The Effects of Additives in Ferric Oxide Catalysts

I. Electrical Measurements and Electron Probe Microanalysis on Mg-Doped Ferric Oxide

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Catalysts prepared from high-purity ferric oxide (normally weakly n-type) by incorporating 0.01–2.0 at. % Mg showed p-type semiconducting properties. The catalysts were characterized by electrical measurements and by electron probe micro analysis. The variation of dc conductivity with temperature showed three well-defined regions including a plateau between 450 and 900°C. From a semiquantitative description of the mixed conduction system a linear relationship is expected between conductivities in the plateau region and the number of Mg^{2+} incorporated, and this applied up to 0.1–0.2% Mg. Seebeck voltages showed that each Mg^{2+} introduced one p-carrier up to a limit of 0.2% Mg, beyond which anomalies again appeared, although catalysts were still p-type.

Electron probe microanalysis provided clear evidence for the separation of the spinel phase, magnesium ferrite, in catalysts containing as little as 0.2% Mg confirming conclusions drawn from the electrical measurements (in air). A special study was made into the effects of firing temperature (to induce Mg incorporation) on the Seebeck voltage in ferric oxide catalysts with 0.3 or 0.5% Mg, i.e., just beyond the critical doping level.

Catalysts pellets exposed to the standard reaction mixture used for methanol conversion, or to methanol + argon mixtures, showed a large decrease in conductivity for p-type catalysts, and a smaller increase with the pure oxide, both reversed by methanol removal. The effect of grain size on the rate of conductivity change was also examined and the nature of the changes discussed with regard to electron transfer/permanent changes in the catalyst and the relative importance of surface/bulk conductivities. The use of Mg-doped ferric oxide catalysts for N_2O decomposition and for the conversion of methanol to formaldehyde is reported in Part II.

INTRODUCTION

For many years now attempts have been made to understand the catalytic activity of the metal oxides in terms of their semiconducting properties (1), e.g., the classification of the rates of N_2O decomposition or CO oxidation over a variety of oxides according to whether they are n- or p-type or insulators. Another approach has been to show that changes in electrical conductivity caused by incorporating, e.g., Li_2O or Cr_2O_3 into the lattice of nickel oxide are accompanied by changes in catalytic activity. Also changes in the number of charge carriers may occur in chemisorption and during catalytic reactions over oxides, e.g., in the dehydrogenation of ethanol and isopropanol (2). However, this approach has been less than successful with reactions involving hydrogen, e.g., H_2–D_2 exchange (3). The characteristic twin-peak activity pattern, also observed for the disproportionation and dehydrogenation of cyclohexene (4), over the oxides of the first series of transition elements has been correlated with the effects of the crystal field of these oxides on the electronic levels of the metal ions. Activity for ammonia de-

composition is not related to the difference in conductivity between Eu_2O_3 and Gd_2O_3, chosen for comparison because exchange effects are minimal (5). More recently, dilute solutions of NiO in a matrix of MgO have been studied (6), since they appear amenable to discussion in terms of the localized viewpoint.

However, it has been shown recently that ferric oxide, which is generally recognized as an n-type semiconductor, can be made p-type by incorporating small amounts of magnesium (7) and it seemed worthwhile to explore the catalytic properties of the p-type oxide because iron oxide forms the basis of various technical catalysts. The conductivity and Seebeck voltage of both very pure ferric oxide and the n-type made by the induced valency technique are also reasonably well understood (8–10). Hence a range of n-type and p-type ferric oxides is available. The re-combination of oxygen atoms has been studied over Ti- and Ca-doped ferric oxide (11).

Further, electrical measurements are apparently sensitive to the onset of magnesium ferrite formation above a certain critical doping level and the separation of the spinel structure is an important feature of some mixed oxide catalysts. A special study was made of the effect of firing temperature during the incorporation of amounts of MgO at the critical doping level, on both the electrical and catalytic properties. In addition, because of the part which the appearance of the spinel phase plays in discussing the results, direct evidence for its existence in catalyst samples was sought by electron probe microanalysis.

The catalytic reactions studied and reported upon in the following paper [Pt. II, (15)] were N_2O decomposition and the selective production of formaldehyde from methanol/air mixtures.

