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SOLID–SOLID INTERACTIONS IN PURE AND Li_2O-DOPED MANGANESE AND MAGNESIUM MIXED OXIDES SYSTEM

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Abstract

The solid–solid interactions between manganese and magnesium oxides in absence and in presence of small amounts of Li_2O have been investigated. The molar ratios between manganese and magnesium oxides in the form of Mn_2O_3 and MgO were varied between 0.05:1 to 0.5:1. The mixed solids were calcined in air at 400–1000°C. The techniques employed were DTA, XRD and H_2O_2 decomposition at 20–40°C.

The results obtained revealed that solid–solid interactions took place between the reacting solids at 600–1000°C yielding magnesium manganates (Mg_2MnO_4, Mg_6MnO_8, $MgMnO_4$ besides unreacted portions of MgO, Mn_2O_3 and Mn_3O_4). Li_2O-doping (0.75–6 mol%) of the investigated system followed by calcination at 600 and 800°C decreased progressively the intensity of the diffraction lines of Mn_2O_3 (Bixbyite) with subsequent increase in the lattice parameter '*a*' of MgO to an extent proportional to the amount of Li_2O added. This finding might suggest that the doping process enhanced the dissolution of Mn_2O_3 in MgO forming solid solution. This treatment led also to the formation of Li_2MnO_3. Furthermore, the doping with 3 and 6 mol% Li_2O conducted at 800°C resulted in the conversion of Mn_2O_3 into Mn_3O_4, a process that took place at 1000°C in absence of Li_2O. The produced Li_2MnO_3 phase remained stable by heating at up to 1000°C. Furthermore, Li_2O doping of the investigated system at 400–1000°C resulted in a progressive measurable increase in the particle size of MgO.

The catalytic activity measurements showed that the increase in the molar ratio of Mn_2O_3 in the samples precalcined at 400–800°C was accompanied by a significant increase in the catalytic activity of the treated solids. The maximum increase in the catalytic activity expressed as reaction rate constant measured at 20°C ($k_{20°C}$) attained 3.14, 2.67 and 3.25-fold for the solids precalcined at 400, 600 and 800°C, respectively. Li_2O-doping of the samples having the formula 0.1 Mn_2O_3/MgO conducted at 400–600°C brought a progressive significant increase in its catalytic activity. The maximum increase in the value of $k_{20°C}$ due to Li_2O attained 1.93 and 2.75-fold for the samples preheated at 400 and 600°C, respectively and opposite effect was found for the doped samples preheated at 800°C.

Keywords: H_2O_2 decomposition, Li_2MnO_3, Li_2O-doping, Mg_6MnO_8, MgO, Mn_2O_3

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Introduction

The dopant agent may affect the solid–solid interaction between the oxide and its support [1–3]. This influence may be accompanied by significant changes in the catalytic activities of the doped supported catalysts [4]. The effect of doping with some foreign cations such as Li^+, Na^+, K^+, Zn^+, Ag^+ on physicochemical, surface and catalytic properties of different transition metal oxides supported on alumina or magnesia such as Co_3O_4/MgO [5], Mn_2O_3/Al_2O_3 [6], Co_3O_4/Al_2O_3 [7] and NiO/Al_2O_3 [8] made the object of several investigations. The results showed that the doping process exert significant changes on the degree of dispersion of the catalytically active constituents, on their specific surface areas, on the solid–solid interactions between the metal oxides and support material, and consequently on their catalytic activities [9, 10].

Manganese carbonate is known to decompose readily on heating in air or under a reduced pressure of 10^{-5} Torr at moderate temperatures (300–400°C) yielding MnO_2, which converts simultaneously into Mn_2O_3 [11–14]. Mn_2O_3 remained thermally stable up to 900°C then decomposed to form Mn_3O_4 [15]. The presence of Li_2CO_3 or NaOH was found to enhance the decomposition of both MnO_2 and Mn_2O_3 [11, 15]. The KOH-treatment of $MnCO_3$ was found to decrease the decomposition temperature of $MnCO_3$, MnO_2 and Mn_2O_3 to an extent proportional to the amount of potassium hydroxide present [16]. These results have been attributed to an induced increase in the hygroscopic nature of the treated manganese carbonate and to an effective decrease in the oxidation state of the doped oxides [15]. The effect of aluminum oxide support on the thermal behavior of manganese carbonate was also investigated [17]. The results obtained showed that the employed support material retards the thermal decomposition of $MnCO_3$ due to the formation of a manganese/aluminum adduct which decomposes readily at 350 instead of 250°C in the absence of the support material, to give γ-MnO_2. This compound decomposed at 500°C to Mn_2O_3 (partridgeite) [17, 18].

The present investigation reports a study on the effect of loading of different amounts of manganese carbonate on active magnesia on the thermal decomposition of the supported solids. Also, the present work is devoted to study the effect of doping with Li_2O on the thermal decomposition of supported manganese carbonate and on the catalytic activity of the produced manganese oxides. The techniques employed in this work were DTA, X-ray diffraction and catalytic decomposition of H_2O_2 at 20, 30 and 40°C.

Experimental

Materials

Four specimens of manganese oxide loaded on active magnesia were prepared by mechanical mixing of a known mass of finely powdered magnesium basic carbonate with different amounts of manganese carbonate. The obtained mixed solids were heated in air for 5 h at 400–1000°C. The amount of manganese, expressed as Mn_2O_3 varied between 16.0 and 65.6 mass%. The nominal compositions of these solids were $0.05Mn_2O_3$:MgO, $0.1Mn_2O_3$:MgO, $0.2Mn_2O_3$:MgO and $0.5Mn_2O_3$:MgO. The doped mixed solids were prepared by treating a known mass of basic $MgCO_3$ with a solution containing different proportions of lithium nitrate then dried at 100°C. A fixed quantity of manganese basic carbonate was mixed with different treated magnesium carbonate followed by calcination in air at 400–1000°C for 5 h. Four the series of doped catalysts, manganese content was fixed at 28.6 mass%, expressed as Mn_2O_3, while the amounts of lithium, expressed as Li_2O, were 1.5, 3, 6 and 12 mol% which correspond to 0.75, 1.5, 3 and 6 mol% Li_2O, respectively. All chemicals employed in the preparation of the pure and doped catalysts were of analytical grade as supplied by the Riedel–De Haen Company, Germany.

