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Solid–solid interactions in Co_3O_4–MoO_3/MgO system

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Abstract

Cobalt/magnesium mixed oxide solids and cobalt–molybdenum/magnesium mixed oxide solids were prepared by thermal decomposition of basic magnesium carbonate pretreated with different proportions of cobalt nitrate and then with calculated amounts of ammonium molybdate. The proportions of cobalt expressed as Co_3O_4 were 0.1, 0.2 and 0.3 mol while the concentrations of molybdenum expressed as mol% MoO_3 were 2.5 and 5.0. The prepared mixed solid specimens were calcined in air at 400–1000 °C. The solid–solid interactions in Co_3O_4–MoO_3 were investigated using DTA, TG and X-ray powder diffraction (XRD) techniques.

The results obtained revealed that MgO dissolved cobalt oxide in its lattice forming CoO–MgO solid solution. The amount of cobalt dissolved increases by increasing the temperature in the range 800–1000 °C. This finding was confirmed by X-ray diffractograms in which all the diffraction lines of cobalt oxide disappeared at 1000 °C. MoO_3 present interacted readily with MgO and cobalt oxide by heat treatment at temperature starting from 400 °C producing $MgMoO_4$ and $CoMoO_4$ which remained stable by heating at 1000 °C.

The impregnation of basic magnesium carbonate with cobalt nitrate much enhanced its thermal decomposition yielding MgO, which decomposed completely at 395.5 °C instead of 525 °C. The formation of magnesium cobaltite ($MgCo_2O_4$) has been ruled out via XRD investigation at relatively high diffraction angles.

Keywords: $MgMoO_4$; $CoMoO_4$; Solid solution; CoO–MgO; Co_3O_4; MgO; MoO_3

1. Introduction

Thermally decomposed metal nitrates and metal carbonates have been used as precursors in the chemical industry, as catalysts, in metallurgical processes and as electrochemical power sources [1–11]. The structures formed when metals are deposited on the surfaces of metal oxides can be quite complex. The initial monolayers may involve the formation of a different oxides, leading effectively to an oxide/oxide interfaces. These interfaces are of great importance in a variety of technological areas, including heterogeneous catalysis, adhesion, etc. [12–16].

The phase transformations are determined by several factors, which are often in very complex mutual interactions and because of that they can influence the phase compositions differently. The mutual interactions of support components can also affect the phase composition significantly and therefore the behaviour of the support [17–25].

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A nominal 12 wt.% MoO_3 was impregnated over the calcined (500 °C) support by a wet impregnation method. The initial characterization by X-ray powder diffraction (XRD), Fourier transform-infrared (FT-IR) and O_2 chemisorption techniques revealed that the impregnated MoO_3 is in a highly dispersed state on the surface of the support [26]. XPS electron binding energy (EB) values indicate that the MoO_3/Al_2O_3–TiO_2 catalyst contains the mixed oxide elements in the highest oxidation states [26]. In case of MoO_3/TiO_2–ZrO_2 catalyst, the molybdenum oxide is in highly dispersed state on the support surface when calcined at 500 °C [27]. However, at temperature above 500 °C MoO_3 interacted with ZrO_2 which led to the formation of $ZrMo_2O_8$ compound.

The catalysts Mo–V–Mg–O have been prepared by impregnation of a calcined V–Mg–O mixed oxides with an aqueous solution of ammonium heptamolybdate and then calcined at different temperatures and further characterized by several physico-chemical techniques. Magnesium molybdate ($MgMoO_4$) in addition to $Mg_3V_2O_8$ and MgO have been detected in all the Mo-doped samples [28]. A series of V_2O_5–MoO_3 catalysts with varying MoO_3 content ranging from 1 to 5% (w/w) were prepared by impregnation of previously prepared 10% V_2O_5/Al_2O_3 with different amounts of known concentrations of ammonium molybdate solutions [29]. Dispersion of vanadia was found to decrease with the increase of molybdena loading. The XRD results suggested that the formation of vanadium aluminate with the addition of MoO_3 to V_2O_5/Al_2O_3 catalyst [29]. The nature of surface species and the phases composition of different systems, Mo–V–W mixed oxides [30], MoO_3–Al_2O_3, MoO_3–TiO_2, MoO_3–SiO_2, CaO–MgO and V_2O_5/CaO–MgO [31–38] were investigated by different techniques. The systems CoO–MgO, NiO–MgO, MnO–MgO and ZnO–MgO forming solid solutions were investigated by different techniques [39–42].

The present investigation reports a study of the solid–solid interactions in the Co_3O_4–MoO_3/MgO system. The techniques employed were DTA, TG and XRD. These techniques allowed us to clarify the effects of MoO_3 treatment on the thermal behaviour of mixed solids prepared by wet impregnation and to identify the different phases produced by heating the mixed solids at various temperatures.