EXPERIMENTAL METHODS

Catalyst preparation. The electrical properties of these semiconducting oxides are sensitive to minute traces of cation impurities and considerable care must be taken to ensure that contamination will be negligible. All samples were prepared from the same batch of high-purity ferric oxide (Johnson Matthey and Co. Ltd.), made by calcining thin layers of ferrous oxalate at about 450°C. Analysis by emission spectroscopy for impurities detected only the following elements: Ag, Cu < 1; Mg, 1; Mn, Ni, 2; Si, 10 ppm. Calculated volumes of a standard dilute magnesium nitrate solution were mixed with 60-g samples of ferric oxide to give the required cation concentrations. The resultant pastes were dried, crushed and fired for 15 hr in air at 450°C to decompose the nitrate, followed by further crushing and mixing. Magnesium was then partially incorporated in the ferric oxide lattice by firing at 750°C; this temperature was still sufficiently low to leave these ferric oxide samples relatively unsintered.

Rectangular pellets were formed by compacting the powders at 26 ton in.$^{-2}$; 44 s.w.g. platinum wires and Pt/13% Rh–Pt thermocouples were embedded in some of the pellets during this stage. A series of pellets containing 0–2.0 at. % magnesium were fired in air at 1300°C for 15 hr (unless otherwise stated) and then allowed to cool slowly in the furnace. The pellets were fired on a bed of ferric oxide powder containing the same magnesium concentration to avoid possible loss of magnesium by diffusion at this high temperature. The catalyst charge for the reactor was prepared by crushing pellets and sieving out a 2–3-mm fraction. After sample preparation, no increase in the amount of impurities present was detected. Samples of magnesium ferrite were prepared by the same procedure.

Electrical measurements. The dc resistance of complete pellets ($1.5 \times 0.5 \times 0.3$ cm) was measured by a four-probe technique using the platinum wire of the two thermocouples embedded near the ends of the pellet as current leads and two fine platinum wires between them as potential probes. Voltages were measured with a high-impedance vibrating reed electrometer. The resistivity was calculated from the cross-sectional area of the pellet and the separation, 0.55 cm, of the probes.

For measurements of the Seebeck voltage a temperature difference of between 2 and

20°C was established along the pellet between the embedded thermocouples. The thermocouple voltages were measured to the nearest microvolt on a potentiometer and the Seebeck voltage developed was measured between the platinum thermocouple leads on a vibrating reed electrometer. The Seebeck voltage (μV/°C) was found by plotting the temperature difference against the voltage developed; values quoted are relative to platinum. The sign of the Seebeck voltage was taken as the sign of the platinum lead at the lower temperature and is therefore the sign of the predominant charge carrier which diffuses to the cold end of the pellet. The same techniques were used for both the basic electrical measurements in air and those made under reaction conditions.

Electron probe microanalysis. Specimens of oxide catalyst for electron probe microanalysis were prepared by polishing to a flat surface pieces of fired pellet which had been set in a plastic block. Specimens were examined in a "Geoscan" electron probe microanalyser (Cambridge Scientific Instruments Ltd.), for variations in Fe and Mg content, associated with variations in surface appearance.

RESULTS

Pure and Mg-doped ferric oxide catalysts were characterized by electrical measurements (dc conductivity and Seebeck voltage) and by electron probe microanalysis.

Electrical Properties in Air

The catalytic results reported in Pt. II (15) were obtained using catalysts with 10 different Mg-concentrations between 0 and 2.0 at. % (as well as the stoichiometric magnesium ferrite). In a number of cases, at least two entirely separate catalyst preparations for each Mg-concentration were involved and electrical measurements were made on samples from each preparation. The electrical measurements were particularly reproducible and further agreed closely with previously reported results (7) for ferric oxide with Mg-concentrations common to the present work. Electrical measurements used to characterize the catalysts refer to data for pellets which
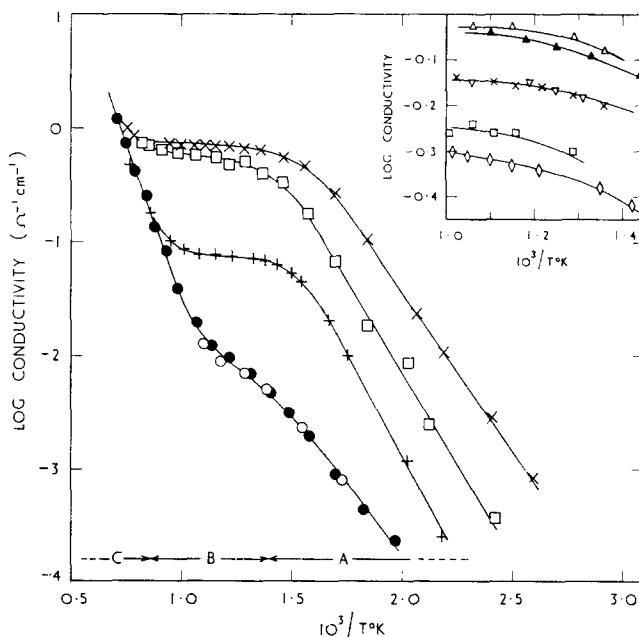

