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THERMAL STABILITY OF COBALT OXIDES DOPED WITH V_2O_5 AND MoO_3

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ABSTRACT

The effect of V_2O_5 and MoO_3 doping on the thermal decomposition of Co_3O_4 to CoO and the re-oxidation of cobaltous to cobaltic oxide was studied using DTA, X-ray diffraction and infrared spectrometry techniques. Pure and doped Co_3O_4 specimens were prepared by the thermal decomposition of pure basic cobalt carbonate and basic carbonate mixed with different proportions of ammonium metavanadate and ammonium molybdate. The decomposition temperatures were varied between 700 and 1100°C. The DTA investigation was carried out during heating to 1000°C and cooling to 500°C. X-Ray diffraction and infrared absorption spectra were conducted for different solids subjected to both sudden and slow cooling.

The results obtained revealed that part of the V_2O_5 and MoO_3 was dissolved in Co_3O_4 lattice, affecting partial stabilization of the solid, and another part of the dopant oxides underwent a chemical interaction with the CoO produced giving cobalt vanadate and cobalt molybdate. The sudden cooling of the doped oxides favoured the formation of molybdate and vanadate phases. The dopant oxides exerted no important effect on the reactivity of CoO for oxidation to Co_3O_4, except the solid treated with 6% MoO_3 which acquired the highest ability towards oxidation.

INTRODUCTION

Cobalt oxide produced from the thermal decomposition of cobalt hydroxide or basic cobalt carbonate under reduced pressure ($P = 10^{-6}$ Torr) at temperatures equal to or higher than 330°C exists in the form of crystalline CoO [1,2], which possesses well-known catalytic and surface properties [1–4]. The thermal decomposition of basic cobalt carbonate in air at temperatures below 900°C leads to the formation of crystalline Co_3O_4 [3]. The cobaltic oxide obtained also exhibits a high catalytic activity [5,6]. The heating of cobaltic oxide at 900°C affects its partial decomposition to CoO [6].

The temperature of the thermal decomposition of Co_3O_4 depends mainly on particle size, the history of the oxide, calcination conditions [7] and doping [8]. It has been shown, in a previous investigation [8], that dissolution of Li_2O (1.5 mole %) in the Co_3O_4 lattice prevented its thermal decomposition even by heating at 1100°C. The incorporation of Li_2O in the Co_3O_4

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lattice has been found to affect greatly the catalytic and surface properties of the doped Co_3O_4 solids [9,10].

In the present investigation, we studied the effect of doping with vanadium pentoxide and molybdenum trioxide on the thermal stability of cobaltic oxide and on the reactivity of the produced cobaltous oxide for oxidation to Co_3O_4. The techniques employed in this work were DTA, X-ray diffraction and infrared absorption spectrometry.

EXPERIMENTAL

Materials

Pure cobalt oxide specimens were obtained by thermal decomposition of basic cobalt carbonate, $5CoCO_3 \cdot Co(OH)_2$, in air at different temperatures between 700 and 1100°C. Details of the method of preparation of the basic carbonate have been given elsewhere [1,8].

Different doped cobaltic oxide samples were prepared by heating the basic cobalt carbonate treated with different proportions of ammonium vanadate or ammonium molybdate in air at 700–1100°C for 4 h. A concentrated solution of ammonium vanadate or molybdate was added to a given weight of a basic cobalt carbonate to make a paste. After drying at reduced pressure at room temperature, the paste was dried at 100°C to constant weight. Six doped Co_3O_4 solids were prepared. These solids contained 1.5, 3 and 6 mole % V_2O_5 or MoO_3.

Techniques

Differential thermal analysis (DTA) of pure and doped basic cobalt carbonate was carried out using a DuPont 990 thermal analyzer with a differential scanning calorimeter cell. The rate of heating was 20°C min^{-1} and the sensitivity was 1 mV $in.^{-1}$. The rate of cooling was not controlled and each specimen was allowed to cool from 1000 to 500°C and the cooling curves recorded. A 30 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 iron-filtered cobalt radiation, $\lambda = 1.7889$ 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 1300 and 300 cm^{-1} were considered in this 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. The sample disks were placed in the holder of a double-grating IR spectrometer.

