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QUANTITATIVE ANALYSIS BY DERIVATIVE THERMOGRAVIMETRY OF OXIDIZABLE CATIONS FOR FINELY-DIVIDED MANGANESE SUBSTITUTED MAGNETITES

M. LAARJ[1], I. PIGNONE[1], M. EL GUENDOUZI[1], P. TAILHADES[2], A. ROUSSET[2], and B. GILLOT[1].

[1]Faculté des Sciences Mirande, Laboratoire sur la Réactivité des Solides,
associé au C.N.R.S., U.A. 23, B.P. 138, 21004 DIJON CEDEX.

[2]Laboratoire de Chimie des Matériaux Inorganiques, Université Paul Sabatier,
Toulouse III, 118, route de Narbonne, 31062 TOULOUSE CEDEX.

SUMMARY

A quantitative analysis of cations is presented for finely divided manganese substituted magnetites containing several oxidizable cations. This analysis is based on the difference of reactivity of iron and manganese cations in relation to occupied sites (octahedral or tetrahedral) and is achieved from the determination of oxidation peaks areas obtained by derivative thermogravimetry (DTG). Examples of this quantitative analysis are reported to study reactivity versus time dependence or crystallite size.

INTRODUCTION

During a detailed study on the reactivity of several finely grained magnetites substituted by divalent, trivalent or tetravalent ions (1-3), it was found that these mixed oxides, whose crystallite sizes are less than about 200 nm could be oxidized to metastable defect γ-phases with the same spinel structure. In a recent paper we pointed out (4) that the oxidation rate of octahedral site (B-site) Fe^{2+} ions is greater than that of tetrahedral site (A-site) Fe^{2+} ions because of the weaker ionic bonding of the B-site as compared with the stronger A-site covalent bond. From very precise thermogravimetric (TG) measurements, this discrepancy of reactivity has been used to determine the iron cation distribution between the sublattices (4) in divided titanomagnetites $(Fe^{3+}_{2-2x}Fe^{2+}_{1+x}Ti^{4+}_{x})O^{2-}_{4}$ $(0 < x < 1)$. This approach has been possible as titanium exists solely in the Ti^{4+} state and only on the octahedral site. For manganese substituted magnetites $(Mn^{2+}_{0.8x}Fe^{3+}_{2-0.2x}Fe^{2+}_{1-0.8x}Mn^{3+}_{0.2x})O^{2-}_{4}$ where three cations are oxidized (Fe^{2+} and Mn^{3+} ions on B-sites and Mn^{2+} ions on A sites) it was also found from derivative thermogravimetric (DTG) studies (5) that the availability for oxidation of Fe^{2+} and Mn^{3+} ions on B site is greater than that of an A-site Mn^{2+} ions. However, in this case to determine the distribution of oxidizable cations in A and B sites of the spinel structure, it is necessary to gain a fundamental understanding of the effect of their distribution between B

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and A site on the oxidation characteristics.

As a contribution to this goal, a quantitative analysis of cations from the determination of oxidation peaks areas obtained by derivative thermogravimetry has been investigated. When considering some general factors affecting the reactivity as the tendency for oxidation in air at room temperature, the influence of crystallite sizes on oxidation mechanism or the presence of Mn ions which leads to oxidation-reduction phenomena, it becomes possible from quantitative analysis to make a systematic study of the oxidation process in relation to the nature, charge and position of cations in spinel lattice. Until now, among the analytical methods proposed for quantitative analysis of ferrous ions in iron oxides, the electrochemical method seems the most adequate. It has specially been used to evaluate the nonstoichiometry of Fe_2O_3, Fe_3O_4 and FeO inserted in carbon paste electrode (6) and to dose Fe^{2+} and Fe^{3+} ions in FeO,Fe_2O_3 spinel resulting from FeO decomposition below 540°C (7). Recently Lenglet et al. (8) have also reported the analysis of the X-ray absorption line to characterize the oxidation states in several manganese spinel oxides.