Techniques

An X-ray diffractograms of pure and doped mixed solids precalcined in air at 400–1000°C were obtained using a Philips diffractometer (type PW 1390). The patterns were run with iron radiation without filter (λ =1.9373 Å) at 36 kV and 16 mA with scanning speed of 2° in 2θ min^{-1}.

The particle size of MgO phase in pure and doped solids was calculated using Schrer equation [19]:

$$d=\frac{B\lambda}{\beta_{1/2}\cos\theta}$$

where d is average particle size of the phase under investigation, B is the Schrer constant (0.89), λ is wavelength of the X-ray beam used, $\beta_{1/2}$ is the full width half maximum (FWHM) of diffraction peak and θ is the diffraction angle.

The lattice parameter 'a' of MgO (cubic structure) Mn_2O_3/MgO mixed solids preheated at 500–1000°C was determined from the equation: $a=d\sqrt{h^2+k^2+l^2}$ where a for the diffraction line at d-spacing 2.095 Å(200) [20].

DTA analysis was carried out for various mixed solids using Shimadzu DTA-50. The measurements were done in a current of nitrogen flowing at a rate of 20 mL min^{-1}. The rate of heating was kept at 10°C min^{-1}. A 40 mg samples of each solid specimen was employed in each case.

The catalytic activity of the various catalysts was determined by studying the decomposition of H_2O_2 in their presence at 20°C. 30 and 40°C using 10 mg of a given catalyst sample with a 0.5 mL volume of H_2O_2 of known concentration diluted to 20 mL with distilled water. Measuring the volume of oxygen gas liberated at different time intervals until equilibrium was attained monitored the reaction kinetics.

Results and discussion

Thermal investigation of pure and doped uncalcined mixed solid samples

The DTA and dDTA curves of manganese carbonate, pure and doped mixtures of manganese and magnesium carbonates were determined. Figure 1 depicts the DTA and dDTA curves of manganese carbonate hydrate and magnesium basic carbonate

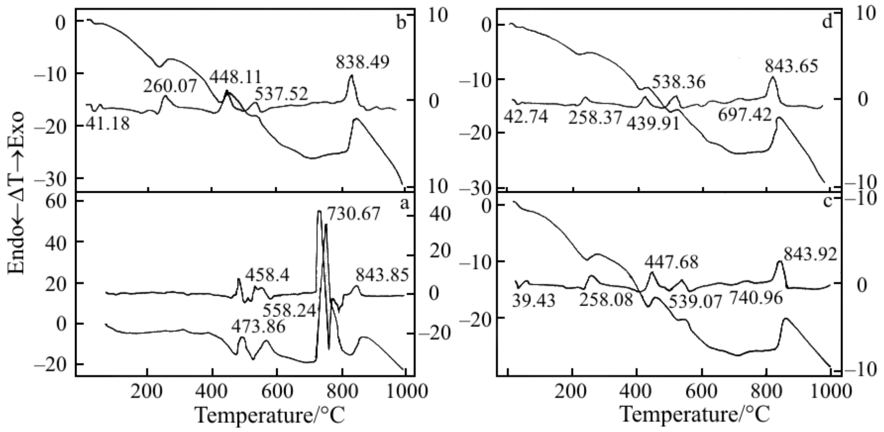

Fig. 1 DTA and dDTA of a – hydrated manganese carbonate, b – 0.2 manganese carbonate : basic magnesium carbonate, c – 0.4 manganese carbonate : basic magnesium carbonate and d – manganese carbonate : basic magnesium carbonate

mixed with different proportions of manganese carbonate (0.2, 0.4 and 1 mol mol^{-1}). The DTA and dDTA curve of manganese carbonate consists of three endothermic peaks located at 473.9, 558.2 and 843.9°C together with very strong and sharp exothermic peak at 730.7°C.

The endothermic peaks correspond to thermal decomposition of $MnCO_3$ into MnO_2, Mn_2O_3 and Mn_3O_4 according to:

$$2MnCO_3+O_2\xrightarrow{473.9\,°C}2MnO_2+2CO_2;\ 2MnO_2\xrightarrow{558.2\,°C}Mn_2O_3+\tfrac{1}{2}O_2;$$

$$3Mn_2O_3\xrightarrow{843.9\,°C}2Mn_3O_4+\tfrac{1}{2}O_2\ .$$

The exothermic peak at 730.7°C might characterize the crystallization of Mn_2O_3 into Mn_2O_3 (bixbyite) phase. The DTA curves of different mixtures of manganese and magnesium carbonates consist of five endothermic peaks at 39–43, 258–260, 439–448, 537–539 and 838–844°C. The first set of peaks correspond to removal of water of crystallization of magnesium and manganese carbonates, the second peak prefers to dehydroxylation of magnesium basic carbonate yielding $MgCO_3$ [11, 16], the third and fourth peaks correspond to thermal decomposition of $MgCO_3$ into MgO. The last peak refers to thermal transformation of Mn_2O_3 to Mn_3O_4 [17, 18].

