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The formation and physicochemical characterization of Al_2O_3-doped manganese ferrites

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Abstract

Mn/Fe mixed oxide solids doped with Al_2O_3 (0.32–1.27 wt.%) were prepared by impregnation of manganese nitrate with finely powdered ferric oxide, then treated with different amounts of aluminum nitrate. The obtained samples were calcined in air at 700–1000 °C for 6 h. The specific surface area (S_{BET}) and the catalytic activity of pure and doped precalcined at 700–1000 °C have been measured by using N_2 adsorption isotherms and CO oxidation by O_2. The structure and the phase changes were characterized by DTA and XRD techniques. The obtained results revealed that Mn_2O_3 interacted readily with Fe_2O_3 to produce well-crystallized manganese ferrite ($MnFe_2O_4$) at temperatures of 800 °C and above. The degree of propagation of this reaction increased by Al_2O_3-doping and also by increasing the heating temperature. The treatment with 1.27 wt.% Al_2O_3 followed by heating at 1000 °C resulted in complete conversion of Mn/Fe oxides into the corresponding ferrite phase. The catalytic activity and S_{BET} of pure and doped solids were found to decrease, by increasing both the calcination temperature and the amount of Al_2O_3 added, due to the enhanced formation of $MnFe_2O_4$ phase which is less reactive than the free oxides (Mn_2O_3 and Fe_2O_3). The activation energy of formation (ΔE) of $MnFe_2O_4$ was determined for pure and doped solids. The promotion effect of aluminum in formation of $MnFe_2O_4$ was attributed to an effective increase in the mobility of reacting cations.

Keywords: Al_2O_3-doped; $MnFe_2O_4$; Catalytic activity

1. Introduction

Most divalent metal oxides (MO) interact with Fe_2O_3 yielding the corresponding ferrite with the formula MFe_2O_4 [1]. Ferrites are important materials due to their several applications in the technological and the catalytic fields [2–6]. Transition metal ferrites have a cubic spinel structure, in which oxygen ions form a face centered cubic lattice and two different interstitial sites occupied by the cations are of two kinds as tetrahedral or A sites and octahedral or B sites [1–10]. The spinel crystal structure is only formed when the ionic radius of the cation (M) is less than about 1 Å. If it is >1 Å, then the electrostatic coulomb forces are insufficient to ensure the stability of crystal [11]. However, the spinel structure can be classified into: (i) Normal spinels in which M^{2+} ions occupy the A sites and Fe^{3+} ions occur on the B sites. (ii) Inverse spinels in which M^{2+} ions occupy the B sites together with half Fe^{3+} ions, the other half being on the A sites. (iii) Random spinels in which both M^{2+} and Fe^{3+} ions occur on the A and B sites. Ferrites can be prepared by ceramic or co-precipitation techniques depending on their end use [1,7]. Deraz [12] reported that solid–solid interaction between α-Fe_2O_3 and

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Mn_2O_3, resulted from thermal decomposition of manganese carbonate, to produce manganese ferrite occurred at temperatures of 900 °C and above. However, it has been shown that Li_2O or ZnO-doping enhanced the formation of copper and manganese ferrites by increasing the mobility of thermal diffusion of the reacting cations through the early ferrite film [12]. Several authors reported that the rate of the solid state reaction between Fe_2O_3 and various transition metal oxides depends on both the contact area of the reacting particles and their mobility through the early ferrite film [12–20].

The present work reports a study of the effect of addition of Al_2O_3 on manganese ferrite formation at different temperatures. The techniques employed were DTA, XRD, N_2 adsorption at −196 °C and catalysis of CO oxidation by O_2 at 350 °C over the investigated mixed solids preheated at different temperatures.

2. Experimental

2.1. Materials

Pure mixed oxide solids were prepared by impregnating equimolar proportions of manganese nitrate tetrahydrate and α-Fe_2O_3, then dried and subjected to thermal treatment in air at 700–1000 °C for 6 h. Three doped mixed solid samples were obtained by treating known amounts of both manganese nitrate tetrahydrate and α-Fe_2O_3 with calculated amounts of aluminum nitrate non-hydrate dissolved in the minimum amounts of distilled water then dried and calcined in air at 700–1000 °C. The amounts of aluminum, expressed as Al_2O_3, were 0.32, 0.64 and 1.27 wt.%. All the employed chemicals were of analytical grade and supplied by Fluka company.

2.2. Techniques

Differential thermal analysis (DTA) of the various specimens was carried out using Perkin-Elmer thermal analysis apparatus. The rate of heating was kept at $10\,^{\circ}C\,min^{-1}$ and the mass of solid specimen was 40 mg in each run. The measurements were carried out in a current of N_2 flowing at a rate of $50\,cm^3\,min^{-1}$.

An X-ray investigation of the different mixed solids preheated in air at 700, 800, 900 and 1000 °C was carried out using a Philips diffractometer (type PW 1390). The patterns were run with Fe Kα radiation at 36 kV and 16 mA with scanning speed in 2θ of $2^{\circ}\,min^{-1}$.

