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X-ray and electrical conductivity studies on iron–aluminium mixed oxides

B. MANI, V. SITAKARA RAO, H. S. MAITI
Department of Chemistry and Materials Science Centre, Indian Institute of Technology, Kharagpur-721302, India

Co-precipitated iron–aluminium mixed oxide catalysts containing 0 to 100 mol % alumina have been studied by X-ray diffraction and electrical conductivity measurements. Formation of solid solution has been observed. At lower concentrations, aluminium ions occupy the interstitial sites while at higher alumina contents, it forms a substitutional solid solution. Electrical conductivity of the specimens has been measured in air and nitrogen atmospheres in the temperature range room temperature to 400° C. The influence of moisture is found to be significant and it increases with increasing alumina content. A straight line relationship exists between log σ and $1/T$ for all the specimens. The activation energies for conduction in air and nitrogen are observed to be in the range 0.25 to 0.35 and 0.24 to 0.29 eV, respectively. Electron holes are found to be responsible for electrical conduction in these materials.

1. Introduction

Iron–aluminium mixed oxides have been widely used as dehydration–dehydrogenation catalysts [1–3]. These are also excellent catalysts for the polymerization of ethylene oxide compared to the oxides of beryllium, magnesium, aluminium and iron [4]. It is observed that iron–aluminium oxide catalysts possess maximum catalytic activity when they are prepared by co-precipitation of the hydroxides followed by calcination at around 400° C in air [5]. Furthermore, it is well known that the catalytic properties of the oxide catalysts are very closely related to their semiconducting behaviour [6]. Electrical properties of pure and doped iron oxide prepared at high temperatures have been studied by several investigators [7–11]. However, not much attention has been paid so far to the co-precipitated mixed oxide catalysts. The present paper embodies the study of electrical conductivity in iron–aluminium mixed oxides and determination of their structural characteristics by X-ray diffraction analysis.

2. Experimental procedure

Iron–aluminium mixed oxide catalysts in the composition range 0 to 100 mol % were prepared by the co-precipitation method. To obtain the required composition, suitable volumes of ferric ammonium sulphate (E. Merck-G.R.) and aluminium ammonium sulphate (B.D.H.-A.R.) solutions were mixed together. The mixtures were heated to boiling with concentrated nitric acid and the hydroxides were then precipitated at 60° C by adding 6 N ammonium hydroxide (B.D.H.-A.R.) solution. The precipitated hydroxides were filtered, washed free from other ions with distilled water and dehydrated at 110° C for 4 h. The hydroxides were then heated at 420° C for 4 h to convert them into the corresponding oxides. The mol % aluminium oxide in different samples S1–S12 are given in Table I. X-ray diffraction patterns were obtained from a ΔPOH-I(USSR) type diffractometer using Fe$K\alpha$ radiation.

TABLE I Composition of samples

Sample no.	Mol % Al_2O_3	Sample no.	Mol % Al_2O_3
S1	0.00	S7	8.33
S2	0.43	S8	20.0
S3	0.76	S9	40.0
S4	1.52	S10	60.0
S5	2.06	S11	80.0
S6	3.43	S12	100.0

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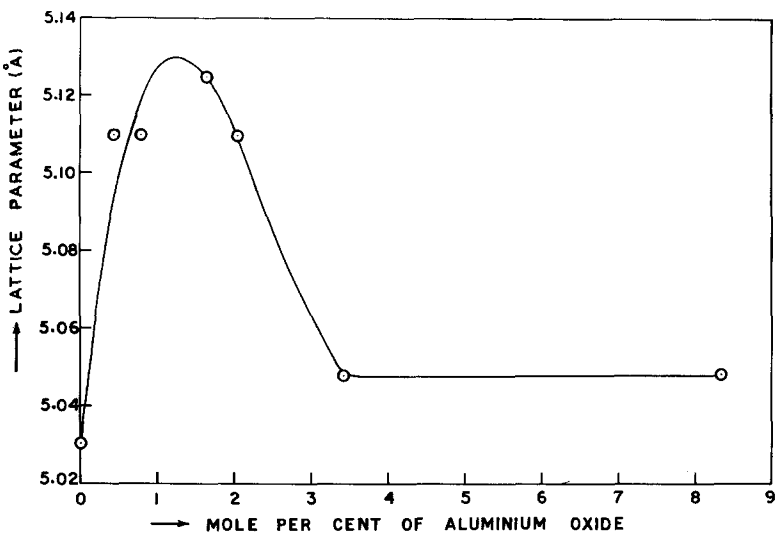

Figure 1 Variation of lattice parameter with alumina content.