2. Experimental

2.1. Materials

Pure Co_3O_4/MgO samples were prepared by treating a known mass of finely powdered basic magnesium carbonate, $MgCO_3Mg(OH)_2 \cdot 2.5H_2O$, solid with different amounts of cobalt nitrate dissolved in the least amount of distilled water making pastes. The proportions of cobalt nitrate were calculated so that the molar compositions of the calcined solids were $0.1Co_3O_4$/MgO, $0.2Co_3O_4$/MgO and $0.3Co_3O_4$/MgO. The pastes thus obtained were dried at 120 °C and then calcined for 5 h in air at 400, 600, 800 and 1000 °C. The mixed solids Co_3O_4–MoO_3/MgO were prepared by treating a known mass of basic magnesium carbonate with cobalt nitrate solution containing different proportion of it, drying at 120 °C and then treating the dried solids with ammonium molybdate solution. The resulting materials were then dried at 120 °C and calcined for 5 h in air at 400, 600, 800 and 1000 °C. The concentrations of ammonium molybdate solution employed corresponded to the addition of 2.5 and 5.0 mol% MoO_3 (with respect to the sum of MgO and Co_3O_4).

The nominal molar compositions of the calcined mixed solids were $0.1Co_3O_4$/MgO (I), $0.2Co_3O_4$/MgO (II) and $0.3Co_3O_4$/MgO (III). The prepared mixed solid specimens were designated CoMg-I, CoMg-I-2.5Mo, CoMg-I-5Mo, CoMg-II, CoMg-II-2.5Mo, CoMg-II-5Mo, CoMg-III, CoMg-III-2.5Mo and CoMg-III-5Mo. All chemicals employed were of analytical grade and supplied BDH company.

2.2. Techniques

DTA and TG analyses of various uncalcined materials were carried out using Shimadzu DTA-50H and TGA-50H systems. The rate of heating was kept at 10 °C min^{-1}. The analyses were followed at temperatures between room temperature and 1000 °C with α-Al_2O_3 as a reference material. A 40 mg sample of each solid specimen was employed in each case. The measurements were carried out in a current of nitrogen flowing at a rate of 50 $cm^3 min^{-1}$.

An X-ray investigation of the thermal products of the different mixed solids was performed with a Philips diffractometer (type PW 1390). The patterns were run with iron filtered cobalt radiation ($\lambda = 1.7889$ Å) at 36 kV and 16 mA with scanning speed of 2° in 2θ min^{-1}.

3. Results and discussion

3.1. Thermal behaviour of pure and doped mixed solids

DTA curves of various pure and treated uncalcined materials were determined and the results obtained are summarized in Table 1. The DTA curves of basic magnesium carbonate and uncalcined CoMg-I, CoMg-I-2.5Mo and CoMg-I-5Mo samples are illustrated in Fig. 1. It is clear from Fig. 1 that basic magnesium carbonate exhibited three main endothermic peaks besides two small peaks at 51 and 113 °C. The first and last peaks are sharp and strong, while the second peak is broad and weak with their maxima located at 285.4, 417.8 and 525.5 °C. The small endothermic peaks at 51 and 113 °C correspond to removal of water of crystallization of basic magnesium carbonate.

Table 1
DTA results for pure and treated uncalcined materials

Solid	DTA/$\Delta T/T$	T_{max}/°C	Corresponding reaction
Basic $MgCO_3$	Endo, vw[a]	51,113	Dehydration of water of crystallization
	Endo, vs[b]	285	Dehydroxylation of basic $MgCO_3$
	Endo, w[c]	417	Dehydroxylation of basic $MgCO_3$
	Endo, vs	525	Complete decomposition of $MgCO_3$
Basic $MgCO_3$ + 0.3cobalt nitrate	Endo, s[d]	90	Dehydration of water of crystallization
	Endo, vs	174	Decomposition of cobalt nitrate
	Endo, s	285	Dehydroxylation of basic $MgCO_3$
	Endo, vs	395	Complete decomposition of $MgCO_3$
Basic $MgCO_3$ + 0.3cobalt nitrate + 2.5 mol% ammonium molybdate	Endo, s	140	Dehydration of water of crystallization
	Endo, w	205	Decomposition of cobalt nitrate
	Endo, s	294	Dehydroxylation of basic $MgCO_3$ + decomposition of ammonium molybdate
	Endo, vs	410	Complete decomposition of $MgCO_3$ + formation of $MgMoO_4/CoMoO_4$
Basic $MgCO_3$ + 0.3cobalt nitrate + 5 mol% ammonium molybdate	Endo, vs	142	Dehydration of water of crystallization
	Endo, w	205	Decomposition of cobalt nitrate
	Endo, w	285	Dehydroxylation of basic $MgCO_3$ + decomposition of ammonium molybdate
	Endo, vs	410	Complete decomposition of $MgCO_3$ + formation of $MgMoO_4/CoMoO_4$
Basic $MgCO_3$ + 0.9cobalt nitrate	Endo, w	110	Dehydration of water of crystallization
	Endo, w	140	Dehydration of water of crystallization
	Endo, vs	180	Decomposition of cobalt nitrate
	Endo, s	325	Dehydroxylation of basic $MgCO_3$
	Endo, s	395	Complete decomposition of $MgCO_3$
Basic $MgCO_3$ + 0.9cobalt nitrate + 5 mol% ammonium molybdate	Endo, s	85	Dehydration of water of crystallization
	Endo, w	140	Dehydration of water of crystallization
	Endo, s	170	Decomposition of cobalt nitrate
	Endo, s	280	Decomposition of ammonium molybdate
	Endo, s	330	Dehydroxylation of basic $MgCO_3$
	Endo, vs	390	Complete decomposition of $MgCO_3$ + formation of $MgMoO_4/CoMoO_4$