FIG. 1. Logarithm of dc conductivity in air as a function of reciprocal temperature for pure ferric oxide (○, ●) (separate preparations); ferric oxide with 0.01 at. % Mg (+); 0.1% (×); 0.2% (▲); 0.3% (△); 0.5% (▽); 1.0% (◇); 2.0% (□).
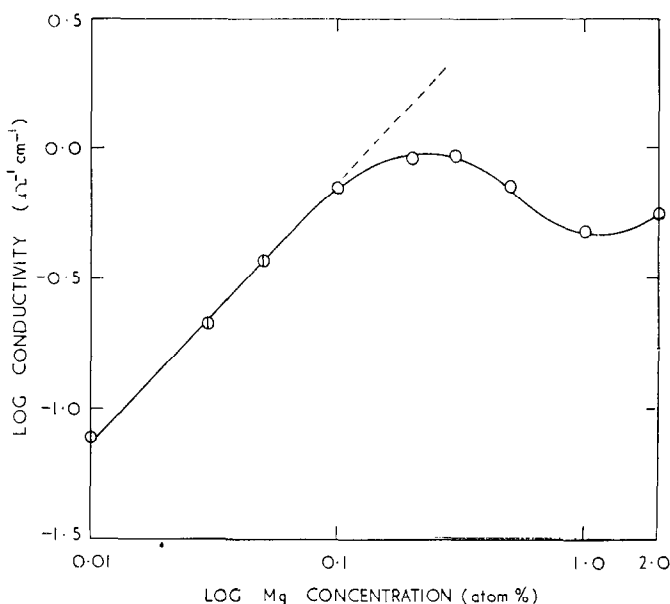
FIG. 2. Logarithm of dc conductivity in air at $10^3/T°K = 1.1$ (plateau region, B, in Fig. 1) as a function of Mg content in ferric oxide catalysts, present work (O); from Ref. (7) (⊕).

had not been exposed to reaction conditions. In a later section, conductivity changes which occurred when pellets were exposed to methanol/air mixtures are reported.

Figure 1 shows plots of the variation of dc conductivity with temperature for various catalysts in air. Samples of ferric oxide doped with magnesium always gave nonlinear conductivity plots in which three regions could be distinguished, i.e. (A) a linear part below 400–450°C, then (B) a plateau, followed by (C) a further sharp increase above ~900°C.