The specific surface area (S_{BET}) of different mixed solids precalcined at 700–1000 °C were determined from N_2 adsorption isotherms at −196 °C by using a conventional volumetric apparatus. Before carrying out the measurements, each sample was degassed under a reduced pressure of 10^{-5} Torr at 150 °C for 3 h.

The catalytic activity of pure and doped mixed solids preheated in air at 700–1000 °C was estimated by following the kinetics of CO oxidation by O_2 at 350 °C over each solid by using a static method and a stoichiometric mixture of CO and O_2 at a pressure of 2 Torr. The product of the catalytic oxidation (CO_2) was removed from the reaction mixture by freezing in a liquid-nitrogen trap. A 400 mg of fresh catalyst sample was employed for each catalytic experiment. The carbon monoxide and oxygen gases were produced via the dehydration of formic acid by concentrated H_2SO_4 and thermal decomposition of $KMnO_4$, respectively. These gases were purified by passing them through KOH solution and over P_2O_5.

3. Results

3.1. Thermal behavior of pure and alumina-doped manganese nitrate/ferric oxide

The differential thermal analysis curves of pure and different doped mixed solids are given in Fig. 1. Three sets of endothermic peaks were observed in the DTA curves of various mixed solids, the first set of peaks is weak and broad, locating at 50 °C. The second set of peaks is strong and sharp, having maximum at 300 °C. The third set of peak is weak and broad extending between 800 and 950 °C. The first set of peaks correspond to the desorption of physisorbed water of manganese nitrate tetrahydrate. The strong endothermic peaks at 300 °C indicate a complete thermal decomposition of both the employed manganese and aluminum nitrates into Mn_2O_3 and Al_2O_3, respectively, with simultaneous formation of nitrogen oxides. The last set of peaks for pure and doped mixed might indicate solid–solid interaction between the thermal products

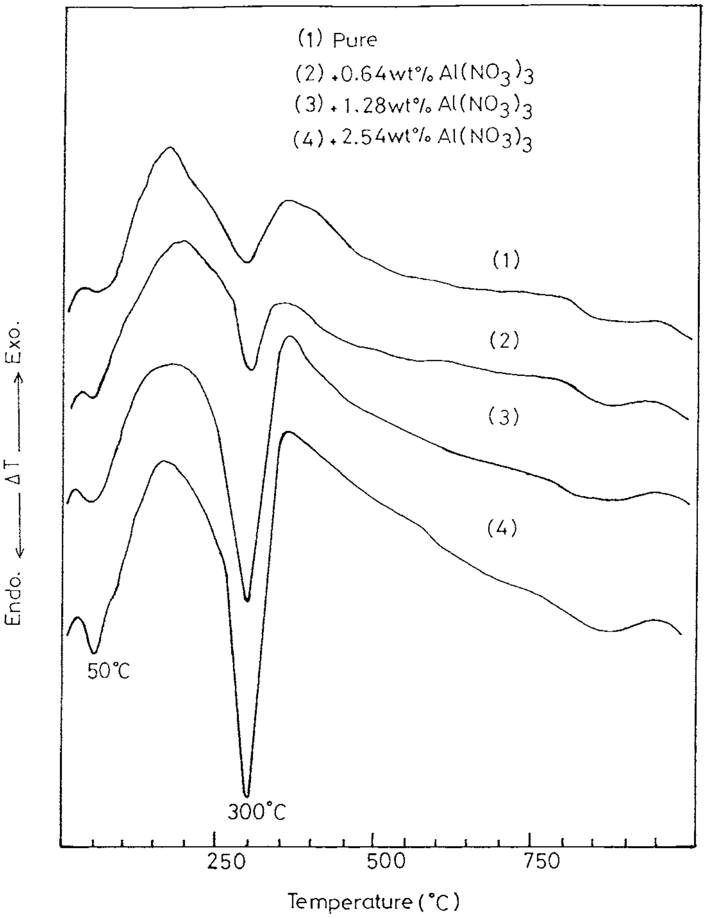

Fig. 1. DTA curves of equimolar proportions of manganese nitrate and α-Fe_2O_3 and those treated with various amounts of aluminium nitrate.

of manganese/iron mixed solids and/or transformation process of one of the produced product.

Since the weight of pure and doped mixed solids was constant in each DTA run, the area of various endothermic peaks for the different solids could be looked as a measure of the amount of solid undergoing a chemical change. Inspection of the DTA curves of the different investigated solids are given in Fig. 1 and reported that addition of the increasing amounts of aluminum nitrate led to an increase in the area of all investigated peaks to an extent proportional to the amount of $Al(NO_3)_3$. This indicates an increase in the amount of physisorbed water and stimulation of the thermal decomposition of manganese nitrate in the presence of aluminum nitrate. However, alumina-treatment brought about an increase of solid–solid interaction between Mn/Fe mixed oxide solids and/or phase transformation process of one of the resulted products. These findings will be confirmed later by XRD measurements.