[a] Very weak.
[b] Very strong peaks.
[c] Weak.
[d] Strong.

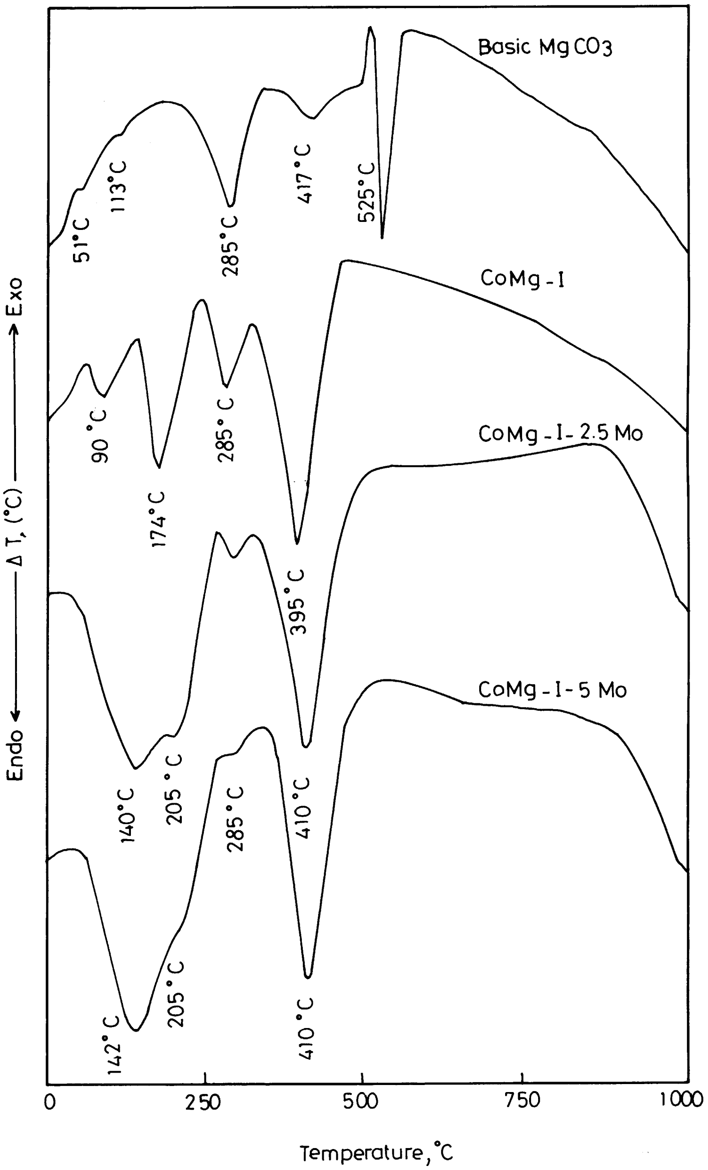

Fig. 1. DTA curves of uncalcined basic $MgCO_3$, CoMg-I, CoMg-I-2.5Mo and CoMg-I-5Mo solid samples.

The peak at 285.4 °C indicates dehydroxylation of basic magnesium carbonate yielding $MgCO_3$ and MgO while the second and third peaks are indicative for the thermal decomposition of $MgCO_3$ into MgO [43]. It is also seen from Fig. 1 that the DTA curves of pure and treated mixed solids exhibited four sets of endothermic peaks having their maxima located at 90–142, 174–205, 285–294 and 395–410 °C. Most of these peaks are sharp and strong. The first sets of peaks are indicative for removal of water of crystallization of cobalt nitrate and ammonium molybdate. The presence of ammonium molybdate led to an effective increase in the area of this peak. The second and third peaks correspond to the thermal decomposition of cobalt nitrate. The third peak is also indicative for dehydroxylation of basic magnesium carbonate into $MgCO_3$ and MgO and for decomposition of ammonium molybdate into MoO_3. The last peak characterizes the thermal decomposition of magnesium carbonate into MgO [43] and the formation of $MgMoO_4$ and/or cobalt molybdate ($CoMoO_4$). Inspection of DTA curves of the investigated solid samples revealed that: (i) cobalt nitrate treatment of basic magnesium carbonate much enhanced its thermal decomposition and it lowered down the temperature of its thermal decomposition from 525.5 to 395 °C, (ii) ammonium molybdate treatment of the investigated solids enhanced the thermal decomposition of cobalt nitrate and dehydroxylation of basic magnesium carbonate, which occurred simultaneously.