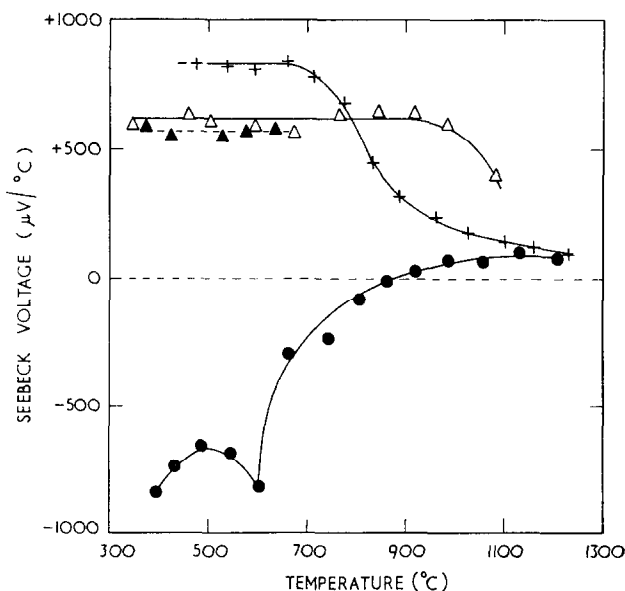At temperatures below 900°C, the elec-

FIG. 3. Seebeck voltage as a function of temperature for pure ferric oxide (●); ferric oxide with 0.01 at. % Mg (+); 0.2% Mg (▲); 0.3% Mg (△).
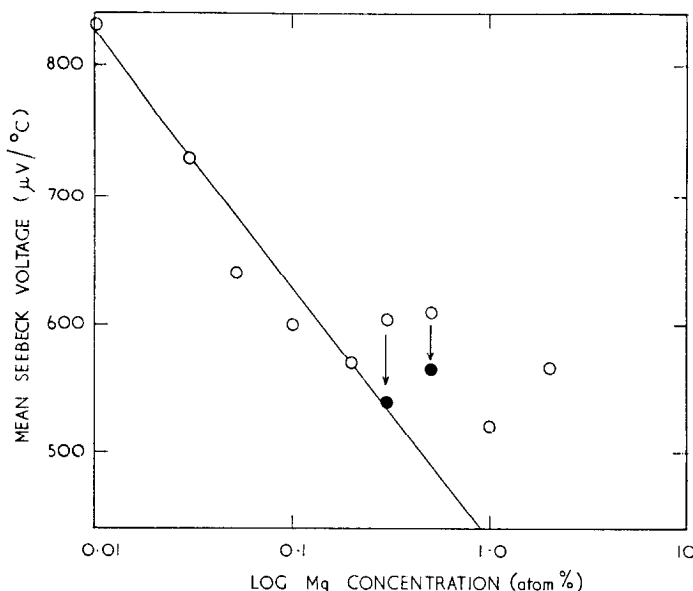
FIG. 4. Mean value of Seebeck voltage in plateau region, B (see Fig. 1) as a function of Mg content in ferric oxide catalysts fired at 1300°C (O); "best" values for 0.3% and 0.5% Mg from Table 1 (●); theoretical (————).

trical conductivity of ferric oxide samples containing magnesium was greater than the conductivity of the pure oxide, with a maximum at 0.2–0.3 at. %. Above this concentration, the conductivity decreased, but was still substantially greater than that for the undoped oxide; cf. data for 2.0% in Fig. 1. The inset in Fig. 1 shows, on a larger scale, data for all magnesium-doped catalysts approaching and on the plateau region, except for the 0.01% shown on the main part of Fig. 1.

As discussed later, a linear relationship should exist between conductivity in the plateau region (B) and the Mg content. Conductivities (logarithm) at the mid-point of the temperature range B, $10^3/T°K = 1.1$, are plotted against the logarithm of the Mg content in Fig. 2. Data reported previously (7) for Fe_2O_3 + 0.03 or 0.05% Mg are also included.

Values of the Seebeck voltage observed in pure ferric oxide and catalyst samples containing 0.01, 0.2, and 0.3% Mg are shown in Fig. 3; the p-type nature of the Mg-doped samples is apparent. Seebeck voltages in p-type samples also exhibit a well-defined "plateau," before decreasing at

higher temperatures due to oxygen loss and the production of n-carriers (8). At the lowest Mg-content, 0.01%, the decrease occurred above 700°C, but otherwise the "plateau" region is between 400–450° and 900°C.

The mean value of the Seebeck voltage in the "plateau" region is shown in Fig. 4 as a function of Mg content, for Mg-doped catalysts fired at 1300°C (open circles). Seebeck voltage measurements were also made on catalysts fired under different conditions (Table 1) and containing approximately the critical Mg content above which phase-separation is observed (see discussion below). Here, the idea was to incorporate the Mg without attendant ferrite formation. Three samples of catalyst containing either 0.3 or 0.5% Mg were examined; only sample B of the 0.3% Mg catalysts, after firing for 10-hr periods at 1100 and 1150°C, gave approximately the theoretical Seebeck voltage expected from the Mg content, i.e. 540 μV/°C observed compared with 535 μV/°C expected. This observed value and the "best" value for the 0.5% Mg-doped catalysts are also shown in Fig. 4 (filled circles).

TABLE 1
EFFECT OF FIRING TEMPERATURE ON SEEBECK VOLTAGE ($\mu V/°C$)

Catalyst (% Mg conc)	Firing time (hr)	Firing temperatures and Seebeck voltages in plateau region						Theor. θ
		(A)		(B)		(C)		
		T (°C)	θ	T (°C)	θ	T (°C)	θ	
0.3	10	1000	560	1100	550			535
		+1050	585	+1150	540			
		+1200[a]	585	+1200	565			
		+1240[b]	630	+1300	735	1300[b]	605	
0.5	15	900	655	1100	565			490
		+1000	620	+1150	580			
		+1100	605					
		+1200	735			1300	610	

[a] Firing time, 5 hr.
[b] 15 hr.