Figure 2 shows the DTA and dDTA curves of pure and lithium oxide-doped mixed solids. The DTA curves of doped mixed solid samples consist of six endothermic peaks located at 40–41, 260–267, 440–448, 480–537, 735–838 and 887–960°C. The first five sets of peaks indicate removal of water of crystallization of manganese and magnesium carbonates, dehydroxylation of magnesium basic carbonate, decomposition of $MgCO_3$ and transformation of Mn_2O_3 into Mn_3O_4, respectively. The last set of peaks might characterize possible solid–solid interactions between Li_2O with manganese and magnesium oxides yielding lithium/manganese and lithium/magnesium compounds. The identification of such compounds will be done via XRD investigation of variously doped mixed solids precalcined at different temperatures.

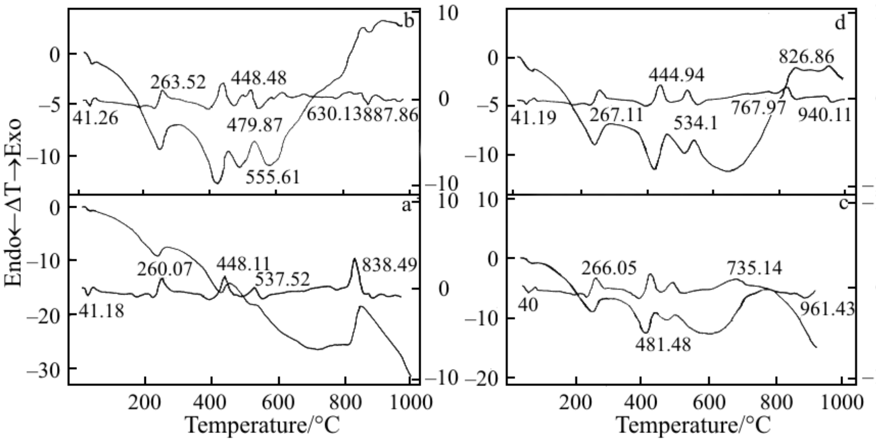

Fig. 2 DTA and dDTA of a – pure solid, 0.2 manganese carbonate : basic magnesium carbonate, b – pure solid doped with 3 mol% $LiNO_3$, c – pure solid doped with 6 mol% $LiNO_3$ and d – pure solid doped with 12 mol% $LiNO_3$

XRD investigation of $MnCO_3$ preheated at different temperatures

Figure 3 depicts X-ray diffractograms of $MnCO_3$ hydrate subjected to heat treatment at 400, 500, 600, 800 and 1000°C. This figure showed that the diffraction lines of MnO_2 (major phase) together with some diffraction lines of Mn_2O_3 appeared in the diffractograms of the samples precalcined at 400°C [16]. The rise in calcination temperature in the range of 400–800°C led to a complete conversion of MnO_2 into Mn_2O_3 (bixbyite). It can also be seen from Fig. 3 that the diffractogram of the solid preheated at 1000°C consisted of all diffraction lines of well-crystallized Mn_3O_4 (Hausmannite) [21].

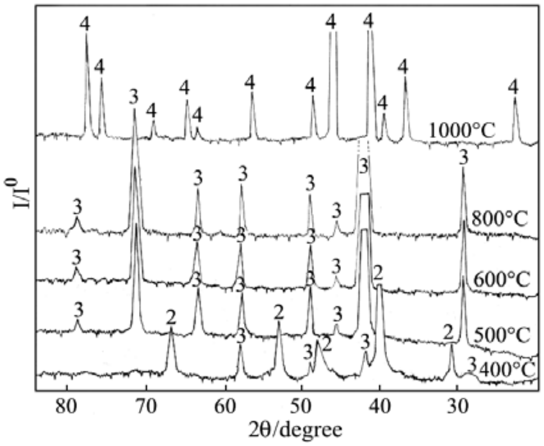

Fig. 3 X-ray diffractograms of manganese carbonate precalcined in air at 400, 500, 600, 800, 1000°C. Lines 2 – MnO_2, 3 – Mn_2O_3 and 4 – Mn_3O_4

XRD investigation of pure manganese and magnesium mixed carbonate precalcined at different temperatures

The X-ray diffractograms of pure manganese and magnesium mixed carbonates precalcined at 400 to 1000°C was determined. The crystalline phases produced are summarized and given in Table 1. Figures 4 and 5 depict representative diffractograms of different solids preheated at 400 and 600°C. It can be seen from Table 1 and Figs 4, 5 that: (*i*) MgO and MnO_2 constituted the crystalline phases present in the mixed solids precalcined at 400°C. (*ii*) The relative intensities of the diffraction lines of MnO_2 increases and those of MgO decreases by increasing the amount of manganese oxide added. The diffraction patterns of the sample having a molar ratio of manganese oxide : MgO of 0.5:1 and calcined at 400°C consisted of the diffraction lines of MnO_2 indicating a possible retardation effect of thermal decomposition of $MgCO_3$ or the formation of finely divided MgO phase that could not be detected easily by XRD. (*iii*) The mixed solids precalcined at 600°C consisted of the diffraction lines of MgO, Mn_2O_3 and Mg_2MnO_4. The formation of magnesium manganate compound took place according to:

$$4MgO+Mn_2O_3+1/2O_2\xrightarrow{600^\circ C}2Mg_2MnO_4 \tag{1}$$

(*iv*) The heat treatment of the investigated solids at 800°C led to formation of Mg_6MnO_8 together with Mg_2MnO_4, MgO, Mn_2O_3 and Mn_5O_8 phases [20]. The formation of Mg_6MnO_8 was produced according to:

$$12MgO+Mn_2O_3+1/2O_2\xrightarrow{800^\circ C}2Mg_6MnO_8 \tag{2}$$

(*v*) The heat treatment of different mixed solids at 1000°C led to the formation of Mn_3O_4 [16], Mg_6MnO_8, Mg_2MnO_4, MgO and $MgMnO_4$. The formation of the last compound took place according to:

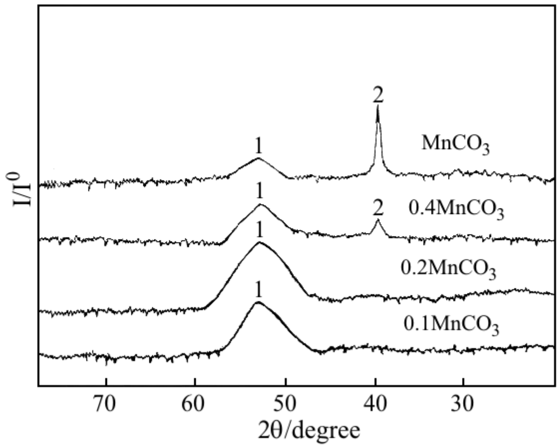

Fig. 4 X-ray diffractograms of magnesium carbonate mixed with different proportions of manganese carbonate and precalcined in air at 400°C. Lines 1 – MgO and 2 – MnO_2

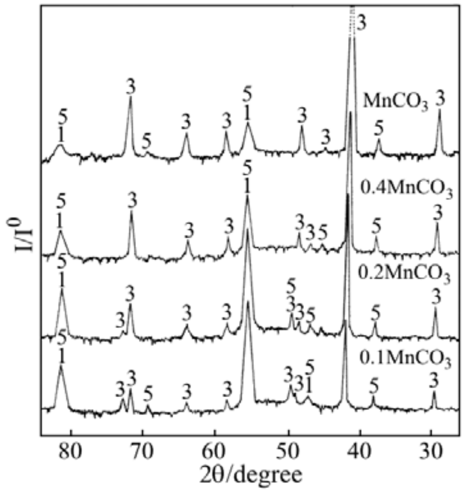

Fig. 5 X-ray diffractograms of magnesium carbonate mixed with different porportions of manganese carbonate and precalcined in air at 600°C. Lines 1 – MgO, 3 – Mn_2O_3 and 5 – Mg_2MnO_4

$$3MgO+Mn_3O_4+5/2O_2 \xrightarrow{1000°C} 3MgMnO_4 \qquad (3)$$

The effects of mol ratios of manganese oxide: MgO and calcination temperature on the lattice parameter '*a*' of MgO and on its particle size have been investigated and the results obtained are given in Table 2. Inspection of Table 2 revealed the following: (*i*) The particle size of MgO phase increases progressively by increasing the calcination temperature and amount of manganese oxide present. (*ii*) The lattice parameter of MgO phase present in different investigated solids precalcined at 500–1000°C increases progressively by increasing the amount of manganese oxide present. This increase was, however, more pronounced in the case of the mixed oxide solids precalcined at 500, 600 and 800°C.

The observed increase in the lattice parameter due to treatment with increasing amounts of manganese oxide might be attributed to dissolution of some of manganese oxide in the lattice of MgO forming MnO–MgO solid solution having the formula $Mn_xMg_{1-x}O$. In fact, the ionic radii of Mg^{2+} and Mn^{2+} are 0.65 and 0.80 Å, respectively [22]. So, the dissolution of a small portion of manganese oxide in the lattice of MgO should be normally accompanied by an expansion in its lattice with subsequent increase in the lattice parameter of MgO phase. The fact that the extent of increase in the lattice parameter of MgO decreases progressively by increasing the precalcination temperature of the investigated solids, suggesting that the amount of manganese oxide dissolved in MgO lattice decreases by increasing the temperature of heat treatment within the range 500–1000°C. This conclusion simply seems logical, because solid–solid interactions between manganese and MgO took place at temperature within the range 600–1000°C (Table 1).

Table 1 Different crystalline phases produced by heating $MnCO_3$ and manganese/magnesium mixed carbonates precalcined at 400–1000°

Chemical composition	Calcination temperature/°C	Formed phase*
	400	MnO_2 (different structure, small amount of Mn_2O_3)
	500	Mn_2O_3
$MnCO_3$	600	Mn_2O_3
	800	Mn_2O_3
	1000	Mn_3O_4
0.05 Mn/Mg	400	MgO
0.1 Mn/Mg		MgO, MnO_2
0.2 Mn/Mg		MgO, MnO_2
0.5 Mn/Mg		MgO, MnO_2
0.05 Mn/Mg	500	MgO, Mn_2O_3
0.1 Mn/Mg		MgO, Mn_2O_3
0.2 Mn/Mg		MgO, Mn_2O_3
0.5 Mn/Mg		MgO, Mn_2O_3
0.05 Mn/Mg	600	MgO, Mn_2O_3
0.1 Mn/Mg		MgO, Mn_2O_3, Mg_2MnO_4
0.2 Mn/Mg		MgO, Mn_2O_3, Mg_2MnO_4
0.5 Mn/Mg		MgO, Mn_2O_3, Mg_2MnO_4
0.05 Mn/Mg	800	MgO, Mn_2O_3
0.1 Mn/Mg		MgO, Mn_2O_3, Mg_6MnO_8
0.2 Mn/Mg		MgO, Mn_2O_3, Mg_6MnO_8
0.5 Mn/Mg		MgO, Mn_2O_3, Mg_6MnO_8
0.05 Mn/Mg	1000	MgO, Mn_3O_4, $MgMnO_4$
0.1 Mn/Mg		MgO, Mn_3O_4, $MgMnO_4$
0.2 Mn/Mg		MgO, γ-Mn_3O_4, $MgMnO_4$, Mg_2MnO_4
0.5 Mn/Mg		MgO, Mn_3O_4, Mg_6MnO_8, $MgMnO_4$, Mg_2MnO_4

*Mn_2O_3 (Bixbyite)
*Mn_3O_4 (Hausmannite)

XRD investigation of manganese and magnesium mixed oxides doped with Li_2O and precalcined at 400–1000°C

The X-ray diffractograms of the sample having the formula $0.1Mn_2O_3/MgO$ doped with small amounts of Li_2O followed by calcination at 400–1000°C have been carried out. The crystalline phases produced are given in Table 3.