RESULTS

Thermal behaviour of pure basic cobalt carbonate and cobalt carbonate treated with ammonium vanadate and molybdate

Figures 1 and 2 represent the DTA of pure basic cobalt carbonate and cobalt carbonate treated with different proportions of ammonium vanadate and molybdate. Four endothermic peaks are observed in the case of pure basic cobalt carbonate, the first 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,

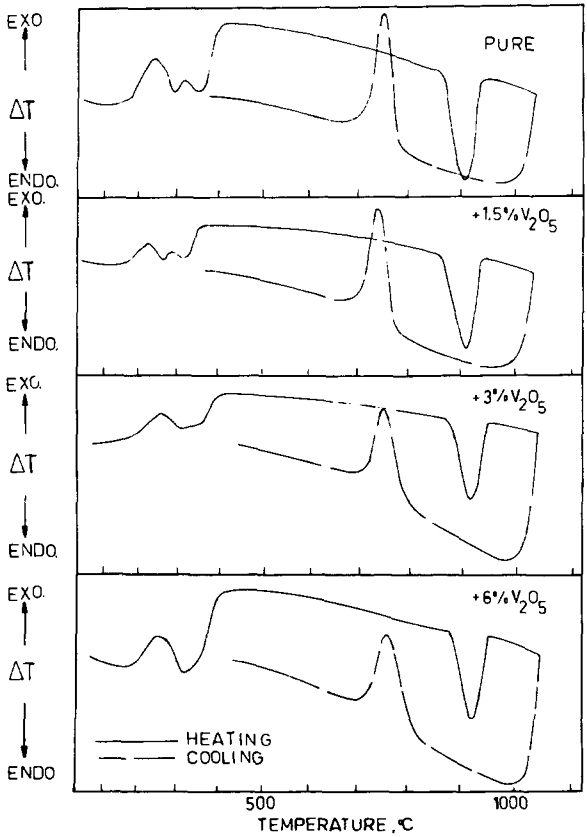

Fig. 1. DTA heating and cooling curves of pure and ammonium vanadate-treated specimens of basic cobalt carbonate.

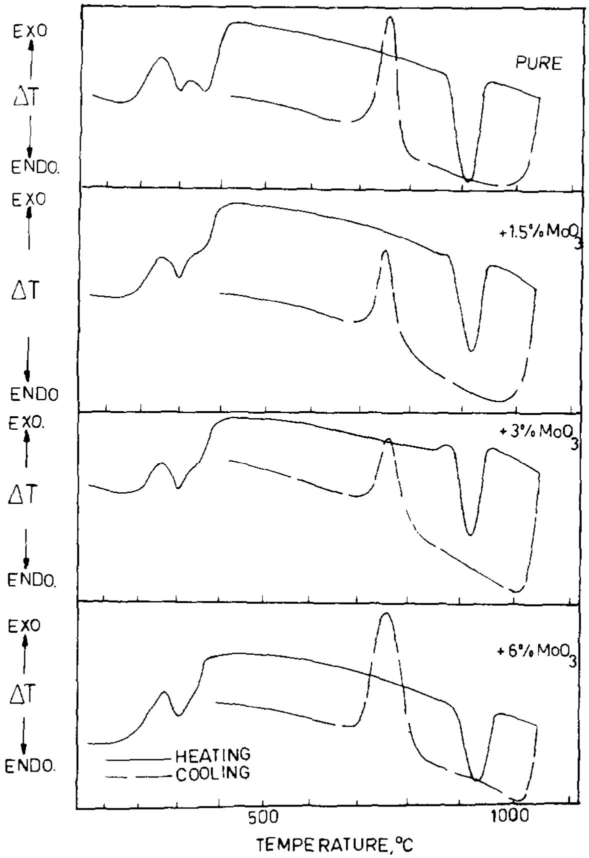

Fig. 2. DTA heating and cooling curves of pure and ammonium molybdate-treated specimens of basic cobalt carbonate.

correspond to the loss of water of crystallization and decomposition of $CoCO_3$ to Co_3O_4 [3,11]. The last peak, with its maximum at 910°C, indicates the decomposition of Co_3O_4 to CoO. These results will be confirmed later in this investigation. A strong exothermic peak was observed during the cooling of the thermal products of pure solid heated at 1000°C. The maximum of the recorded exothermic peak was located at 755°C and it indicates the oxidation of CoO to Co_3O_4.