Conductivities under Reaction Conditions

Single catalyst pellets were exposed to the standard reaction mixture used in testing catalyst performance for the conversion of methanol, i.e., 14% methanol in air flowing at 150 ml/min. Figure 5 shows the change in conductivity, $\Delta \log \sigma$, with time at fixed reaction temperatures, where

$$\Delta \log \sigma = \log(\text{initial conductivity in air}) \\ -\log(\text{observed conductivity}).$$

The sample contained 0.2 at. % Mg and was fired at 1300°C; it shows characteristic behavior for Mg-doped ferric oxide catalysts, viz., a very large decrease in conductivity on exposure to methanol vapor in air. In similar experiments the change in
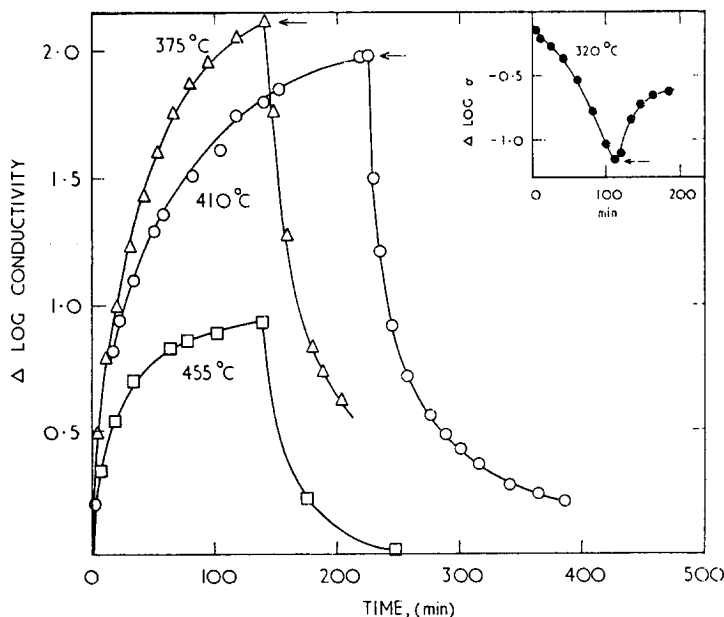

FIG. 5. Changes in dc conductivity with time in catalyst pellets of ferric oxide + 0.2 at. % Mg fired at 1300°C, when exposed to methanol + air; inset shows conductivity change in a pure ferric oxide catalyst exposed to methanol + argon. Arrows indicate removal of methanol from air or argon stream.

conductivity was followed until a constant value was reached. When the methanol supply was removed, so that air alone was flowing over the catalyst (arrows in Fig. 5), much of the conductivity change was reversed. Between experiments, the sample was held overnight at reaction temperature in air, restoring the original conductivity.

It should be noted, however, that the methanol supply was *not* removed in the experiment at 455°C, but on approaching the constant value, the conductivity increased sharply, i.e., $\Delta \log \sigma$ decreased. This effect was observed a number of times and the surface of the pellet was visibly changed. After one such experiment, the presence of magnetite was detected by X-ray diffraction.

Experiments were also carried out (with Mg-doped catalysts fired at 1300°C) where the methanol vapor was carried in argon over the catalyst instead of in air. Similar changes in conductivity were observed and again when the methanol supply was shut off, leaving only argon flowing, there was a sharp reversal of the conductivity change.

When pure (*n*-type) ferric oxide catalysts were exposed to methanol + air mixtures, only small conductivity changes were observed. Further, the pellet temperature increased sharply which would itself raise the conductivity. However, the conductivity change is probably in the opposite direction compared with magnesium-doped catalysts. Experiments with methanol + argon mixtures over the pure oxide showed conductivity changes which were comparable in magnitude to changes observed in magnesium-doped catalysts but, again, in the opposite direction, Fig. 5 (inset).

Further experiments were carried out where the surface-to-bulk ratio was varied, as both surface and bulk conductivity contribute to the total. A catalyst containing 0.3% Mg was fired at temperatures between 1000 and 1300°C, i.e., over the temperature range where marked changes in grain size are known to occur—cf. Ref. (7), Fig. 3 (a) and (b). Table 2 shows the changes in conductivity when the catalyst was exposed to a stream of methanol in argon at 315°C. The conductivity of the pellet after firing at 1000°C responded rapidly on exposure to methanol ($\Delta \log \sigma = 2.74$ after 1 min). With additional firing at higher temperatures, the speed of response was slower and the constant value was only attained after longer periods of exposure to methanol vapour. Again, withdrawal of methanol from the argon reversed the conductivity change.