Table 2 Lattice parameter and particle size of MgO phase present in different manganese/magnesium mixed oxides preheated at 500–100°C

Mn/Mg molar ratio	Calcination temperature/°C	Lattice parameter/Å	Particle size/Å
0.05	500	4.2135	85
0.1	500	4.2191	99
0.2	500	4.2261	110
0.5	500	4.2290	112
0.05	600	4.2121	108
0.1	600	4.2173	116
0.2	600	4.2191	145
0.5	600	4.2265	150
0.05	800	4.2129	202
0.1	800	4.2169	209
0.2	800	4.2188	215
0.5	800	4.2233	285
0.05	1000	4.1220	295
0.1	1000	4.2121	296
0.2	1000	4.2140	298
0.5	1000	4.2146	302

Figure 6 depicts X-ray diffractograms of pure and variously doped solids precalcined at 400°C. It is seen from this figure that Li_2O-doping of the investigated system followed by calcination at 400°C stimulated the thermal decomposition of $MnCO_3$ yielding MnO_2. The stimulation effect ran parallel to the amount of the dopant added. The doping process effected also a measurable increase in the degree of ordering and particle size of MgO phase as evidenced from the observed measurable increase in peak height of the main diffraction lines of MgO phase (d=2.095 Å) which measured the values 40, 49, 54, 58 and 94 a.u. for the pure sample and those doped with 0.75, 1.5, 3 and 6 mol% Li_2O, respectively. These results could be attributed to an enhanced increase in the mobility of magnesium and manganese ions thus facilitating the thermal decomposition of $MnCO_3$ producing MnO_2 [11] and increasing the degree of crystallinity of MgO phase. These findings agree with the refluxing effect of Li_2O.

Inspection of Table 3 revealed the following: (*i*) The rise in precalcination temperature to above 400°C led to the formation of Li_2MnO_3 [11, 23] besides Mn_2O_3, MgO and Mg_2MnO_4. The formation of Li_2MnO_3 took place according to:

$$2Li_2O+Mn_2O_3+1/2O_2 \xrightarrow{>400^\circ C} 2Li_2MnO_3 \quad (4)$$

Table 3 Crystalline phases present in the thermal products of pure and Li_2O-doped manganese/magnesium mixed oxide solids preheated at 400–1000°C

Li_2O concentration/ mol%	Calcination temperature/°C	Phases*
0	400	MgO, MnO_2
0.75		MgO, MnO_2
1.5		MgO, MnO_2
3		MgO, MnO_2
6		MgO, MnO_2
0	500	MgO, Mn_2O_3
0.75		MgO, Mn_2O_3
1.5		MgO, Mn_2O_3, Li_2MnO_3
3		MgO, Mn_2O_3, Li_2MnO_3
6		MgO, Mn_2O_3, Li_2MnO_3
0	600	MgO, Mn_2O_3, Mg_2MnO_4
0.75		MgO, Mn_2O_3, Mg_2MnO_4, Li_2MnO_3
1.5		MgO, Mn_2O_3, Mg_2MnO_4, Li_2MnO_3
3		MgO, Mn_2O_3, Mg_2MnO_4, Li_2MnO_3
6		MgO, Mn_2O_3, Mg_2MnO_4, Li_2MnO_3
0	800	MgO, Mn_2O_3, Mg_2MnO_4, $MgMnO_4$
0.75		MgO, Mn_2O_3, Mg_2MnO_4, $MgMnO_4$
1.5		MgO, Mn_2O_3, Mg_6MnO_8, Li_2MnO_3
3		MgO, Mn_2O_3, Li_2MnO_3
6		MgO, Mn_2O_3, Mn_3O_4, Li_2MnO_3
0	1000	MgO, Mn_3O_4, Mg_6MnO_8
0.75		MgO, Mn_3O_4, Mg_6MnO_8
1.5		MgO, Mn_3O_4, Li_2MnO_3
3.0		MgO, Mn_3O_4, Li_2MnO_3
6.0		MgO, Mn_3O_4, Li_2MnO_3

*Mn_2O_3 (Bixbyite)
*Mn_3O_4 (Hausmannite)

The fact that the diffraction lines of Li_2MnO_3 (*d*=4.75, 2.03, 2.02) [20] phase were detected in the diffractograms of the solids doped with very small amounts of Li_2O which are much below the detection limit of XRD suggested that most of the dopant added was retained in the uppermost surface layers of the treated solids.