Treating the basic cobalt carbonate with ammonium vanadate or molybdate mainly 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. However, the maximum of the endothermic peak indicating the decomposition of Co_3O_4 to CoO was shifted, in the case of the solid treated with 6 mole % MoO_3, from 910 to 940°C.

Once a constant weight of pure and treated basic cobalt carbonate was taken in each DTA run, the area of endothermic and exothermic peaks for

TABLE 1

Effect of V_2O_5 and MoO_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 units)		% 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	14.53	14.90	0.0	1.02
Basic carbonate + 1.5% V_2O_5	12.70	13.98	12.59	1.10
+ 3% V_2O_5	10.92	11.00	24.85	1.01
+ 6% V_2O_5	11.34	13.22	21.95	1.16
Basic carbonate + 1.5% MoO_3	11.47	10.78	20.37	0.93
+ 3% MoO_3	11.26	10.40	22.51	0.92
+ 6% MoO_3 [b]	10.78	25.50	25.81	2.36
+ 6% MoO_3 [b]	10.35	23.80	28.77	2.30

[a] The data of this column were obtained by subtracting the area of the endothermic peak for each solid from 14.53 (that of the pure solid).

[b] A duplicate specimen was taken to check the reproducibility of the results.

each solid could be taken as a measure of the amount of the 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 corresponding to the decomposition of cobaltic to cobaltous oxide and oxidation of cobaltous to cobaltic oxide for pure and doped solids are given in Table 1. This table also includes the % decrease in the area of the endothermic peak due to doping with V_2O_5 and MoO_3 and the ratio between the area of the exothermic and endothermic peaks. It can be seen from Table 1 that doping of Co_3O_4 with V_2O_5 and MoO_3 effected a decrease in the area of the endothermic peak proportional to the amount of dopant oxide added. In other words, incorporation of V_2O_5 or MoO_3 in the lattice of Co_3O_4 decreased the fraction of the solid that underwent decomposition to CoO, thus leading to partial thermal stabilization of cobaltic oxide. This partial stabilization is, however, more pronounced in case of MoO_3-doped solids.

Table 1 shows also that doping with V_2O_5 (up to 3 mole %) and MoO_3 (up to 3 mole %) exerted no important influence on the area of the exothermic peak characterizing the oxidation of CoO to Co_3O_4. Doping with 6 mole % MoO_3 resulted in an approximately 2-fold increase in the area of the exothermic peak, i.e. the amount of heat evolved during cooling, in air, of the doped solid heated to 1000°C was considerably increased by doping with 6 mole % MoO_3. It can be concluded that doping with V_2O_5 and MoO_3 (up to 3 mole %) exerted a small effect on the reactivity of CoO towards oxidation with O_2 giving Co_3O_4, the first dopant oxide increased such reactivity slightly, while the second decreased it slightly. In contrast, the solid doped with 6 mole % MoO_3 acquired the greatest ability for oxidation.