Electron probe Microanalysis

Figure 6 shows the characteristic features observed when ferric oxide catalysts containing between 0 and 2% Mg were examined by electron probe microanalysis. In the pure ferric oxide sample, Fig. 6a, the upper trace showing Fe concentration records a minimum when the electron probe, scanning along the horizontal line, passes over a pore in the surface; the lower trace for Mg shows no significant variation. Similar results were obtained with ferric oxide samples containing 0.03, 0.05, and 0.1% Mg, used in catalytic reaction.

A new feature appears in the sample containing 0.2% Mg Fig. 6b, and is also detected in samples with 0.3, 0.5, 1.0, and 2.0% Mg, viz., dark grey areas (see Fig.

TABLE 2

EFFECT OF FIRING CONDITIONS ON RATE OF CONDUCTIVITY CHANGE

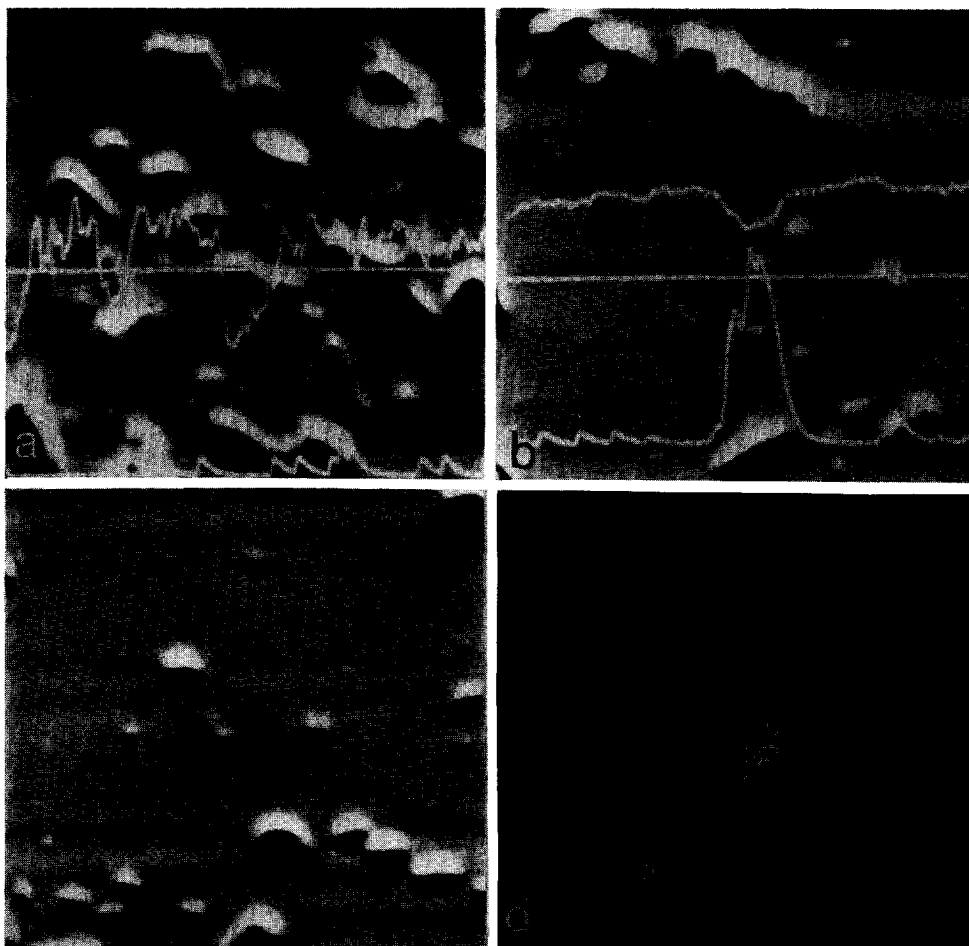| Firing conditions		$\Delta \log \sigma$					
		Time (min):					
(°C)	(hr)	1	3	9	15	30	50
1000	15	2.74	3.12	3.23	3.31	3.31	3.31
+1100	15	1.21	2.62	2.85	2.86	2.86	2.86
+1200	10	0.52	1.34	2.60	3.14	3.34	3.40
+1300	5	0.29	0.91	1.78	2.27	2.68	2.87

FIG. 6. Electron probe microanalysis of pure and Mg-doped ferric oxide catalysts: (a) pure ferric oxide, and (b) ferric oxide + 0.2 at. % Mg; [upper trace] in (a) and (b) shows Fe concentration, [lower trace], Mg concentration, scanning along horizontal line; (c) electron image, and (d) corresponding Mg analysis from catalyst with 0.5% Mg.