SAMPLES AND EXPERIMENTAL METHOD

Samples

The preparation conditions of finely-grained manganese substituted magnetites have already been reported (2). The thermal decomposition of mixed iron manganese oxalates leads, through appropriate thermal treatments at low temperature (< 500°C), to the solid solutions $Fe_3O_{4(1-x)}MnFe_2O_{4x}$ $(0 < x < 1)$. Although several models have been proposed for the distribution of manganese cations (9,10) a first structural investigation by radiocrystallographic analysis (2) indicated that the distribution at room temperature can be formulated as follows :

$$(Mn^{2+}{}_{0.8x}\ Fe^{3+}{}_{1-0.8x})_A(Fe^{3+}{}_{1+0.6x}\ Fe^{2+}{}_{1-0.8x}\ Mn^{3+}{}_{0.2x})_B\ O_4^{2-}$$

with the totality of Mn^{2+} ions on A-sites and a small amount of Mn^{3+} ions on B-sites.

Crystallite size measurements by electron microscopy and from specific surface areas show that the samples consist of almost spherical grains of average 30 nm. Much annealing on original spinel were carried out to study the influence of crystallite size on oxidation process.

Measurements

The samples were oxidized in a Setaram MTB 10-8 microbalance at a constant rate of 2.5°C min^{-1} from 20 to 700°C. The material weighed 6 mg and the powder was spread out so that it would be oxidize in the same way as N independent particles of equal mean radius. Before every reaction, great care had to be taken while degassing to ensure that the powder was not even partly oxidized. This necessitated a vacuum of $< 10^{-4}$ Pa and a very slow temperature rise so that no weight change occurredduring the heating period.

RESULTS AND DISCUSSION

Behavior in air of Mn-substituted magnetites and quantitative analysis of oxidizable cations

An example of the use of TG for the determination of oxidation characteristics in air is shown in Fig. 1 when three regions can be distinguished.

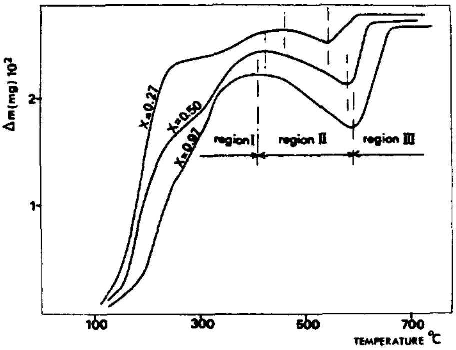

Fig. 1. TG curves for manganese substituted magnetite heated in air at 2.5°C min^{-1}.

As already reported (5), in region I the weight gain is due to total oxidation of Fe^{2+} (about 200°C) and Mn^{3+} (about 270°C) on B-sites and an incomplete oxidation of Mn^{2+} into Mn^{3+} ions (about 350°C) on A-sites. Above 400°C, the compound loses weight (region II) which corresponds to the reduction of Mn^{4+} to Mn^{3+} ions. For the two regions, X-ray diffraction shows a single phase spinel structure. Above 550°C (region III) we again have a weight gain due to oxidation of Mn^{2+} ions that were not completely oxidized at a lower temperature. This oxidation is accompanied by a phase change from a spinel to a corundum structure.

Quantitative analysis from DTG curves in region I

The effect of the distribution of Fe^{2+}, Mn^{3+} and Mn^{2+} ions between B-and A-sites and the effect of the substitution extent x below 450°C were demonstrated directly by plotting dΔm/dt against temperature (curves a, b, c, Fig. 2). However, as the peaks obtained exhibit a tendency to overlap, we have carried out a deconvolution of spectra which is based on several assumptions :

- For the first peak, we consider that in the domain of the ascending curve, one phenomenon exists, i.e. the oxidation of Fe^{2+} ions on B-sites.

- Likewise for the third peak, the descending curve may be interpreted as only due to the oxidation of Mn^{2+} ions on A-sites.

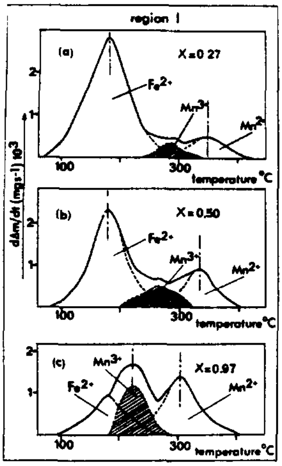

Fig. 2. DTG curves $d\Delta m/dt = f(T)$ (________) in region I and deconvolution spectra (------) of oxidation processes (Fe^{2+} and Mn^{3+} ions on B-sites and Mn^{2+} ions and A-sites).