3.2. X-ray investigation of the thermal products of pure and Al_2O_3-doped mixed solids

The crystalline phases of pure and doped mixed solids precalcined at different temperatures were determined from XRD measurements. XRD investigation revealed that the ferric oxide solid employed in the present investigation consisted entirely of the well-crystallized α-Fe_2O_3 and remained thermally stable even by firing in air at 1000 °C. The thermal treatment of pure manganese/iron mixed solids in air at 700 °C did not conduct any solid–solid interaction between ferric and manganese oxides as indicated from the XRD investigation which showed the presence of well-crystallized Mn_2O_3 (Partridgeite) and α-Fe_2O_3 phases only at 700 °C. On the other hand, new diffraction lines beside those of Mn_2O_3 and α-Fe_2O_3 phases were detected in the patterns of pure mixed solids precalcined at 800–1000 °C. The newly detected lines characterize the manganese ferrite ($MnFe_2O_4$, Jacobsite) spinel phase.

X-ray diffractograms of pure and doped mixed solids preheated in air at 700, 800, 900 and 1000 °C are given in Figs. 2–5. Inspection of these figures revealed that: (i) Solid–solid interaction between α-Fe_2O_3 and Mn_2O_3 to produce $MnFe_2O_4$ takes place at temperatures starting from 800 °C. (ii) The addition of small amount of dopant oxide (0.32 wt.% Al_2O_3) followed by heating at 700 °C resulted in an early formation of manganese ferrite. (iii) The augmentation in the calcination temperature of various mixed solids up to 1000 °C led to an important increase in the amount of $MnFe_2O_4$ produced with subsequent decrease in the extent of both the unreacted portions of α-Fe_2O_3 and Mn_2O_3. (iv) Al_2O_3-doping enhanced the formation of manganese ferrite to an extent proportional to the amount of dopant oxide added. The presence of 1.27 wt.% Al_2O_3 in the mixed solids preheated at 1000 °C resulted in complete conversion of ferric and manganese oxides into manganese ferrite. (v) The aluminum oxide treatment resulted in a small shift in the position of diffraction lines of the investigated oxides precalcined at different temperatures.

The enhancement effect of alumina-doping in manganese ferrite formation is better investigated by comparing the peak height of some diffraction lines characterized for α-Fe_2O_3, Mn_2O_3 and $MnFe_2O_4$ phases. This conclusion is reached from the fact that all diffraction lines of various phases are sharp and only their relative intensity (I/I_0) alter by changing both the extent of Al_2O_3 added and precalcination temperature of the investigated solids. The relative intensity of key-lines or characteristic lines of manganese ferrite and those of unreacted α-Fe_2O_3 and Mn_2O_3 are located at '*d*' spacing of 2.56, 2.69 and 2.72 Å, respectively. The choice of these lines is based on the fact that they are not in common with the diffraction lines of α-Fe_2O_3, Mn_2O_3 and $MnFe_2O_4$ phases.

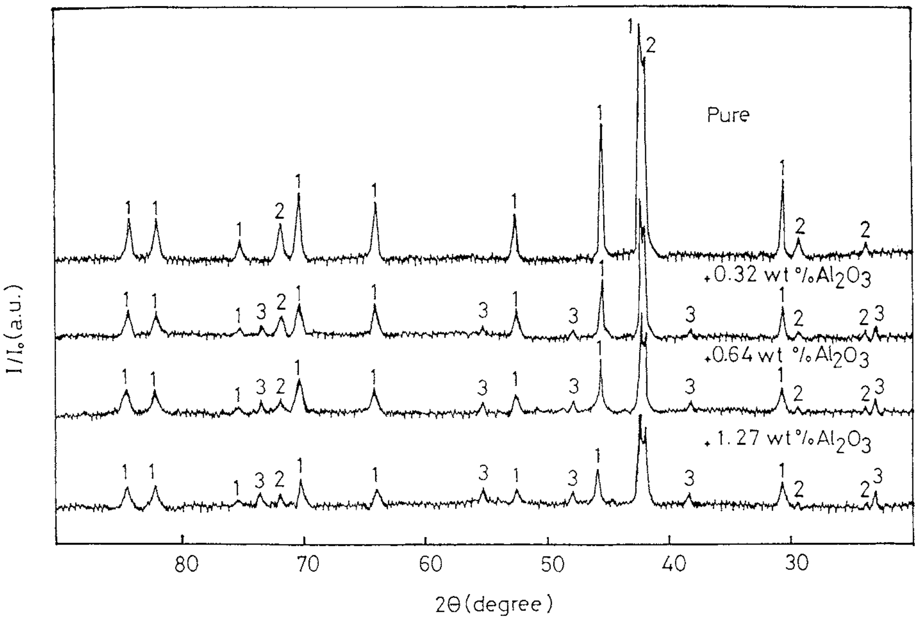

Fig. 2. X-ray diffractograms of Mn/Fe mixed oxide solids precalcined at 700 °C. Lines (1) α-Fe_2O_3, (2) Mn_2O_3 [Partridgeite], and (3) $MnFe_2O_4$.