6b just below center). The upper trace (Fe) shows a minimum while the lower trace (Mg) shows a maximum across the dark grey area. Dark grey areas also feature in Fig. 6c obtained from a $Fe_2O_3 + 0.5\%$ Mg catalyst, as well as a number of pores. When the total field of this electron image was analyzed for Mg, Fig. 6d, the Mg concentration indicated by the density of white spots was highest in some of the pores as well as in the dark grey areas.

Table 3 shows the quantitative analysis of some dark grey areas in a sample of $Fe_2O_3 + 1\%$ Mg. As an alternative to applying the otherwise necessary corrections, count rates due to iron and magnesium are compared with standard samples of mag-

nesium ferrite. The agreement between the two sets of values provides evidence that the dark grey areas observed in Fig. 6b and c have approximately the same Fe and Mg concentrations as the spinel, magnesium ferrite.

DISCUSSION

Electrical measurements (dc conductivities and Seebeck voltage) on catalyst pellets in air serve to characterize the catalysts, i.e., they provide information on the number and nature of the charge carriers when magnesium is incorporated into ferric oxide and, further, they indicate sensitively the onset of phase-separation.

Catalyst performance was measured (*15*)

TABLE 3

ELECTRON PROBE MICROANALYSIS OF DARK GREY
AREAS IN Fe_2O_3 + 1% Mg CATALYST
(COUNTS/SEC)[a]

| | Catalyst sample | | $MgO \cdot Fe_2O_3$ standard | |
Area	Fe	Mg	Fe	Mg
1	9550	1415	9255	1295
2	9690	1350		
3	9845	1405	9740	1275
4	9775	1415		

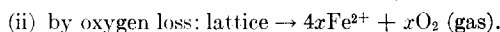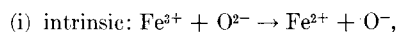[a] Background counts: Fe 65–70, Mg ~20.

over the temperature ranges ~500–750°C (N_2O decomposition) and ~300–600°C (methanol conversion). Only the lower temperatures for the latter reaction fall in the linear part of the conductivity-reciprocal temperature plot, Fig. 1 (designated region A), where the interference of grain boundaries with the dc conductivity of polycrystalline specimens is well known. The conductivity in region A is markedly affected by the temperature at which the pellets have been fired (7); for example, firing at 1300°C (the standard incorporation temperature in the present work) instead of 1000°C increased the conductivity corresponding to the increased grain growth. However, relative levels of conductivity, associated with the various Mg contents, remain the same as in the plateau region (cf. Fig. 1).

The higher temperatures used in measuring catalyst performance, viz., above 400–450°C, fall in the plateau region of the conductivity plots for magnesium-doped samples (designated region B). Here it is believed that the conductivity is relatively free from grain boundary effects. The evidence for this is the correspondence of conductivity values observed in polycrystalline compacts containing the same amount of magnesium but fired at different temperatures (7) and the agreement between data for pure compacts and single crystals of ferric oxide (12). The small temperature coefficient associated with the conductivity in the plateau region is probably due only to changes in the carrier mobility. Some increase in carrier mobility is expected and hence the plateau is in-

dicative of a relatively fixed carrier concentration. For these reasons, the magnitude of the conductivity in region B is of most interest for this work.

At still higher temperatures (designated region C) above the plateau, the conductivities of both pure and magnesium-doped ferric oxide come together as they are increasingly dominated by carriers arising by two possible mechanisms (8).

In the conduction process, n-carriers or electrons are believed to jump to neighboring cations; and the p-carrier, holes on oxygen ions (O^-) to neighboring anions.

(i) intrinsic: $Fe^{3+} + O^{2-} \rightarrow Fe^{2+} + O^-$,

(ii) by oxygen loss: lattice $\rightarrow 4xFe^{2+} + xO_2$ (gas).

Incorporation of magnesium introduces additional p-carriers into the Fe_2O_3 lattice and a fair semiquantitative description of this mixed conduction system (7), in regions B and C, is given by:

$$\sigma_{obs} \simeq \mu_p e p + \sigma_n$$

Where σ_{obs} is the total observed conductivity, μ_p is the mobility and p is the number of p-carriers, and σ_n can be represented by the conductivity of the pure oxide. Examination of the conductivity curve for the pure oxide shows that the contribution of σ_n to the total is small *in region B* for magnesium-doped samples. Therefore a linear relationship is expected between the conductivities in the plateau region (B) and the number of Mg^{2+} incorporated, if each introduces one p-carrier. Figure 2 shows that the relationship holds up to a magnesium concentration of 0.1% but deviation sets in a 0.2% Mg.