X-Ray investigation of the thermal products of pure basic cobalt carbonate

The X-ray diffraction patterns of the thermal products of pure basic cobalt carbonate heated in air at 700 and 800°C and subjected to both sudden and slow cooling revealed that the solids produced were composed entirely of the very crystalline Co_3O_4 phase. The solids obtained at 900°C and cooled suddenly were composed of a mixture of cobaltic and cobaltous oxide phases, indicating a partial decomposition of Co_3O_4 to CoO. The oxides produced at 1000 and 1100°C and subjected also to sudden cooling consisted of the very crystalline CoO phase, indicating a complete decomposition of Co_3O_4 to CoO. In contrast, the characteristic lines of cobaltic oxide appeared only in the X-ray diffraction patterns of pure Co_3O_4 heated at 900°C and cooled slowly, indicating a complete oxidation of the produced CoO to Co_3O_4. These results agree well with DTA results previously presented [8]. The X-ray diffraction patterns of cobaltic oxide heated in air at 1000 and 1100°C followed by slow cooling revealed that the oxides obtained were composed of a mixture of Co_3O_4 and CoO. These results indicate that pure CoO produced at 1000–1100°C was capable of undergoing partial oxidation yielding Co_3O_4. And in order to prevent such an oxidation process, the cobaltous oxide might be heated at temperatures above 1100°C. The ability of CoO towards oxidation with O_2 yielding Co_3O_4 could be related to the sinterability of cobaltous oxide phase; the higher the temperature of heating in air, the greater the sinterability of CoO, the smaller will be its ability for oxidation.

X-Ray investigation of thermal products of basic cobalt carbonate treated with ammonium vanadate and ammonium molybdate

The X-ray diffraction patterns were carried out for the doped solids heated in air at 700–1100°C and subjected only to slow cooling. The diffraction patterns of all doped oxides prepared at 700, 800 and 900°C were similar to those found for pure solids. However, two new diffraction lines were observed in the case of MoO_3-doped solids prepared at temperatures equal to or higher than 800°C. The *d* spacings of these lines were calculated at $d = 3.13_x$ and 1.65_5. These lines correspond to the $CoMoO_4$ phase [12].

The characteristic lines of free MoO_3 and V_2O_5 phases were not detected in the diffraction patterns of any doped solid.

The doped oxides prepared at 1000 and 1100°C differ from the pure oxides prepared at the same temperatures. At 1000°C, the doped solids were composed entirely of the Co_3O_4 phase and at 1100°C, they consisted of a mixture of Co_3O_4 and CoO, except for the 6% MoO_3-doped solid, which was composed entirely of Co_3O_4.

The disappearance of cobaltous oxide in all doped solids prepared at 1000°C may result from an effective thermal stabilization of cobaltic oxide and/or from a complete oxidation, during slow cooling in air, of CoO produced by partial decomposition of cobaltic oxide. The absence of cobaltous oxide in the 6% MoO_3-doped solid heated at 1100°C may indicate the enhanced thermal stabilization of cobaltic oxide induced by doping with MoO_3.