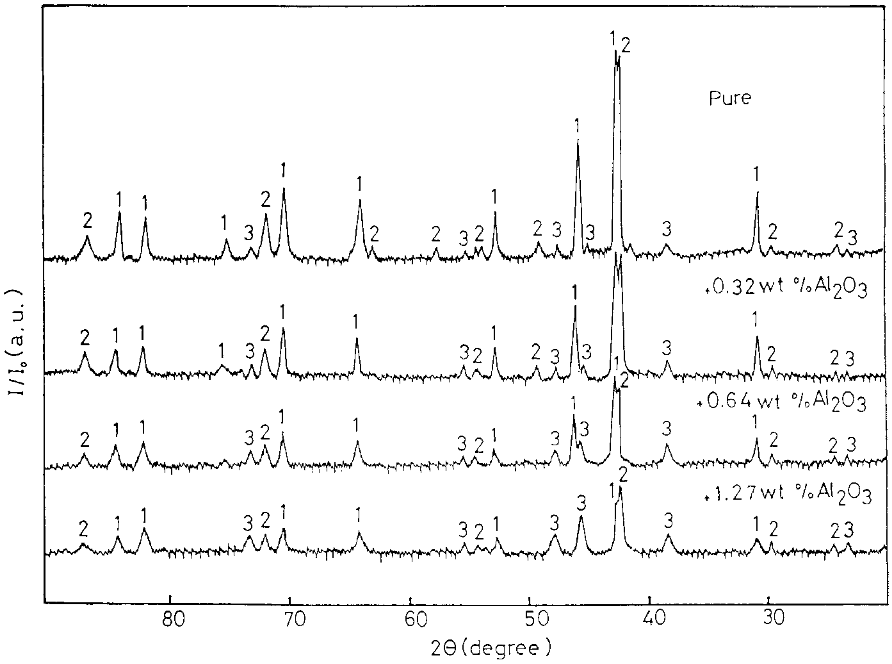

Fig. 3. X-ray diffractograms of Mn/Fe mixed oxide solids precalcined at 800 °C. Lines (1) α-Fe_2O_3, (2) Mn_2O_3 [Partridgeite], and (3) $MnFe_2O_4$.

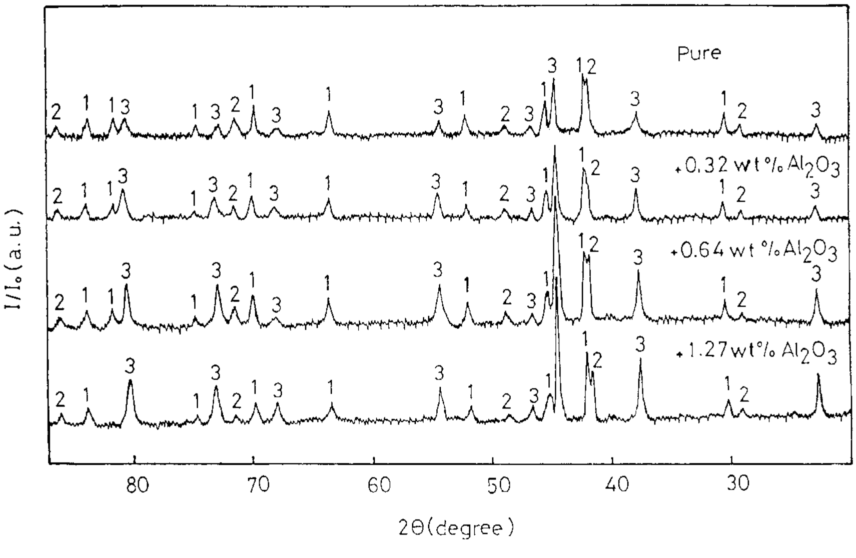

Fig. 4. X-ray diffractograms of Mn/Fe mixed oxide solids precalcined at 900 °C. Lines (1) α-Fe_2O_3, (2) Mn_2O_3 [Partridgeite], and (3) $MnFe_2O_4$.

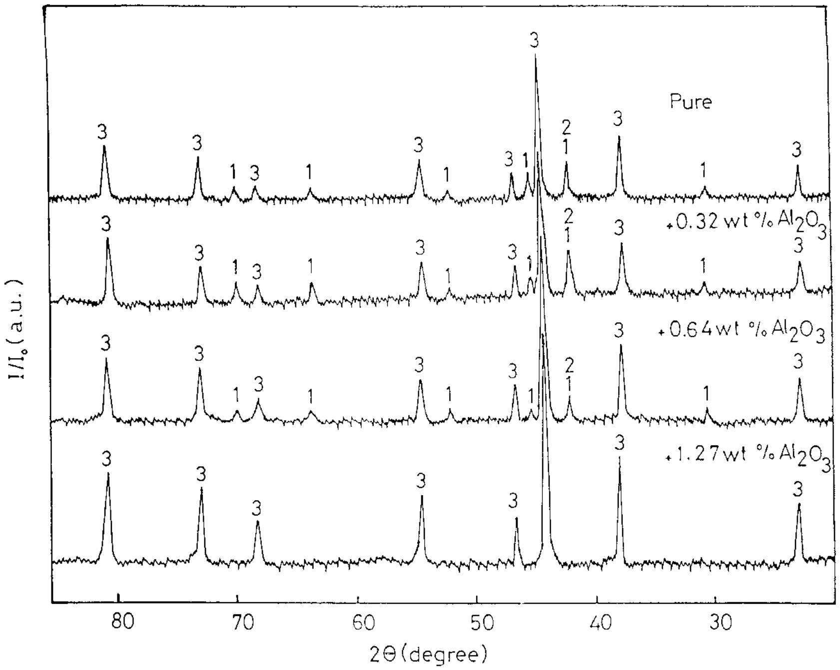

Fig. 5. X-ray diffractograms of Mn/Fe mixed oxide solids precalcined at 1000 °C. Lines (1) α-Fe_2O_3, (2) Mn_2O_3 [Partridgeite], and (3) $MnFe_2O_4$.

