cobalt ions according to [22]

$$Al_2O_3 + \tfrac{1}{2}\, O_2(gas) \rightarrow 2\, Al(Co^{4+}) + 2\, Co^{3+} \qquad (3)$$

$Al(Co^{4+})$ is trivalent aluminium ion located in the position of the host cation, Co^{4+}, of the Co_3O_4 lattice; Co^{3+} is trivalent cobalt ion (charge carrier). Dissolution of Al_2O_3 in solid cobaltic oxide according to the mechanism expressed by eqn. (3) is accompanied by transformation of some of the host cations, Co^{2+}, to Co^{3+} followed by fixation of O_2 into the oxide lattice which increases its oxidation character to a great extent and thus it acts as a barrier to the reduction of Co_3O_4 to CoO. According to such a mechanism, aluminium oxide doping exerted a similar effect on the thermal stability of Co_3O_4 as did lithium oxide-doping [8]. The dissolution of Al^{3+} ions in the cobaltic oxide lattice via substitution of some divalent cobalt ions might be accompanied by a decrease in the thermal stability of cobaltic oxide. The fact that a marked increase was observed in the thermal stability of cobaltic oxide due to Al_2O_3 doping might indicate that the substitution of tetravalent cobalt ions by Al^{3+} ions was energetically more favourable than the substitution of divalent cobalt ions. It seems that the similarity between the ionic radii of Co^{4+} and Al^{3+}, which are 0.56 and 0.50 Å [23], respectively, had a decisive role in the dissolution of Al^{3+} ions according to the mechanism given by eqn. (3). The limited thermal stability of Co_3O_4 due to Al_2O_3-doping (58%) might indicate that a substitution of some cobalt ions in the divalent positions became effective at higher Al_2O_3 content.

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