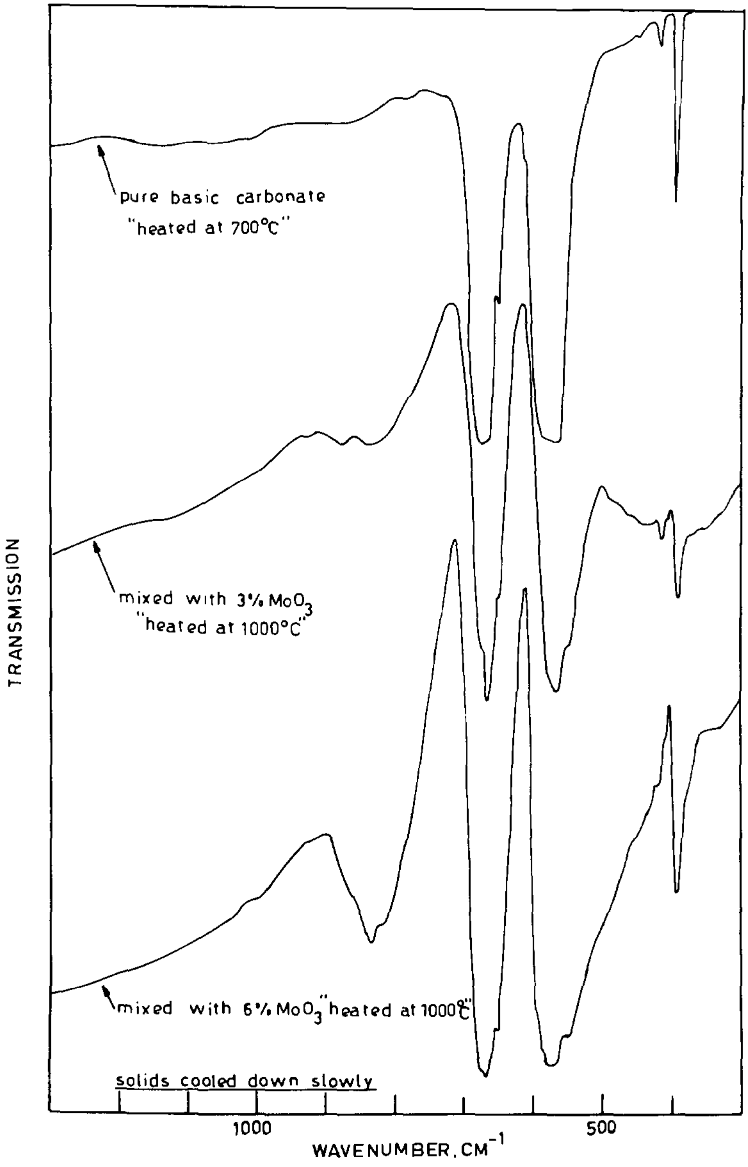

Fig. 3. Infrared absorption spectra of pure basic cobalt carbonate heated at 700°C and ammonium molybdate-treated basic cobalt carbonate heated at 1000°C and cooled slowly.

Infrared spectrometric investigation of the thermal products of pure basic cobalt carbonate

The IR absorption spectrum of pure basic cobalt carbonate heated in air at 700°C is shown in Fig. 3. Seven absorption bands were detected at 670, 660, 645, 588, 575, 420 and 390 cm^{-1}. These bands correspond to a cobalt oxide structure in the form of Co_3O_4 [13–15]. The basic cobalt carbonate heated at 1000 and 1100°C and allowed to cool suddenly exhibited identical absorption spectra which are completely different from that observed for the solid heated at 700°C. All the absorption bands found for the oxide heated at 700°C disappeared in the case of the oxides heated at 1000 and 1100°C except for the band at 660 cm^{-1} (cf. Fig. 4), which appeared with a very small percent transmission. A very broad band extending between 300 and 600 cm^{-1} was also observed in the spectra of the solids heated at 1000 and 1100°C and 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 temperature is CoO. The presence of a weak band at 660 cm^{-1} in the spectra of the solids heated at 1000 and 1100°C and cooled suddenly may indicate the presence of a trace amount of cobaltic oxide undetectable by X-ray diffraction techniques.

The IR absorption spectrum of pure basic cobalt carbonate heated in air at 1000°C and cooled slowly is similar to that observed for the solid heated at 700°C, i.e. all the absorption bands corresponding to Co_3O_4 were detected. This indicates that the oxide produced from the thermal decomposition of basic cobalt carbonate at 1000°C, which is mainly in the form of CoO, was completely oxidized, yielding Co_3O_4, during the process of slow cooling. These results agree with those of X-ray investigations and DTA studies previously presented [8].

Infrared spectrometric investigation of the thermal products of basic cobalt carbonate treated with ammonium vanadate and ammonium molybdate

The IR absorption spectra were measured for the doped solids heated in air at 1000°C and subjected to both sudden and slow cooling. Figure 4 shows the absorption spectra of 3 and 6 mole % V_2O_5-doped solids heated at 1000°C and allowed to cool suddenly. It is observed from this figure that the vanadium pentoxide-doped solids are mainly in the form of CoO together with trace amounts of Co_3O_4, as indicated by the presence of a weak band at 660 cm^{-1}. Two additional bands at 880 and 825 cm^{-1} were also observed in the IR spectra of the V_2O_5-doped solids. These bands correspond to VO_3^- [16], thus revealing the presence of cobalt vanadate. It seems that the amount of V_2O_5 involved in the formation of the cobalt vanadate compound was too small to be detected by X-ray diffraction.