From these assumptions, symetrical profiles for the first and third peaks can be obtained by using an axis through the top. The symetrical profile has been demonstrated elsewhere (1) during the oxidation of spinels containing solely an oxidizable cation (for example Fe^{2+}) and only located on one site (A or B). An optimum choice of the experimental conditions (amount of sample, heating rate, oxygen pressure) can in principle be used to obtain suchsymmetry. For example it is necessary to carry out the oxidation with a small amount of powder (between 4 and 6 mg) in order to avoid the heating up caused locally by the exothermicity of the reaction. The second peak (that of medium) is obtained by deconvolution from the total curve.

The results of this method are given in Fig. 2 (dotted lines for a, b, c curves) for three different manganese contents ($x = 0.27$, $x = 0.50$ and $x = 0.97$). Fig. 2 shows three separated peaks where the variation in intensity of each peak with iron and manganese contents is indicative of the quantities of Fe^{2+}, Mn^{3+} and Mn^{2+} ions within the spinel. Table 1 gives the S_i/S_0 ratios where S_i represents the area of each peak and S_0 the area of peak corresponding to pure magnetite ($x = 0$). The S_i/S_0 ratio of the first and second peak agrees well with the concentration of Fe^{2+} and Mn^{3+} ions calculated from structural formula (values in brackets). On the other hand, the S_i/S_0 value corresponding to third peak does not agree with the concentration of Mn^{2+} ions and is always lower than that calculated (Table 1) indicating an incomplete oxidation of Mn^{2+} ions.

TABLE 1

Dependance of S_i/S_o ratio and oxidation temperature of each peak on composition x in region I. The values in brackets are values calculated from structural formula.

Substitution extent x	REGION I						% Mn^{2+} oxidized
	First Peak		Second Peak		Third Peak		
	S_i / S_o	T_{ox}(°C)	S_i / S_o	T_{ox}(°C)	S_i / S_o	T_{ox}(°C)	
0.14	0.84(0.89)	180	0.01(0.03)	280	0.07(0.11)	347	64
0.27	0.78(0.78)	181	0.05(0.05)	287	0.12(0.22)	347	54
0.37	0.67(0.70)	184	0.08(0.08)	279	0.15(0.30)	344	50
0.50	0.54(0.60)	182	0.11(0.11)	260	0.18(0.40)	334	44
0.97	0.22(0.22)	180	0.19(0.19)	225)	0.35(0.78)	305	43

Table 1 also shows that the percentage of oxidized Mn^{2+} ions diminishes with increasing x and that the position of the second and third maximum shifted toward lower temperature with increasing of Mn content.

Quantitative analysis in II and III regions

The DTG curves recorded during the heating in air of Mn-substituted magnetites in region II and III are shown in Fig. 3 and the S_i/S_o ratios are listed in table 2.. It is of interest to compare the present results with those obtained for the region I.

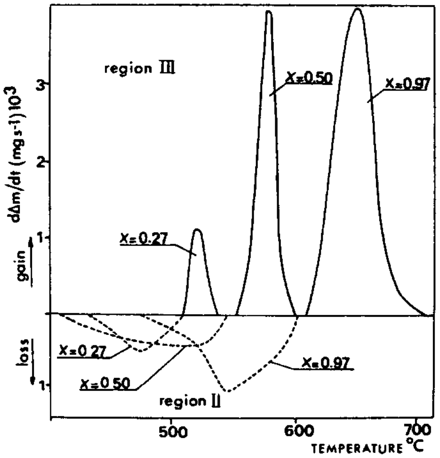

Fig. 3. DTG curves dΔm/dt = f(T) in regions II and III.

TABLE 2

Dependence of S_i/S_o ratio and oxidation temperature of fourth and fifth peak on composition x in regions II and III. The values in brackets are the values calculated from structural formula.