For electrical conductivity measurements, pellets of 2 cm diameter and around 1.5 mm thickness were made in a steel die-punch applying a pressure of about 560 kg cm^{-2} with a hydraulic press. The opposite sides of the pellet were coated with silver paint and dried in an air oven at 150° C. The coated pellets were held between two stainless steel electrodes in a sample holder with arrangements of temperature variation and gas flow. The resistances of the pellets were measured with a 10^6 megohmmeter at d.c. fields of 100, 200 and 500 V. Resistances less than $10^7\ \Omega$ were measured using a LCR bridge. Preliminary measurements showed that the d.c. conductivity values were very close to those of a.c. Hence, only d.c. values are reported here.

Conductivity measurements of the specimens were carried out in moist air, dry air and dry nitrogen gas. The gases were dried by passing them through towers containing anhydrous calcium chloride and phosphorous pentoxide. The temperature of the specimen was controlled within ± 1° C by an electronic feed-back controller. The exact temperature was measured with a chromel–alumel thermocouple and a potentiometer. The conductivity measurements were taken after allowing the pellet to stand at a constant temperature for at least 2 h.

3. Results and discussions

Iron–aluminium mixed hydroxides obtained after calcination at 110° C do not show any X-ray diffraction peaks. Similar is the case with samples containing more than 8.33 mol% alumina even after calcination at 420° C. However, samples containing less than this amount (samples S1 to S7) show definite X-ray diffraction peaks after the same heat treatment. Comparison of *d* values of these samples with the standard data indicates the presence of α-Fe_2O_3 in these samples. Shifting of the peak positions and the consequent change in lattice parameter confirm the formation of solid solution even at this low temperature. Formation of such solid solutions at low temperatures in the co-precipitation method has been reported earlier, in the case of other oxides [12]. It has also been reported that about 8 mol% Al_2O_3 can form a solid solution with iron oxide when sintered at 1300° C [13, 14]. Fig. 1 shows the variation of lattice parameter with the alumina content of the samples as observed in the present investigation. The lattice parameter initially increases with increasing concentration of alumina up to about 1.5 mol%, followed by a decrease up to about 3.5 mol% and remains practically constant thereafter. The close values of ionic radii of Fe^{3+} (0.64 Å) and Al^{3+} (0.59 Å) and similarity in the crystal structure of these sesquioxides suggest that possibility of the formation of a substitutional solid solution in these samples. Formation of such a solid solution would result in a decrease in lattice parameter of Fe_2O_3 as the ionic radius of Al^{3+} is slightly less than that of Fe^{3+}. This is observed only at alumina concentrations higher than 1.5 mol%. The initial increase of lattice parameter below this concentration can only be explained if one assumes the formation of an interstitial type solid solution at these concentrations. It is known that the aluminium ion can occupy either a tetrahedral or an octahedral site

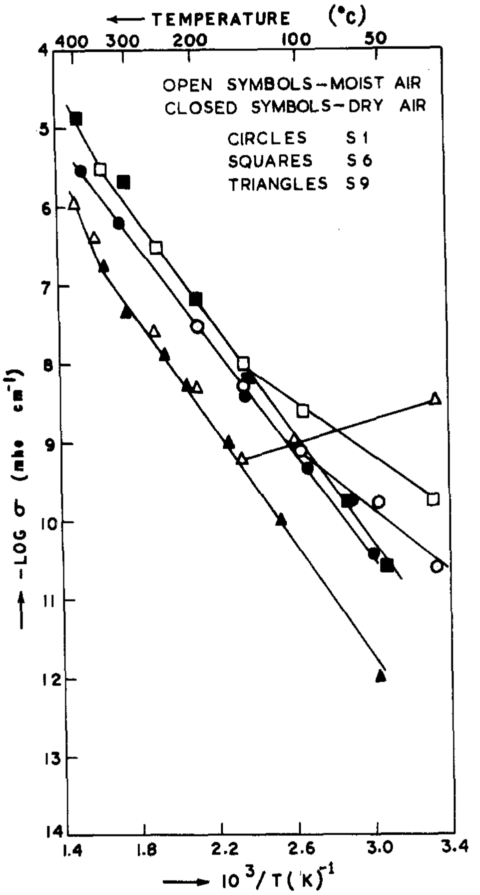

Figure 2 Effect of moisture on the electrical conductivity of samples S1, S6 and S9.