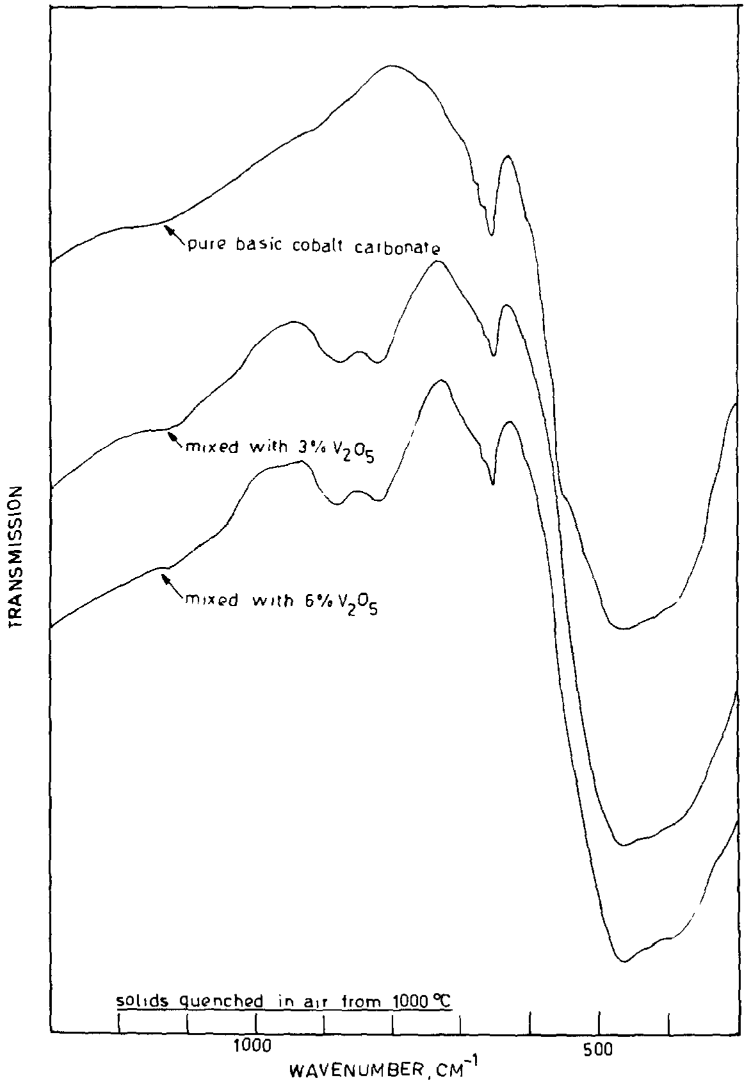

Fig. 4. Infrared absorption spectra of pure and ammonium vanadate-treated specimens of basic cobalt carbonate heated at 1000°C and subjected to sudden cooling in air.

It can be concluded that the IR results, which agree with those of the X-ray and DTA studies previously presented, offered the advantage of detecting the formation of cobalt vanadate in the V_2O_5-doped solids.

Figure 5 shows the IR spectra of 3 and 6 mole % MoO_3-doped solids heated in air at 1000°C and subjected to sudden cooling in air. It can be seen that the doped solids are mainly in the form of CoO together with a minute amount of Co_3O_4 as revealed by the presence of a weak band at 660 cm^{-1}. Two additional strong bands at 840 and 820 cm^{-1} were also observed. Moreover, the percent transmission of these bands increases by increasing