Substitution extent x	Region II Fourth Peak		Region III Fifth Peak		Third + Fifth Peak
	S_i/S_o	T_{ox}(°C)	S_i/S_o	T_{ox}(°C)	S_i/S_o
0.14	0.04(0.03)	480	0.03(0.11)	560	0.10(0.11)
0.27	0.06(0.05)	475	0.80(0.22)	525	0.20(0.22)
0.37	0.06(0.07)	485	0.13(0.30)	575	0.28(0.30)
0.50	0.10(0.11)	500	0.18(0.40)	580	0.36(0.40)
0.97	0.19(0.19)	550	0.40(0.78)	658	0.75(0.78)

For region II, it can be seen that the S_i/S_o ratio of the fourth peak (column 2) corresponds closely to S_i/S_o ratio of the second peak (column 4, table 1) except for x = 0.14. Thus, it is possible to assume that the amount of Mn^{4+} ions created by oxidation of Mn^{3+} ions in region I must be totally reduced to lower valency i.e. to Mn^{3+} during the reduction process in region II.

The reoxidized amount in region III was explained by examining the S_i/S_o ratio of the fifth peak (column 4) with that of third peak (column 6,table 1). Total amount of oxidized Mn^{2+} ions can be determined from the sum of the ratios of 4th(table 2) and 6th(table 1) columns. From these calculated values (column 6, table 2) it can be seen that the amount of oxidized Mn^{2+} is comparable to the concentration of Mn^{2+} ions calculated from structural formula (values inbrackets). This implies that the tetrahedral Mn^{2+} ions not completely oxidized in region I could be totally oxidized in region III. The top temperature of fourth and fifth peak slightly vary with the substitution extent x.

Influence of time and crystallite size on oxidation characteristics

Oxidation with time of freshly synthesized samples

The tendency for oxidation of Fe^{2+} ions with time is called "maghemitization" and finely divided ferrous spinels can be partially oxidized in air at room temperature (4). As the oxidation reaction at low temperature is essentially due to the absorbed oxygen ionized by the extra electron of the Mn^{2+} ions which diffuse through the solid at higher temperatures, it may be seen that for cubic crystal of about 100 nm approximately 3% of all the unit cells in each crystallite will be exposed on the exterior faces ; the rates of the earliest stage in the oxidation will be large.

It is then important to know the degree of nonstoichiometry versus time and the nature of oxidized cations in function of occupied site to reproduce the same initial state comparatively to a freshly sythesized specimen. The nature of the DTG curves of a sample stored under static air for different times is shown in figure 4 for the composition x = 0.67. Compared with a freshly prepared sample (curve 1, figure 4) the S_i/S_0 ratio of the first and second

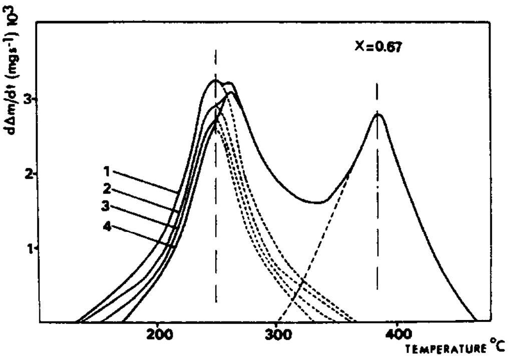

Fig. 4 DTG curves dΔm/dt = f(T) for the composition x = 0.67 and evolution with time in air at room temperature ; 1 : freshly prepared sample ; 2 : after 5 months in ambiant air ; 3 : after 14 months in ambiant air ; 4 : after 19 months in ambiant air.

peak is diminished as a result of the decrease in the amount of oxidized phase. The S_i/S_0 ratio of the third peak is unchanged. These observations indicate that the decrease of the first and second peak is associated with the oxidation of Fe^{2+} and Mn^{3+} ions when the sample was exposed during long periods at room temperature in static air which is consistent with the availability for oxidation of M^{2+} ions located on B-sites.