Fig. 2 shows the DTA and TG curves of uncalcined CoMg-III and CoMg-III-5Mo samples. The

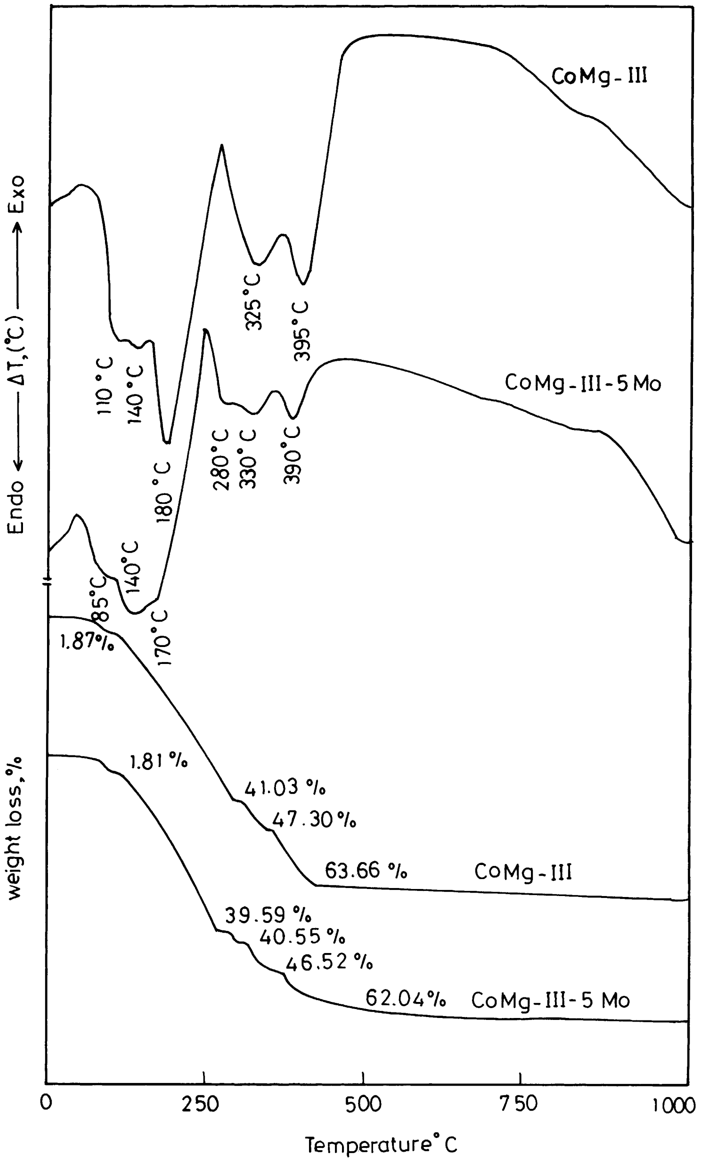

Fig. 2. DTA and TG curves of uncalcined CoMg-III and CoMg-III-5Mo solid samples.

DTA curve of CoMg-III exhibited five sets of endothermic peaks while DTA curve of CoMg-III-5Mo consists of six endothermic peaks. The maxima of these peaks are found at 85–110, 140, 170–180, 280, 325–330 and 390–395 °C. Most of these peaks are sharp and strong. The first and second peaks indicate the departure of water of crystallization of cobalt nitrate and ammonium molybdate. The set of peaks located at 170–180 and 325–330 °C correspond to thermal decomposition of cobalt nitrate. Also this peak (325–330 °C) is indicative for dehydroxylation of basic magnesium carbonate into $MgCO_3$ and MgO while the peak located at 280 °C characterizes the thermal decomposition of ammonium molybdate into MoO_3. The last sets of peaks are indicative for the thermal decomposition of magnesium carbonate into MgO and the formation of $MgMoO_4$ and/or $CoMoO_4$. Fig. 2 depicts also the TG curves of uncalcined solid samples CoMg-III and CoMg-III-5Mo. The calculated total weight loss accompanying the thermal decomposition of $Co(NO_3)_2/MgCO_3Mg(OH)_2$ mixed solids to the corresponding oxides (Co_3O_4 and MgO) is 63.66% while the thermal decomposition of $Co(NO_3)_2$–$(NH_4)_6Mo_7O_{24}/MgCO_3Mg(OH)_2$ mixed solids to the corresponding oxides (Co_3O_4, MoO_3 and MgO) leads to a total weight loss of 62.04%. These calculated values of total weight loss are very close to those found experimentally (Fig. 2), and so the following reactions in case of cobalt nitrate treated with basic magnesium carbonate can be written as