The peak heights of some diffraction lines of α-Fe_2O_3 (d = 2.69 Å), Mn_2O_3 (d = 2.72 Å) and $MnFe_2O_4$ (d = 2.56 Å) phases for pure and variously doped mixed solids precalcined at 800, 900 and 1000 °C were determined and given in Table 1. This table suggests that Al_2O_3-doping much enhances the conversion of Mn_2O_3 into $MnFe_2O_4$ via a solid–solid interaction with α-Fe_2O_3 at different temperatures. In addition, the thermal treatment of the mixed solid sample doped with 1.27 wt.% Al_2O_3 at 1000 °C for

Table 1

Effect of Al_2O_3-doping on the heights of some diffraction lines of α-Fe_2O_3, Mn_2O_3 and $MnFe_2O_4$ phases for Mn/Fe mixed oxide solids precalcined at various temperatures

Dopant concentration (wt.%)	Calcination temperature (°C)	Peak height (a.u.)		
		α-Fe_2O_3 (2.69 Å; 100%)	Mn_2O_3 (2.72 Å; 100%)	$MnFe_2O_4$ (2.56 Å; 100%)
0.00	800	136	135	12
0.32	800	84	84	18
0.64	800	60	52	26
1.27	800	44	40	37
0.00	900	36	36	46
0.32	900	30	26	68
0.64	900	25	20	85
1.27	900	15	12	102
0.00	1000	28	28	144
0.32	1000	20	16	150
0.64	1000	10	8	186
1.27	1000	0	0	199

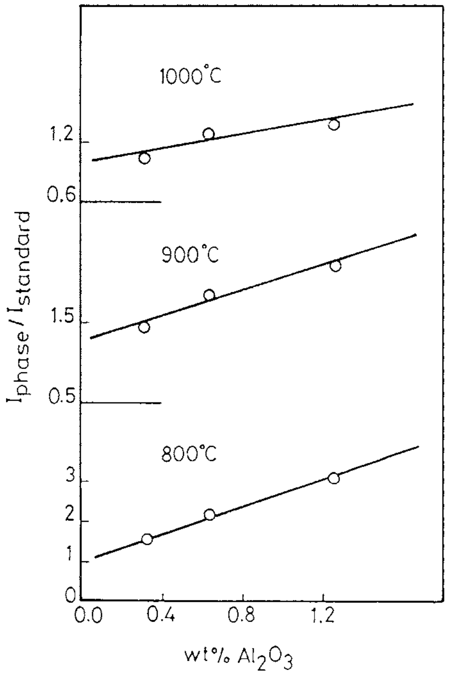

Fig. 6. Variation of $I_{phase}/I_{standard}$ for the solids calcined at various temperatures against the amount of Al_2O_3.

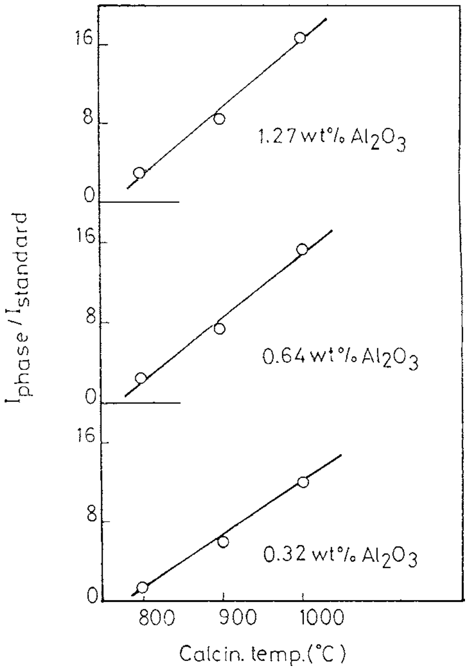

Fig. 7. The relationship between $I_{phase}/I_{standared}$ and calcination temperatures for the doped solids.

6 h led to the disappearance of the unreacted portions of both α-Fe_2O_3 and Mn_2O_3 phases. However, the change of $I_{phase}/I_{standard}$ (the ratio between the peak height of the lines at "*d*" spacing of 2.56 Å relative to manganese ferrite phase for pure mixed solids and those treated with Al_2O_3) is plotted versus both the precalcination temperature and the amount of dopant added to the mixed solids and is shown in Figs. 6 and 7. It is seen from these figures that the increase in both the amount of dopant added and the heat treatment of various solids investigated resulted in a progressive increase in the value of $I_{phase}/I_{standard}$ indicating a progressive increase in the extent of produced $MnFe_2O_4$ phase.