This conclusion comes from the fact that the doped samples were prepared by wet impregnation method. (*ii*) The heat treatment of the doped samples at 800°C brought about the appearance of diffraction lines of Mn_3O_4 phase [11]. The formation of this

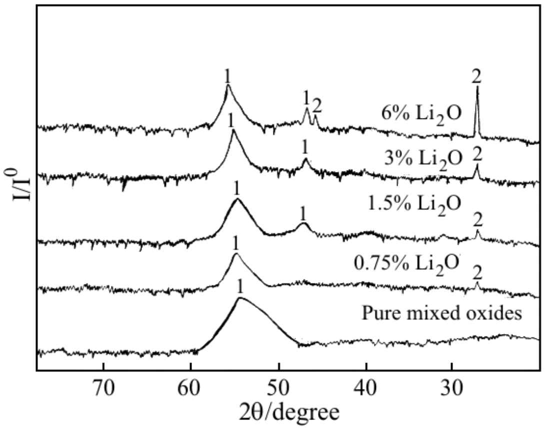

Fig. 6 X-ray diffractograms of pure 0.2 manganese carbonate: basic magnesium carbonate and doped with Li_2O and preheated in air at 400°C. Lines 1 – MgO and 2 – MnO_2

oxide required a heat treatment of pure manganese oxide above 900°C [16, 17]. So, Li_2O-doping enhanced the thermal conversion of Mn_2O_3 into Mn_3O_4 according to:

$$3Mn_2O_3 \xrightarrow{Li_2O;\ 800°C} 2Mn_3O_4 + 1/2O_2 \qquad (5)$$

This effect clarifies the role of Li_2O as a reflux material, which lowers the thermal conversion process of Mn_2O_3 into Mn_3O_4 according to the above equation. (*iii*) Li_2MnO_3 compound produced at 500°C remained thermally stable even by heating at 1000°C (Fig. 7).

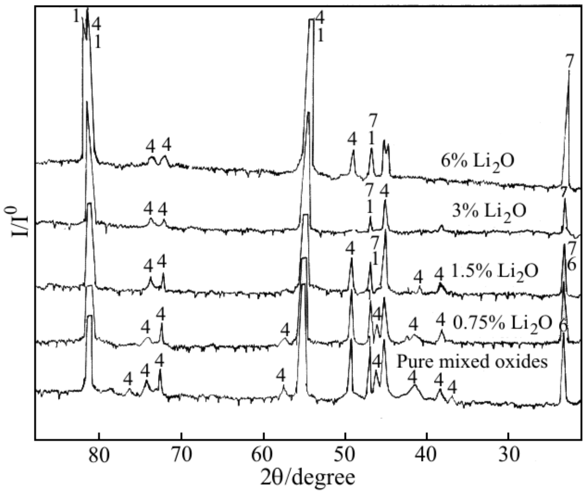

Fig. 7 X-ray diffractograms of pure 0.2 manganese carbonate: basic magnesium carbonate and doped with Li_2O and preheated in air at 1000°C. Lines 1 – MgO, 4 – Mn_3O_4 and 7 – Li_2MnO_3

Table 4 Particle size of MgO phase present in pure and Li_2O-doped manganese/magnesium mixed oxide solids precalcined at 400-1000°C

Li_2O concentration/mol%	Calcination temperature/°C	Particle size/Å
0	400	40
0.75	400	45
1.5	400	48
3	400	51
6	400	51
0	500	103
0.75	500	110
1.5	500	115
3	500	119
6	500	128
0	600	118
0.75	600	136
1.5	600	150
3	600	167
6	600	184
0	800	215
0.75	800	243
1.5	800	277
3	800	294
6	800	319
0	1000	240
0.75	1000	296
1.5	1000	307
3	1000	323
6	1000	361

The effect of Li_2O on the particle size of MgO phase was investigated and the results obtained are given in Table 4. It is clearly shown from this table that the particle size of MgO phase increases progressively by increasing the precalcination temperature within the range 400–1000°C and also by increasing the amounts of Li_2O added. The maximum increase in the particle size of MgO phase due to Li_2O-doping with 6 mol% attained 25, 25, 55, 48 and 50% for the solids preheated at 400, 500, 600, 800 and 1000°C, respectively.

The computed values of the particle size of MgO in pure and variously doped solids preheated at 400–1000°C enabled the calculation the activation energy of sintering of MgO using Arrhenius equation:

$$d=A\exp(-E_s/RT) \tag{6}$$

where d is the particle size of MgO preheated at temperature T, A is the frequency factor of Arrhenius equation and E_s is the activation energy of sintering process of MgO. The last equation can be converted into the following form:

$$\ln d=\ln A-E_s/RT \tag{7}$$

By plotting ln$d$ *vs.* $1/T$ a straight line is obtained whose slope and intercept permitted the calculation of E_s and ln$A$. The plots of ln$d$ *vs.* $1/T$ in the range of 400–1000°C for pure and doped solids (not given) are straight lines and the computed E_s values were 32, 28, 25.7 and 21 kJ mol^{-1} for pure sample and those treated with 1.5, 3 and 6 mol% Li_2O, respectively. These results suggested that Li_2O-doping enhanced the grain growth or particle adhesion of MgO crystallites to an extent proportional to the amount of dopant added. Similar results have been reported in the case of Li_2O-doping of NiO, CoO, Co_3O_4 and MgO/Fe_2O_3 solids [24–26].

Catalytic decomposition of H_2O_2 on different pure manganese and magnesium mixed oxides precalcined at different temperatures

Following up the volume of oxygen liberated at different time intervals until equilibrium was attained monitored the kinetic of the catalytic decomposition of H_2O_2 on different catalysts. First-order kinetics were observed in all cases and the slopes of these first order plots enable a direct calculation of the reaction rate constant (k) measured at different temperatures over various catalyst samples. The values of k measured at 20, 30 and 40°C were determined and the data obtained are given in Table 5. Included also in this Table are the values of the apparent activation energy 'E_a', of the catalyzed reaction.