$$0.9Co(NO_3)_2 + 0.5MgCO_3Mg(OH)_2 \cdot 0.5H_2O \xrightarrow{140\,^{\circ}C} 0.9Co(NO_3)_2 + 0.5MgCO_3Mg(OH)_2 + 0.25H_2O \quad (1)$$

$$0.9Co(NO_3)_2 + 0.5MgCO_3Mg(OH)_2 \xrightarrow{140\text{–}180\,^{\circ}C} 0.3Co_3O_4 + 0.5MgCO_3Mg(OH)_2 + 1.8NO_2 + 0.3O_2 \quad (2)$$

$$0.3Co_3O_4 + 0.5MgCO_3Mg(OH)_2 \xrightarrow{180\text{–}325\,^{\circ}C} 0.3Co_3O_4 + 0.5MgCO_3MgO + 0.5H_2O \quad (3)$$

$$0.3Co_3O_4 + 0.5MgCO_3MgO \xrightarrow{325\text{–}395\,^{\circ}C} 0.3Co_3O_4 + MgO + 0.5CO_2 \quad (4)$$

The produced evolved NO_2, O_2, CO_2 and NH_3 have not been detected as evolved gases and their formation was speculatively suggested on the light of the TG measurements. The reactions taking place in cobalt nitrate–ammonium molybdate/basic magnesium carbonate are the same previously mentioned reactions of cobalt nitrate/basic magnesium carbonate except the decomposition of ammonium molybdate into MoO_3 at temperature 280 °C besides the formation of $MgMoO_4$ and $CoMoO_4$ at temperatures >390 °C.

$$(NH_4)_6Mo_7O_{24} \xrightarrow{170\text{–}280\,^{\circ}C} 7MoO_3 + 6NH_3 + 3H_2O \quad (5)$$

$$MgO + CoO + MoO_3 \xrightarrow{>390\,^{\circ}C} MgMoO_4 + CoMoO_4 \quad (6)$$

3.2. XRD investigation of the thermal products of the investigated mixed solid samples precalcined at different temperatures

XRDs of various mixed solids preheated in air at 400, 600, 800 and 1000 °C were measured. Fig. 3 shows the XRD patterns of CoMg-I solid samples and those treated with MoO_3 preheated in air at 400 °C. It can be seen from this figure that the diffractograms of the investigated solids consist of the diffraction lines of well-crystallized MgO phase and Co_3O_4 phase with moderate degree of crystallinity and the mixed solid sample treated with 5.0 mol% MoO_3 consists of $MgMoO_4$ phase and/or $CoMoO_4$ phase besides MgO and Co_3O_4 phases. The absence of all diffraction lines of MoO_3 in the patterns of the mixed oxides indicates its complete transformation into $MgMoO_4$ and/or $CoMoO_4$ (the main diffraction lines of both phases are very close to each other).

Fig. 4 depicts the XRDs of pure mixed solids CoMg-I and those treated with 2.5 and 5.0 mol% MoO_3 precalcined at 600 °C. The diffractograms of pure mixed solids consist of all diffraction lines of well crystalline MgO as a major phase besides the diffraction lines of Co_3O_4 phase. This finding clearly indicates the absence of any appreciable solid–solid interaction between cobalt and magnesium oxides by exposure to heat treatment at 400 or 600 °C. The diffractograms of mixed solids treated with 2.5 and 5.0 mol% MoO_3 include the diffraction lines of

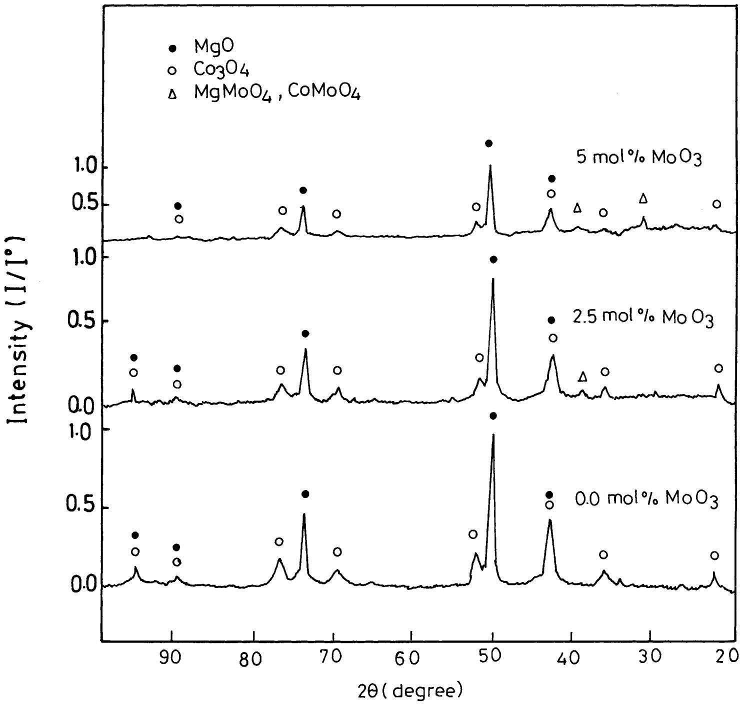

Fig. 3. XRDs of CoMg-I sample and those treated with MoO_3 then precalcined at 400 °C.