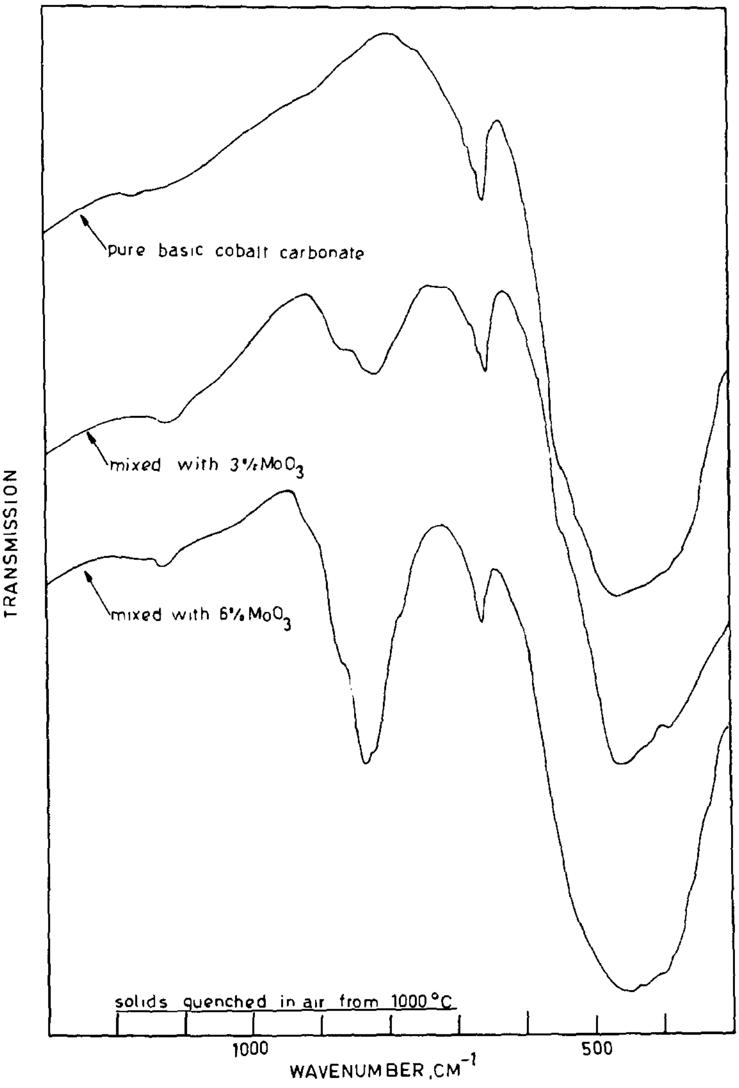

Fig. 5. Infrared absorption spectra of pure and ammonium molybdate-treated specimens of basic cobalt carbonate heated at 1000°C and subjected to sudden cooling in air.

the extent of dopant oxide added. These bands, which characterize the molybdate structure MoO_4^{2-} [16], indicate the presence of cobalt molybdate. An IR spectrum of pure MoO_3 was measured. The spectrum, not presented here, revealed the absence of this oxide in all molybdenum oxide-doped solids. These results agree well with those of X-ray investigation previously presented in this investigation.

The slow cooling of MoO_3-doped solids heated at 1000°C modified considerably the absorption spectra of these solids (cf. Figs. 3 and 5). It can be observed that, similar to the case of pure cobalt oxide heated at 1000°C, all the absorption bands corresponding to Co_3O_4 were detected (Fig. 3). Moreover, the percent transmission of the two additional bands at 840 and 820 cm^{-1} decreased considerably.

It can be concluded that the slow cooling of the thermal products of basic cobalt carbonate treated with ammonium molybdate and heated in air at 1000°C led to a complete oxidation of CoO to Co_3O_4 and considerably decreased the amount of cobalt molybdate formed. These results, which are in a good agreement with those of the X-ray investigation previously presented in this paper, offered the advantage of revealing the role of slow cooling on the formation of cobalt molybdate compound.

DISCUSSION

The evaluation of the partial thermal stability of cobaltic oxide and the formation of cobalt vanadate and molybdate revealed that a portion of V_2O_5 and MoO_3 was effectively incorporated in the cobalt oxide lattice and another portion underwent a chemical interaction with cobalt oxide, yielding vanadate and molybdate phases. However, the portion of V_2O_5 involved in vanadate formation was too small to be detected by X-ray diffraction.