Influence of crystallite size

In region I, the DTG curves (figure 5) show the effect of the crystallite

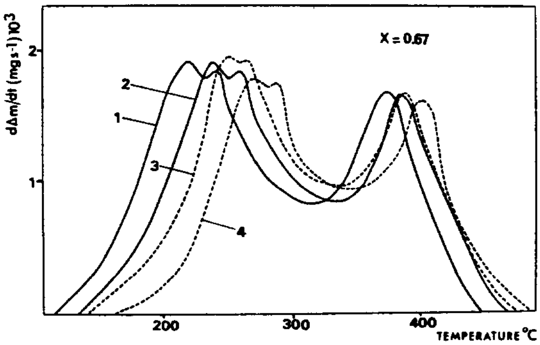

Fig. 5 DTG curves dΔm/dt : f(T) showing the influence of crystallite size on oxidation behavior ; 1 : 25 nm ; 2 : 45 nm ; 3 : 63 nm ; 4 : 78 nm.

size on the oxidation characteristics. In all cases the oxidations proceeded through three distinguishable steps with a shift of the peaks toward higher temperatures with increase in particle size (table 3). From the computer

TABLE 3

Dependence of S_i/S_o ratio and oxidation temperature of each peak on the crystallyte size in region I. The values in brackets are the values calculated from structural formula.

Crystallite size in nm	REGION I					
	First Peak		Second Peak		Third Peak	
	S_i/S_o	T_{ox}(°C)	S_i/S_o	T_{ox}(°C)	S_i/S_o	T_{ox}(°C)
25	0.47(0.46)	219	0.14(0.13)	242	0.32(0.54)	375
45	0.46	239	0.13	260	0.32	387
63	0.45	250	0.12	265	0.31	390
78	0.41	270	0.12	288	0.27	403

fitting it appeared that is only for the samples larger than 65 nm (table 3) that the area ratio has diminished with an appreciable degree suggesting a partial oxidation during the annealing although this thermal treatment results in no change in cation distribution at A- and B-sites.

In contrast, under identical experimental conditions, the region II seems much more affected by the crystallite size since for samples 65 nm and larger (column 2, table 4) the reduction step can be totally removed. In region III, the S_i/S_o ratio is not dependent on the crystallite size (column 4, table 4). These results, together with the availability for oxidation of Mn^{3+} ions in region I do support the presence of Mn^{4+} ions above 700°C for higher particle size.

TABLE 4

Dependence of S_i/S_o ratio and oxidation temperature of fourth and fifth peak on the crystallite size in regions II and III. The values in brackets are the values calculated from structural formula.

Crystallite size in nm	Region II Fourth Peak		Region III Fifth Peak		Third + Fifth Peak
	S_i/S_o	T_{ox}(°C)	S_i/S_o	T_{ox}(°C)	S_i/S_o
25	0.14(0.13)	580	0.25(0.54)	670	0.57(0.54)
45	0.12	580	0.23	650	0.55
63	0.05	570	0.22	630	0.53
78	0	570	0.23	638	0.50

CONCLUSION

The reactivity in air of finely grained manganese substituted magnetites leads to complex phenomenon associated with the charge and position of manganese ions in the spinel structure. Below 450°C the $d\Delta m/dt = f(T)$ curves shows a three stage oxidation process related to the distribution of Fe^{2+} and Mn^{3+} ions on octahedral sites and Mn^{2+} ions on tetrahedral sites. A quantitative analysis of cations from the determination of oxidation peaks areas based on this discrepancy in reactivity is thus possible and in this regard, it has been demonstrated that derivative thermogravimetry can be considered as an accurate method to determine the position and the distribution of cations. The results indicates that octahedrally sited Fe^{2+} and Mn^{3+} ions are totally oxidized whereas tetrahedrally sited Mn^{2+} ions exhibit only a partial oxidation. At higher temperature (>500°C), the quantitative analysis has established that the amount of Mn^{4+} ions formed at about 270°C is reduced to Mn^{3+} ions. It was also found that the proportion of Mn^{2+} ions unoxidized at low temperature reacted with air at about 650°C to produce Mn^{3+} ions. This study reinforces earlier conclusions that bulk reactivity of Mn-substituted magnetites is dominated by the concentration of Mn ions.

To resolve some specific problems as the oxidation in air at room temperature of freshly synthesized samples or the effect of particle size on oxidation characteristics, the quantitative analysis from DTG curves is a particularly well adopted method to take into account the general behavior of submicronic solids in controlling their degree of nonstoichiometry in ambient air associated with the possible variations in cation distribution between the inequivalent sites of the spinel structure, specially in varying crystallite size.

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