$MgMoO_4$ and/or $CoMoO_4$ phases besides the other phases, MgO and Co_3O_4. The disappearance of all diffraction lines of MoO_3 phase suggested its conversion to $MgMoO_4$ and/or $CoMoO_4$ via interacting with cobalt oxide and magnesium oxide. In fact, the addition of increasing amounts of MoO_3 followed by precalcination at 600 °C resulted in a progressive decrease in the intensity of the diffraction lines of free oxides MgO and Co_3O_4. This conclusion was evidenced by following the decrease in the peak height of MgO and Co_3O_4 phases due to this treatment. The peak height of the line at 1.49 Å (MgO phase, 72%) decreased from 87 to 36 (a.u.) while the peak height of the line at 1.43 Å (Co_3O_4 phase, 58%) decreased from 28 to 12 (a.u.) upon the addition of 5.0 mol% MoO_3 (cf. Table 2). Furthermore, the peak height of the lines at 3.38 Å ($MgMoO_4$ phase, 100% and/or $CoMoO_4$ phase, 100%) and 3.83 Å ($MgMoO_4$ phase, 40% and/or $CoMoO_4$ phase, 22%) increased up to 44 and 21 (a.u.), respectively, upon the addition of 5.0 mol% MoO_3.

Fig. 5 illustrates the diffractograms of pure mixed solids CoMg-I, CoMg-II and CoMg-III and those treated with 2.5 and 5.0 mol% MoO_3 and then precalcined at 800 °C. It is seen from Fig. 5 that the diffractograms of pure mixed solids and those treated with MoO_3 followed by precalcination at 800 °C consisted of MgO and Co_3O_4 phases, similar to all investigated mixed solids precalcined at 600 °C. On the other hand, the diffraction lines of $MgMoO_4$ and/or $CoMoO_4$ appeared in the other solid samples treated with 2.5 and 5.0 mol% MoO_3 and preheated at 800 °C. It is clear that the increase in both the precalcination temperature of various investigated mixed solids from 600 to 800 °C and the amounts of MoO_3 added much enhanced the solid–solid interactions between MoO_3 and MgO leading to the formation of $MgMoO_4$ or between MoO_3 and Co_3O_4 yielding $CoMoO_4$ phase as indicated from the progressive increase in the intensity of the diffraction lines of $MgMoO_4$ and/or $CoMoO_4$ with subsequent decrease in the intensity

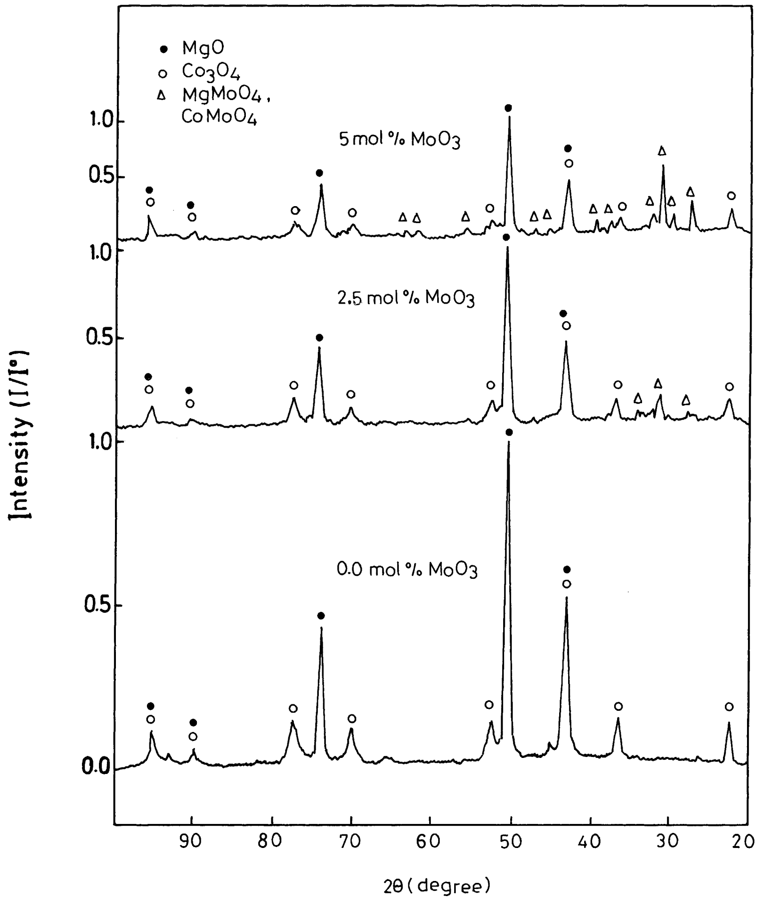

Fig. 4. XRDs of CoMg-I sample and those treated with MoO_3 then precalcined at 600 °C.