3.3. Surface areas of variously doped solids

The BET-surface areas (S_{BET}) of variously doped Mn_2O_3/Fe_2O_3 mixed solids precalcined at 700–1000 °C were determined from nitrogen adsorption isotherms measured at −196 °C. The values of S_{BET} for various mixed solids preheated in air at 700–1000 °C are given in Table 2. It is seen from this table that Al_2O_3-treatment of Mn_2O_3/Fe_2O_3 mixed solids followed by calcination at 700–1000 °C resulted in significant decrease in their BET-surface areas to an extent proportional to the amount of aluminum oxide added. The maximum decrease in the S_{BET} of Mn/Fe mixed oxide solids due to doping with 1.27 wt.% Al_2O_3 attained 53% for the sample precalcined at 1000 °C. The decrease in the S_{BET} of mixed oxide solids due to doping with Al_2O_3 at 700–1000 °C could be attributed to the sintering process. The sintering process might take place according to the collapse of the pore structure and/or grain growth process together with possible phase transformation [21]. Phase transformation which predominates at high temperatures (700–1000 °C) is a major factor leading to a considerable decrease in the surface area. The confirmation of this speculation finds a support from XRD measurements which showed that the thermal treatment and/or Al_2O_3-doping of Mn/Fe mixed oxides enhanced the formation of manganese ferrite. The conversion of α-Fe_2O_3 into $MnFe_2O_4$ via a

Table 2
Effect of Al_2O_3-treatment on both surface area (S_{BET}) and specific catalytic activity ($\bar{k}$) for Mn/Fe mixed oxide solids precalcined at different temperatures

Dopant concentration (wt.%)	Calcination temperature (°C)	S_{BET} ($m^2\,g^{-1}$)	$\bar{k} \times 10^{-4}$ ($min^{-1}\,m^{-2}$)	Calcination temperature (°C)	S_{BET} ($m^2\,g^{-1}$)	$\bar{k} \times 10^{-4}$ ($min^{-1}\,m^{-2}$)
0.00	700	50	15	900	34	9
0.32	700	45	11	900	28	5
0.64	700	35	7	900	22	4
1.27	700	30	5	900	20	2
0.00	800	41	12	1000	26	6
0.32	800	37	8	1000	21	3
0.64	800	29	6	1000	19	2
1.27	800	23	3	1000	17	1

solid–solid interaction with Mn_2O_3 might be accompanied by decrease in the S_{BET} of the treated system. Similar results have been reported that the abrupt decrease in the S_{BET} of V_2O_5–Al_2O_3 system due to the calcination at 400–750 °C could be attributed to the formation of the spinel structure of VAl_2O_4 [22].

The data of S_{BET} measured for the pure and doped mixed oxides calcined at different temperatures allow the calculation of the apparent activation energy of sintering (ΔE_s) by plotting $\log S_{BET}$ versus $1/T$ adopting direct application of the Arrhenius equation [23]. The slopes of the plots obtained allow determination of the values of ΔE_s which were 33, 29, 25 and 22 kJ mol^{-1} for pure and mixed oxides treated with 0.32, 0.64 and 1.27 wt.% Al_2O_3, respectively. These results clearly indicate that ΔE_s decreases considerably by increasing the amount of Al_2O_3 added. In other words, Al_2O_3-doping facilitates the sinterability of the treated solids to an extent proportional to the amount of Al_2O_3 present. These results offer an evidence for the promotion effect of Al_2O_3-doping in the manganese ferrite formation.

3.4. *Catalytic activity of pure and doped mixed solids*

Catalytic activity of pure and doped mixed solids preheated at 700–1000 °C was determined for each solid specimen via oxidation of CO by O_2 at 400 °C under a static conditions. A 400 mg of each solid sample activated by heating at 400 °C under a reduced pressure ($P = 10^{-6}$) for 2 h before carrying out the catalytic reaction. The results showed that the catalytic reaction proceeds according to a first-order law. The plots of $\log P^o/P$ (P^o initial pressure of the reacting gases $CO+1/2O_2$, and P the pressure at time t) against time t enabled the calculation of the reaction rate constant (k) for each catalyst sample by calculating the slopes of these plots. The magnitude of k stands for the catalytic activity of each solid. In order to account for the decrease in the S_{BET} of different catalyst samples, the reaction rate constant per unit surface area ($\bar{k}$) was calculated and the data obtained are given in Table 2. This table shows that the specific catalytic activity ($\bar{k}$) decreases progressively as a function of both amount of Al_2O_3 added and precalcination temperature of the investigated solids. The maximum decrease in the specific catalytic activity due to doping with 1.27 wt.% Al_2O_3 followed by calcination at 700, 800, 900 and 1000 °C attained 66, 75, 78 and 83%, respectively. The rise in the calcination temperature from 700 to 1000 °C brought about a decrease of 2.5, 3.7, 3.5 and 5-folds in the $\bar{k}$ for pure and mixed oxides treated with 0.32, 0.64 and 1.27 wt.% Al_2O_3, respectively.