Preliminary experiments showed that MgO calcined at 400–800°C showed no measurable catalytic activity for H_2O_2 decomposition conducted at temperatures up to 40°C. So, manganese oxide and different magnesium manganate compounds represent the catalytically active constituents of the investigated system. Examination of the results given in Table 5 showed the following: (*i*) The values of k measured at different temperatures increase progressively by increasing the molar ratios of manganese oxide present in different solids preheated at 400, 600 and 800°C. (*ii*) The maximum increase in values of k measured for the reaction conducted at 20°C attained 214, 167 and 225% for the catalysts precalcined at 400, 600 and 800°C, respectively. (*iii*) E_a was found to decrease progressively by increasing the amounts of manganese oxide present in different samples subjected to heat treatment at 400, 600 and 800°C which agree with the observed increase in the catalytic activity of the investigated solids due to increasing the amounts of manganese oxide present. This increase in the catalytic activity could be attributed to the increase in the amount of catalytically active constituents present (manganese oxides and magnesium manganate). All investigated catalysts samples pre-

Table 5 Kinetic parameters for the decomposition of aqueous H_2O_2 on manganese/magnesium mixed oxides precalcined at 400, 600 and 800°C

Catalyst composition	Calcination temp./°C	$k\cdot 10^{-2}$/min^{-1}			E_a/ kJ mol^{-1}
		20°C	30°C	40°C	
0.05 Mn/Mg	400	2	13	20	27
0.1 Mn/Mg	400	11	17	24	20
0.2 Mn/Mg	400	17	25	39	22
0.5 Mn/Mg	400	22	31	46	4.75
0.05 Mn/Mg	600	6	10	18	30
0.1 Mn/Mg	600	8	13	21	26
0.2 Mn/Mg	600	13	22	36	27
0.5 Mn/Mg	600	16	30	42	24
0.05 Mn/Mg	800	4	8	13	35
0.1 Mn/Mg	800	6	10	18	29
0.2 Mn/Mg	800	9	19	31	32
0.5 Mn/Mg	800	13	26	36	26

calcined at 1000°C showed no measurable catalytic activity. The absence of any measurable activity for the investigated solids preheated at 1000°C could be attributed to the complete conversion of manganese oxides into Mn_3O_4 [27] and also to an effective sintering of the treated solids [28].

Effect of Li_2O-doping on the catalytic activity of manganese/magnesium mixed oxides preheated at different temperatures

The catalytic activity of pure and variously doped $0.1Mn_2O_3/MgO$ precalcined at 400, 600 and 800°C was studied. First-order kinetic were also observed in all catalyst samples and the values of k measured at 20, 30 and 40°C were calculated from the first order plots (not given) and the values obtained are cited in Table 6. Included, also in this Table are the values of E_a for the catalyzed reaction.

Inspection of Table 6 showed the following: (*i*) The values of k increased progressively by increasing the amounts of lithia added to the solids preheated at 400 and 600°C. The maximum increase in the values of $k_{20°C}$ due to doping with 6 mol% Li_2O attained 98 and 175% for the solids precalcined at 400 and 600°C, respectively. (*ii*) Li_2O-doping of the employed system followed by calcination at 800°C brought about a progressive drastic decrease in the catalytic activity. The addition of 6 mol% Li_2O to the investigated solids followed by heating at 800°C resulted in a decrease of 75% in the values of $k_{20°C}$. (*iii*) The values of E_a were found to vary slightly for the solids preheated at 400°C. While, E_a values suffer progressives small decrease by increasing the amounts of Li_2O added to the solids precalcined at 600 and 800°C. The slightly different values of E_a for the reaction

Table 6 Kinetic parameters for the decomposition of aqueous H_2O_2 on pure and Li_2O-doped Mn/Mg mixed oxides precalcined at 400, 600 and 800°C

Li_2O/ mol%	Calcination temp./°C	$k\cdot 10^{-2}$/min^{-1}			E_a/ kJ mol^{-1}
		20°C	30°C	40°C	
0	400	11	17	24	20.9
0.75	400	13	19	27	20.9
1.5	400	16	22	32	19
3.0	400	18	26	46	21
6.0	400	22	32	51	23.4
0	600	8	13	21	25
0.75	600	11	16	26	23
1.5	600	15	18	31	20.5
3.0	600	19	23	37	19.2
6.0	600	22	26	44	18.4
0	800	6	10	18	29.3
0.75	800	5.1	9	13	24
1.5	800	4.2	7.2	9	20
3.0	800	2.6	4	6	22
6.0	800	1.5	2	3.9	23.4

catalyzed over variously doped solids preheated at 400°C suggested an increase in the concentration of the catalytically active constituent without much affecting the mechanism of the catalyzed reaction. On the other hand, the observed decrease in the E_a values for the reaction conducted over different doped solids preheated at 600 and 800°C might be attributed to a compensation effect via a decrease in the values of pre-exponential factor in the Arrhenius equation. The observed increase in the catalytic activity of the employed system due to Li_2O-doping conducted at 400 and 600°C could be attributed to creation of new ion pairs acting as active sites for H_2O_2 decomposition. These ion pairs are Li^+–Mn^{4+}, Li^+–Mn^{3+} also, the observed in the activity of the investigated system due to Li_2O-doping could also be attributed to the dissolution of very small amount of Li_2O in lattice of MnO_2 and Mn_2O_3 with subsequent increase in the oxidation state of manganese ions. The dissolution process might take place according to the following reaction adopting Kröger's notion [29]:

$$Li_2O+3Mn^{4+}+3/2O_2\rightarrow 2Li^+ (Mn^{4+})+3Mn^{6+} \qquad (8)$$

$$Li_2O+4Mn^{3+}+O_2\rightarrow 2Li^+(Mn^{3+})+4Mn^{4+} \qquad (9)$$

where $Li^+(Mn^{4+})$ and $Li^+(Mn^{3+})$ represent location of lithium ion in the position of host cation lattice ions of MnO_2 and Mn_2O_3, respectively. Mn^{6+} and Mn^{4+} are created hexavalent and tetravalent manganese ions. Reactions (8) and (9) are accompanied by fixation of atmospheric oxygen in the lattices of manganese oxides. Reaction (9) corresponds to dissolution of Li_2O in Mn_2O_3 (solids calcined at 600°C). However, the formation of Li_2MnO_3 in some doped solids preheated at 500 and 600°C might suggest that very small amount of Li_2O could be dissolved in MnO_2 and Mn_2O_3.