The IR absorption spectra, previously presented, revealed that the slow cooling of MoO_3-doped cobalt oxide heated at 1000°C considerably decreased the amount of cobalt molybdate formed. These results could be attributed to a preferential oxidation of CoO, yielding Co_3O_4, rather than an interaction with MoO_3 producing cobalt molybdate. These reactions could be represented by

$$3\,CoO + 1/2\,O_2(g) \rightarrow Co_3O_4 \tag{1}$$

$$CoO + MoO_3 \rightarrow CoMoO_4 \tag{2}$$

The formation of cobalt vanadate may also take place according to

$$2\,CoO + V_2O_5 \rightarrow 2\,CoVO_3 + 1/2\,O_2(g) \tag{3}$$

The effect of Li_2O doping on the thermal stability of cobaltic oxide has been studied in a previous investigation [8]. The possible mechanisms of dissolution of lithium oxide in the Co_3O_4 lattice have been discussed. The complete thermal stabilization of cobaltic oxide induced by Li_2O-doping has been attributed to substitution of some of cobalt ions of Co_3O_4 in the +4 and +2 valence states by Li^+ ions. The substitution process might be accompanied by the transformation of some Co^{2+} into Co^{3+} with subsequent fixation of atmospheric O_2 in the doped Co_3O_4 lattice.

Assuming that vanadium pentoxide produced from the thermal decomposition of ammonium vanadate at 1000°C existed in the form of V_2O_5 and assuming also that a portion of V_2O_5 was dissolved in Co_3O_4 via substitution of some of cobalt ions in the +4 and +2 valence states, the dissolution process could be simplified [17,18]

$$V_2O_5 + 6\ Co^{3+} \rightarrow 2\ V(Co^{2+}) + 6\ Co^{2+} + 3/2\ O_2(g) \tag{4}$$

$$V_2O_5 + 2\ Co^{3+} \rightarrow 2\ V(Co^{4+}) + 2\ Co^{2+} + 1/2\ O_2(g) \tag{5}$$

$V(Co^{2+})$ and $V(Co^{4+})$ are pentavalent ions located in the positions of the host cations Co^{2+} and Co^{4+} present in the Co_3O_4 lattice.

Similarly, MoO_3 could be dissolved in cobaltic oxide lattice via the same mechanism, which could be simplified to [17,18]

$$MoO_3 + 4\ Co^{3+} \rightarrow Mo(Co^{2+}) + 4\ Co^{2+} + O_2(g) \tag{6}$$

$$MoO_3 + 2\ Co^{3+} \rightarrow Mo(Co^{4+}) + 2\ Co^{2+} + 1/2\ O_2(g) \tag{7}$$

$Mo(Co^{2+})$ and $Mo(Co^{4+})$ are hexavalent ions located in the positions of the host cations Co^{2+} and Co^{4+} of the Co_3O_4 lattice.

The dissolution of V_2O_5 and MoO_3 in cobaltic oxide according to the mechanism represented by eqns. (4)–(7) requires the presence of trivalent cobalt ions in Co_3O_4. These ions may be regarded as the charge carriers responsible for the *p*-type semiconductivity of solid Co_3O_4 [19,20]. The dissolution process is thus restricted by the concentration of these charge carrier ions. Moreover, the incorporation of V^{5+} and Mo^{6+} according to such a mechanism might be accompanied by transformation of some Co^{3+} to Co^{2+} with subsequent removal of O_2 from the cobaltic oxide lattice. The loss of oxygen and the decrease in the oxidation state of the doped oxide (transformation of Co^{3+} to Co^{2+}) might facilitate the reduction of Co_3O_4 to CoO. The results obtained in this investigation revealed a certain degree of thermal stabilization of Co_3O_4 induced by doping with V_2O_5 and MoO_3. It seems that the vanadium and molybdenum ions of V_2O_5 and MoO_3 may exist in several valence states.

Moreover, an important portion of the dopant oxides, especially in the case of MoO_3, participated in solid state reactions with cobalt oxide yielding new compounds, namely cobalt vanadate and cobalt molybdate.

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