Free Mn_2O_3 and Fe_2O_3 are active solids for the catalysis of CO oxidation by O_2 [12]. These solids exhibit higher catalytic activity than manganese ferrite [12]. So, the conversion of Mn_2O_3 and Fe_2O_3 into $MnFe_2O_4$ is expected to be followed by a decrease in the catalytic activity of the mixed oxides. Consequently, the observed decrease in the values of $\bar{k}$ due to doping and/or raising of the calcination temperature of the tested solids could be attributed to the formation of manganese ferrite. In other words, the observed decrease in the values of $\bar{k}$ of the investigated solids could be taken as a measure for the propagation of the solid–solid interaction between Mn_2O_3 and Fe_2O_3 yielding $MnFe_2O_4$. These results offer a further evidence for the role of alumina-doping in stimulating the ferrite formation.

4. Discussion

Manganese ferrite can be prepared via solid–solid interaction between Mn_2O_3 and Fe_2O_3 [12,20]. The propagation of this reaction is controlled by thermal diffusion of manganese and ferric cations through the ferrite film which covers the surfaces of grains of reacting oxides and acts as energy barrier. In addition, the precursor compounds employed to prepare the manganese ferrite have some effects on solid–solid reaction between ferric and manganese oxides. The results obtained in the present work revealed that solid–solid interaction between Fe_2O_3 and Mn_2O_3 resulted from the manganese nitrate took place at temperature starting from 800 °C instead of 900 °C when the manganese carbonate is used as precursor compound in our last investigation [20]. In other words, the use of manganese nitrate as precursor is promising route for manganese ferrite preparation due to an early formation of the produced ferrite as a result of increasing of the contact area of the reacting particles [13]. The fact that the increase in the temperature of heat treatment of Mn/Fe mixed oxides in the range of 700–1000 °C for 6 h brought about an increase in the extent of $MnFe_2O_4$ phase. Moreover, the heating of manganese and iron oxides at 1000 °C for 6 h was not sufficient to effect the complete conversion of the reacting oxides into $MnFe_2O_4$, indicating the necessity of prolonged heating either calcination at temperature above 1000 °C or doping with small amounts of foreign oxides. It has been reported in our last investigation that Li_2O-doping Mn_2O_3 favors its solid–solid interaction with α-Fe_2O_3 to give manganese ferrite [20]. Indeed, the addition of small amount of Al_2O_3 to the reacting solids followed by heating at 700–1000 °C brought about a progressive decrease in the peak height of unreacted oxides with subsequent increase in that of the produced ferrite and also an increase in the value of $I_{\text{phase}}/I_{\text{standard}}$ to an extent proportional to the amount of Al_2O_3 present, indicating an increase in the amount of produced $MnFe_2O_4$ phase. However, the presence of 1.27 wt.% Al_2O_3 in the mixed solids preheated at 1000 °C resulted in complete conversion of ferric and manganese oxides to manganese ferrite. These results clearly indicate the role of Al_2O_3 as an effective material in stimulating the solid–solid interaction between Mn_2O_3 and Fe_2O_3 to yield $MnFe_2O_4$ phase. The enhanced formation of ferrite phase due to the treatment with alumina could result from an induced increase in the concentration of the reacting species and/or increasing their mobility. Similar results have been reported that Li_2O-doping much enhances the solid–solid interaction between Mn_2O_3 and α-Fe_2O_3 to yield $MnFe_2O_4$ [20]. Aluminum oxide can be dissolved in the lattice of each of Fe_2O_3 and Mn_2O_3 at convenient temperatures because of similarity of the ionic radii of Al^{3+}, Mn^{3+} and Fe^{3+} ions. The dissolution of Al^{3+} ions in the lattices of Mn_2O_3 and Fe_2O_3 solids can proceed via substitution of some of host Mn^{3+} or Fe^{3+} ions and also by location in interstitial positions forming solid solution. The substitution process can be simplified by the use of Kröger's notion [24] according to:

$$\tfrac{3}{2}Al_2O_3 \rightarrow 3Al(Mn^{3+}) + C.V.$$

$$\tfrac{3}{2}Al_2O_3 \rightarrow 3Al(Fe^{3+}) + C.V.$$

$Al(Mn^{3+})$ and $Al(Fe^{3+})$ are trivalent aluminum ions located in the positions of host cations Mn^{3+} and Fe^{3+} of Mn_2O_3 and Fe_2O_3 lattices, and C.V. is cationic vacancy. These reactions indicate that the dissolution of $3Al^{3+}$ ions in the lattice of Mn_2O_3 or Fe_2O_3 is followed by creation of one cationic vacancy in each doped solid.