of the diffraction lines of free oxides (MgO and Co_3O_4). The observed increase in the intensity of the diffraction lines of $MgMoO_4$ and/or $CoMoO_4$ by increasing the temperature of heat treatment from 600 to 800 °C might not be attributed to a possible improvement in their degree of crystallinity simply because such treatment decreased the intensity of diffraction lines of unreacted MgO and Co_3O_4 phases.

Preliminary experiments showed that the thermal decomposition of ammonium molybdate in air at 400 °C resulted in the formation of well-crystallized orthorhombic MoO_3 which sublimes completely by heating at 800 °C. The increase in the amount of molybdenum trioxide on the top surface layers of mixed oxides might have a effect on increase in the mobility and diffusion of molybdenum species towards the bulk in order to react with free oxides rather than volatilization. The fact that the amounts of MoO_3 added (2.5 and 5.0 mol% MoO_3 which correspond to 4.0 and 8.0 wt.% MoO_3) is below the detection limit of XRD might suggest that most of molybdenum species added was retained in the uppermost surface layers of the mixed solids. In other words, the concentration of MoO_3 on the top surface layers should be much greater than the nominal amount added because it is prepared by wet impregnation method.

Preliminary experiments showed that the formation of magnesium cobaltite ($MgCo_2O_4$) has been ruled

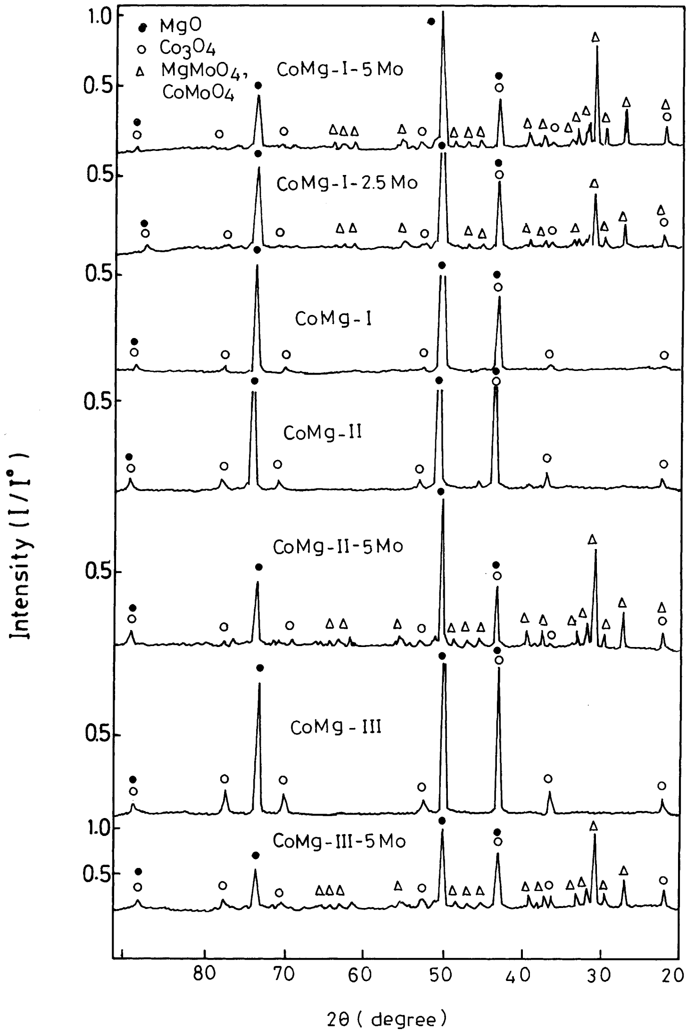

Fig. 5. XRDs of CoMg-I, CoMg-II and CoMg-III samples and those treated with MoO_3 precalcined at 800 °C.

out via XRD investigation at relatively high diffraction angles of 90–130°. In fact, the detected diffraction line at $d = 1.06$ Å showed I/I_0 value (<10%) corresponding to MgO phase instead of 100% in the case of $MgCo_2O_4$. This investigation has been done for different solids investigated precalcined at different temperatures. In other words, most of cobalt species present in the solids precalcined at temperatures ≥800 °C existed as CoO–MgO solid solution having the formula $Co_xMg_{1-x}O$. The diffractograms of the investigated solids precalcined at 1000 °C (not given) consist, only, of the diffraction lines of MgO phase besides the $MgMoO_4$ phase and/or $CoMoO_4$ phase for the solids treated with 2.5 and 5.0 mol% MoO_3. The complete disappearance of all diffraction lines of Co_3O_4 as a separate phase in all solids investigated precalcined at 1000 °C clearly indicates its complete dissolution in MgO lattice forming CoO–MgO solid solution. So the formula of solid solution formed at 1000 °C in the case of CoMg-I, CoMg-II and CoMg-III are as follows: $Co_{0.23}Mg_{0.77}O$, $Co_{0.37}Mg_{0.63}O$ and $Co_{0.47}Mg_{0.53}O$.