Further information on the availability of p-carriers is provided by the Seebeck voltages (Figs. 3 and 4). The Seebeck voltage, θ, is related to the carrier concentration, p, approximately, by the following equation (10):

$$\theta = \frac{k}{e} \ln \left(\frac{N_0}{p} \right) \simeq 198.\log \left(\frac{N_0}{p} \right) \mu V/°C$$

where k is Boltzmann's constant, e the elec-

tronic charge and N_0 is the number of available states. Since p-carriers are identified as holes on oxygen ions, N_0 is taken as the number of anions per cm^3, i.e., 6×10^{22} cm^{-3}.

Using this expression, the Seebeck voltage expected for each catalyst was calculated from its Mg content (straight line, Fig. 4) again assuming that each Mg^{2+} introduces one p-carrier. Comparison of the calculated Seebeck voltage with the mean value observed in the plateau region (open circles, Fig. 4) shows good agreement up to 0.2% Mg. Thus the 0.2% Mg catalyst should contain 8×10^{19} carriers/cm^3 and produce a Seebeck voltage of 567 μV/°C which is in close agreement with the observed value, 570 μV/°C. Such agreement is rather better than can be expected because a variation of 0.1°C in temperature gradient produces a change of $\sim$50 μV in the observed Seebeck voltage. It is clear, however, that calculated and observed Seebeck voltages show a marked divergence for catalysts containing more than 0.2% Mg.

In summary, the electrical measurements in air on these catalysts (fired at 1300°C) can be explained in terms of the incorporation of Mg^{2+} into the hematite lattice, forming a corresponding number of p-carriers, up to a limit of 0.1% Mg (as indicated by conductivity) or 0.2% Mg (as indicated by Seebeck voltage). Table 1 and Fig. 4 (filled circles) show that catalysts containing 0.3% Mg, when fired at a lower incorporation temperature, would also yield the expected Seebeck voltage, but with 0.5% Mg present the expected Seebeck voltage could not be produced. It is believed that beyond 0.1–0.3% Mg, the spinel, magnesium ferrite, is formed and hence anomalies begin to appear in the electrical properties.

A diagram summarizing knowledge of phase relations in the system MgO–iron oxide in air, given by Phillips et al. (13), shows only the coexistence of "magnesioferrite" and hematite at the Mg concentrations and firing temperatures used in the present work. However, a more detailed diagram for the CaO–iron oxide system (14) indicates the solid solution of

<1% CaO in the hematite structure and a limited solubility of MgO in hematite is also indicated by the present electrical measurements.

Previously, evidence for the existence of magnesium ferrite in Mg-doped ferric oxide samples was sought from X-ray diffraction (7) although diffraction from the hematite lattice would be expected to mask almost all the stronger magnesium ferrite diffraction peaks except for $d = 2.96$ Å. This diffraction peak was observed in a sample of ferric oxide containing 2.0% Mg. In the present work, electron probe microanalysis provides good evidence (Fig. 6 and Table 3) for the separation of magnesium ferrite in samples containing as little as 0.2% Mg, confirming the conclusions drawn from the electrical measurements on catalyst pellets in air.

The electrical conductivity changes which occurred when catalysts were exposed to methanol vapor, either in methanol/air or methanol/argon mixtures, are informative with regard to (i) electron transfer/permanent changes in the catalyst, and (ii) the relative importance of surface and bulk conductivities.

When both the pure (n-type) oxide and the (p-type) Mg-doped oxides were exposed to methanol, a net gain of electrons was observed, either donated by the methanol or as a consequence of oxygen loss. The conductivity of the pure oxide is raised due to the increased electron concentration and the conductivity of the Mg-doped oxides decreased by the elimination of positive carriers (Fig. 5). The sharp reversal of the conductivity change when the methanol was removed from methanol/argon mixtures argues against the oxygen-loss mechanism but *rates* of conductivity change for catalysts fired at 1300°C seem to be rather slow. A slow equilibration between surface and bulk and a significant contribution from bulk conductivity to the total is indicated. When the firing temperature was reduced (Table 2) to produce a smaller grain size and a larger contribution from the surface conductivity, then the observed conductivity responded rapidly to methanol vapor.

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