The location of Al^{3+} ions in interstitial position of Mn_2O_3 lattice is normally followed by transformation of some of the host Mn^{3+} ions into Mn^{2+} ions according to:

$$Al_2O_3 + 2Mn^{3+} \rightarrow 2Al_{\blacktriangle} + 2Mn^{2+} + \tfrac{1}{2}O_2(g)$$

$Al_{\blacktriangle}$ is trivalent aluminum ion retained in an interstitial position in Mn_2O_3 lattice. The substitution of some host Mn^{3+} and Fe^{3+} by Al^{3+} ions resulted in creation of cationic vacancies in both Mn_2O_3 and Fe_2O_3 lattices leading to an increase in the mobility of the reacting cations (Mn^{2+} and Fe^{3+}) which contribute directly in the formation of $MnFe_2O_4$ spinel. The location of Al^{3+} ions in interstitial position of Mn_2O_3 lattice brought about an increase of the concentration of the reacting particles. Increasing of the concentration and/or the mobility of reacting species seems to be responsible for the observed enhanced effect of Al_2O_3 in the formation of manganese ferrite spinel. This speculation can be investigated via determination of the activation energy (ΔE) of the formation of $MnFe_2O_4$ phase at temperatures between 800 and 1000 °C for pure and doped mixed solids. This has been tentatively achieved from the results given in Table 1, assuming that the height of the characterized diffraction lines at 3.01, 2.56 and 2.12 Å are a measure of the amount $MnFe_2O_4$ present in a given mixed solids at a definite temperature T. This assumption is based on the fact that the diffraction lines of produced $MnFe_2O_4$ phase are sharp for the investigated solids precalcined at 800–1000 °C. In other words, the rise in precalcination temperature and/or the amount of Al_2O_3 added did not improve the degree of crystallinity of produced ferrite phase but increased its amount. The values of ΔE are determined from the slopes of straight lines for plots of the peak height of one previously line versus $1/T$ via direct application of the Arrhenius equation. This test has been successfully done at 800, 900 and 1000 °C, and the plots obtained are given in Fig. 8. The computed values of ΔE obtained from the diffraction line at 'd' spacing of 2.56 Å are 138, 120, 105 and 92 kJ mol^{-1} for pure mixed solids and those doped with 0.32, 0.64 and 1.27 wt.% Al_2O_3, respectively. These values indicate that aluminum-doping decrease the activation energy of manganese ferrite formation to an extent proportional to the amount of aluminum nitrate added. The maximum decrease in the values of ΔE due to doping with 1.27 wt.% Al_2O_3 attained 33%. This decrease in ΔE values due to the doping process might reflect an effective increase in the mobility of reacting cations through both, whole of the reacting oxides and the early-produced manganese ferrite film.

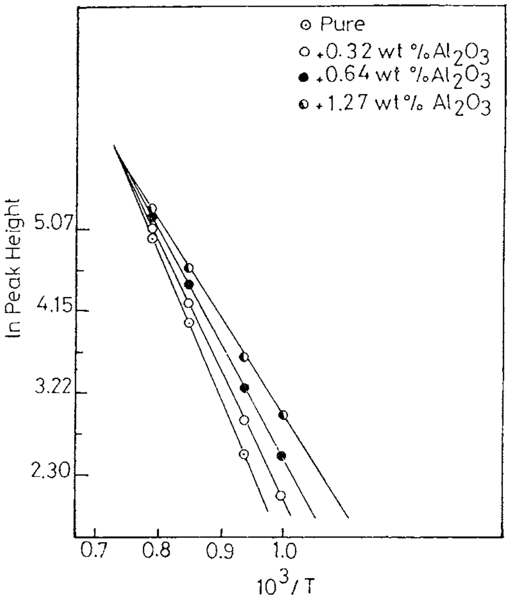

Fig. 8. Change of ln peak height of the diffraction line of $MnFe_2O_4$ (2.56 Å) as a function of $1/T$ of pure and doped mixed oxide solids.

5. Conclusions

These are the main conclusions that can be derived from the experimental results:

1. The aluminum oxide doping was found to stimulate the solid–solid interaction between α-Fe_2O_3 and Mn_2O_3 to produce $MnFe_2O_4$ at temperatures starting from 700 °C instead of 800 °C in case of pure oxides. However, the treatment with 1.27 wt.% Al_2O_3 followed by heating at 1000 °C brought about complete conversion of Mn/Fe oxides into manganese ferrite.
2. Observing the peak height of diffraction line at 2.56 Å followed the formation of $MnFe_2O_4$ phase. The decrease in the extent of the unreacted portions of Mn_2O_3 and α-Fe_2O_3, taken as a measure of formation of manganese ferrite, was followed by observing the peak height of certain diffraction lines at 2.72 and 2.69 Å, respectively. The rise in both, the amount of Al_2O_3 added and precalcination temperature of mixed oxides were found to an increase amount of manganese ferrite to extent proportional to calcination temperature and dopant oxide content.
3. Increasing both the precalcination temperature and the amount of Al_2O_3 added decreased the specific surface area and catalytic activity of pure and doped solids. This decrease can be taken also as measure of manganese ferrite formation.
4. The stimulating effect of Al_2O_3-doping in $MnFe_2O_4$ formation was attributed to an increase in the mobility of the reacting cations due to creation of cationic vacancies in the doped Mn/Fe mixed oxide solids.

5. The activation energy of formation of $MnFe_2O_4$ was determined for pure and Al-doped mixed solids and found to be 138, 120, 105 and 92 kJ mol^{-1} for pure mixed solids and those treated with 0.32, 0.64 and 1.27 wt.% Al_2O_3, respectively.

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