Table 2
The effect of precalcination temperature and composition on the height of some diffraction lines at *d* spacing of 1.49 Å (72% MgO), 1.43 and 2.84 Å (58 and 29% Co_3O_4), 3.38 Å (100% $MgMoO_4$ and 100% $CoMoO_4$) and 3.83 Å (40% $MgMoO_4$ and 22% $CoMoO_4$)

Solids	Precalcination temperature (°C)	Peak height (a.u.)				
		1.49 Å	1.43 Å	2.84 Å	3.38 Å	3.83 Å
Pure $0.1Co_3O_4/MgO$	400	50	22	12	–	–
Pure $0.1Co_3O_4/MgO + 2.5$ mol% MoO_3	400	35	12	9	–	–
Pure $0.1Co_3O_4/MgO + 5.0$ mol% MoO_3	400	27	8	5	11	3
Pure $0.1Co_3O_4/MgO$	600	87	28	27	–	–
Pure $0.1Co_3O_4/MgO + 2.5$ mol% MoO_3	600	51	20	17	18	2
Pure $0.1Co_3O_4/MgO + 5.0$ mol% MoO_3	600	36	12	10	44	21
Pure $0.1Co_3O_4/MgO$	800	134	7	10	–	–
Pure $0.1Co_3O_4/MgO + 2.5$ mol% MoO_3	800	103	4	7	66	30
Pure $0.1Co_3O_4/MgO + 5.0$ mol% MoO_3	800	70	3	6	125	47
Pure 0.2 Co_3O_4/MgO	800	208	21	26	–	–
Pure 0.2 $Co_3O_4/MgO + 2.5$ mol% MoO_3	800	150	12	13	70	35
Pure 0.2 $Co_3O_4/MgO + 5.0$ mol% MoO_3	800	82	6	7	126	47
Pure $0.3Co_3O_4/MgO$	800	164	32	30	–	–
Pure $0.3Co_3O_4/MgO + 2.5$ mol% MoO_3	800	90	21	19	61	23
Pure $0.3Co_3O_4/MgO + 5.0$ mol% MoO_3	800	56	15	15	94	34
Pure $0.1Co_3O_4/MgO$	1000	209	–	–	–	–
Pure $0.1Co_3O_4/MgO + 2.5$ mol% MoO_3	1000	209	–	–	59	19
Pure $0.1Co_3O_4/MgO + 5.0$ mol% MoO_3	1000	190	–	–	57	27
Pure $0.2Co_3O_4/MgO$	1000	228	–	–	–	–
Pure $0.2Co_3O_4/MgO + 2.5$ mol% MoO_3	1000	200	–	–	90	22
Pure $0.2Co_3O_4/MgO + 5.0$ mol% MoO_3	1000	105	–	–	110	39
Pure $0.3Co_3O_4/MgO$	1000	250	–	–	–	–
Pure $0.3Co_3O_4/MgO + 2.5$ mol% MoO_3	1000	210	–	–	105	31
Pure $0.3Co_3O_4/MgO + 5.0$ mol% MoO_3	1000	138	–	–	131	47

4. Conclusions

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

1. Ammonium molybdate treatment of the investigated mixed solids much enhanced the thermal decomposition of cobalt nitrate and dehydroxylation of basic magnesium carbonate, which occurred simultaneously.
2. Cobalt nitrate treatment of basic $MgCO_3$ much enhanced its thermal decomposition and it lowered down the temperature of its thermal decomposition from 525.5 to 395 °C.
3. MoO_3 interacted readily with magnesium oxide and/or cobalt oxide at temperature starting from 400 °C to produce $MgMoO_4$ and/or $CoMoO_4$, which are thermally stable up to 1000 °C.
4. A portion of cobalt oxide reacted with MoO_3 to yield $CoMoO_4$ and the other portion dissolved completely in the matrix of MgO and led to the formation of CoO–MgO solid solution. The complete dissolution occurred at temperature >800 °C producing $Co_xMg_{1-x}O$ (where x varies between 0.3 and 0.47).
5. The complete disappearance of all diffraction lines of cobalt oxide as a separate phase in all solids investigated precalcined at 1000 °C clearly indicates its complete dissolution in MgO matrix forming solid solution.
6. The absence of any appreciable solid–solid interactions between cobalt oxide and MgO yielding

$MgCo_2O_4$ were confirmed by XRD investigation at relatively high diffraction angles.

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