The observed significant decrease in the catalytic activity (75%) of manganese/magnesium mixed oxides due to doping with Li_2O conducted at 800°C could be attributed to the role of Li_2O in catalyzing the thermal conversion of Mn_2O_3 into Mn_3O_4 (Eq. (5)) devoted with very small catalytic activity (Table 3).

Conclusions

The results obtained permitted us to draw the following conclusions:

1) The heat treatment of different mixtures of manganese and magnesium carbonates having various molar ratios at 400–1000°C led to the formation of MnO_2, Mn_2O_3 and different magnesium manganates. These manganate compounds remained stable by heating at 1000°C. This high temperature treatment led to conversion of manganese oxides into Mn_3O_4.

2) MgO dissolved small amount manganese oxide in lattice forming MnO–MgO solid solution with subsequent increase in its lattice parameter.

3) Li_2O-doping of the investigated system conducted at 400–1000°C enhanced the decomposition of manganese carbonate yielding MnO_2 and much increase the particle size of MgO phase. This treatment being conducted at 800°C resulted in conversion of Mn_2O_3 into Mn_3O_4. Furthermore, a portion of Li_2O added interacted with manganese oxide leading to the formation of Li_2MnO_3 at temperature starting from 400°C.

4) The catalytic activities, in H_2O_2 decomposition, increased progressively by increasing the amount of manganese oxide present in different samples preheated at 400–800°C.

5) Li_2O-treatment of the investigated system followed by calcinations at 400 and 600°C effected a measurable increase in the catalytic activity of the treated solids due to creation of new ion pairs and due to an effective increase in the oxidation state of manganese oxides. An opposite effect manifested for the doped solids preheated at 800°C due to transformation of Mn_2O_3 into Mn_3O_4.

References

1 G. A. El-Shobaky, G. A. Fagal, A. M. Ghozza and M. Mokhtar, Colloids Surf., A. Physicochem. Eng. Aspects, 142 (1998) 17.

2 J. Kizenski, M. Marczewski and S. Malinowski, React. Kinet. Catal. Lett., 7 (1977) 157.

3 M. Howalla, J. Lemaitre and B. Delmon, J. Chem. Soc., Faraday Trans., 178 (1982) 1389.

4 G. A. El-Shobaky, Th. El-Nabarawy and G. A. Fagal, Appl. Catal., 52 (1989) 33.

5 N. M. Deraz, Materials Lett., 51 (2001) 470.

6 N. M. Deraz, H. H. Salim and A. A. El-Aal, Materials Lett., 53 (2002) 102.

7 P. Arnoldy and J. A. Moulijn, J. Catal., 51 (1978) 243.

8 G. A. El-Shobaky, A. N. Al-Noaimi and T. N. H. Saber, Bull. Soc. Chim. Fr., 6 (1985) 930.

9 W. M. Shaheen and M. M. Selim, Thermochim. Acta, 322 (1998) 117.
10 N. A. Youssef, T. Farid and M. M. Selim, Afinidad, 50 (443) (1993) 47.
11 G. A. El-Shobaky and K. A. El-Barawy, Thermochim. Acta, 9 (1985) 53.
12 K. S. Irani, A. P. B. Sinka, N. R. San Jena and A. B. Bismas, J. Sci. Ind. Res. Sect. B., 17 (1958) 52.
13 A. Bergstein and J. Vintera, Collect Greh. Chem. Commun., 22 (1957) 884.
14 D. Dollimore and K. H. Tonge, In H. G. Weidemann (Ed.), 3rd Int. Conf. Thermal Analysis Davois, 1971, Birkhaeuser, Basel 1972, p. 91.
15 G. A. El-Shobaky, K. A. El-Barawy and A. A. Ibrahim, Thermochim. Acta, 101 (1986) 195.
16 G. A. El-Shobaky, K. A. El-Barawy and A. A. Ibrahim, Thermochim. Acta, 102 (1986) 21.
17 G. A. El-Shobaky, A. M. Ghozza and H. A. Hassan, J. Therm. Anal. Cal., 51 (1998) 529.
18 M. W. Shaheen and M. M. Selim, J. Therm. Anal. Cal., 59 (2000) 961.
19 B. D. Cullity, ‘Element of X-ray Diffraction’ Adson-Wesly. 3rd Edn. 1967
20 Powder Diffraction File (JCPDS). International Center for Diffraction Data. Swartmore, PA 1979.
21 W. M. Shaheen and K. S. Hong, Thermochim. Acta, 381 (2002) 153.
22 N. N. Greenwood, Ionic Crystal Lattice Deffects and Non-Stoichiometry, Butterworths, London 1968.
23 V. Berbenni and A. Marini, J. Anal. Appl. Pyrol., 62 (2002) 45.
24 G. A. El-Shobaky and N. Petro, Surface Technol., 13 (1981) 19.
25 G. A. El-Shobaky, I. F. Hewaidy and Th. El-Nabarawy, Surface Technol., 12 (1981) 47.
26 G. A. El-Shobaky, N. E. R. Radwan and F. M. Radwan, J. Therm. Anal. Cal., 68 (2002) 275.
27 W. M. Shaheen and M. M. Selim, Afindad, 480 (1999) 129.
28 W. M. Shaheen, N. M. Deraz and M. M. Selim, Mat. Lett., 52 (2002) 130.
29 F. A. Kröger, Chemistry of Imperfect Crystals, North-Holland, Amsterdam 1964.