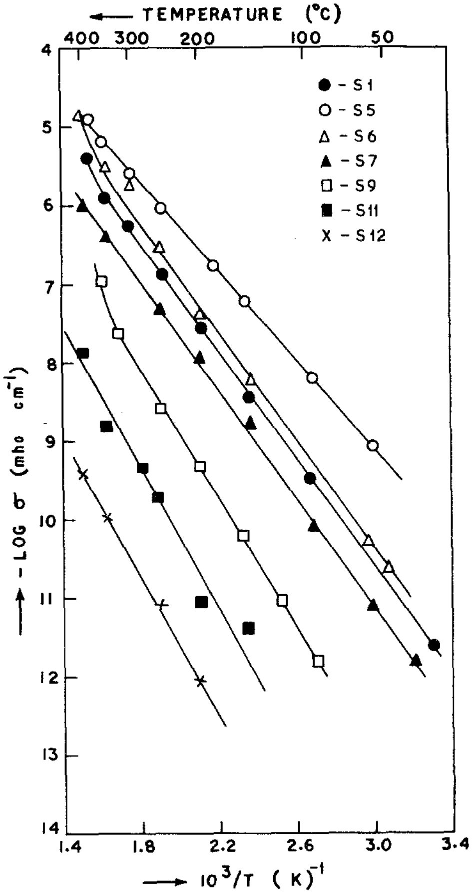

Figure 3 Electrical conductivity of iron–aluminium mixed oxide samples in dry air.

in different oxides due to its near-critical cation-to-anion ratio. The formation of both these types of solid solution has earlier been reported in the NiO–Li_2O system, in which lattice expansion up to an addition of 0.2 mol% Li_2O and a contraction thereafter have been observed [15]. In Fig. 1 the lattice parameter remains practically constant at alumina concentrations higher than 3.5 mol%. Here excess alumina is expected to be separated as the second phase. However, no such second phase has been detected in the present investigation by X-rays probably because it remained in the amorphous hydrated state.

The electrical conductivity of these samples is found to be quite sensitive to moisture content of the surrounding atmosphere especially in the temperature range room temperature to ~ 150° C. Fig. 2 shows the variation of log specific conductivity (σ) with inverse of absolute temperature ($1/T$) for few of the specimens measured both in moist and dry air. The conductivity values of sample S1 ("pure" iron oxide) measured in moist and dry air are found to coincide in the temperature range 110 to 400° C while a small deviation is observed below this temperature range, the values in moist air being higher than those in dry air. Similar behaviour is also observed in samples S6 and S9 which contain different quantities of aluminium oxide. However, the deviation in these cases starts at a slightly higher temperature (~ 150° C). It may also be noted that the deviation becomes more significant as the alumina content is increased. These observations suggest that the water molecules are readily adsorbed on the surface of these specimens and are driven off when heated to about 150° C. Furthermore, the adsorption is enhanced as the alumina content is increased. This is in accordance with the fact that the water retention capacity of alumina, especially at lower temperatures, is higher than that of ferric oxide [16, 17]. This is also evident from the thermogravimetric analysis of the specimens [18].

Fig. 3 shows the results of electrical conduc-

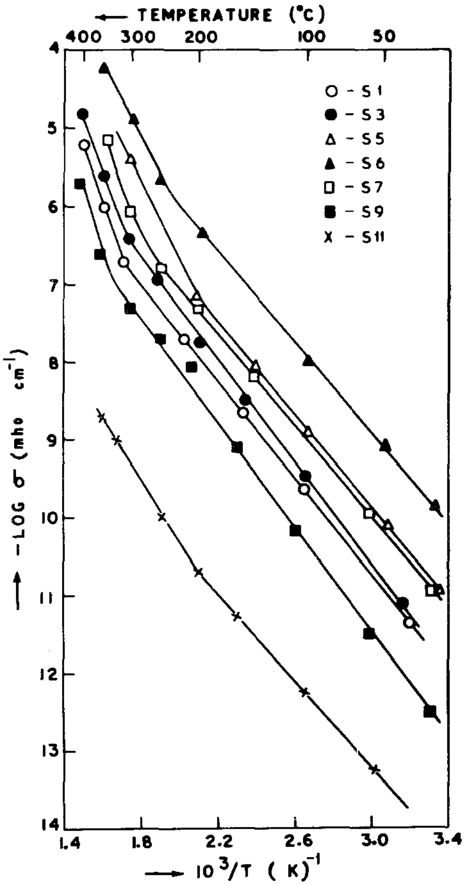

Figure 4 Electrical conductivity of iron–aluminium mixed oxide samples in dry nitrogen.

tivity measurements in dry air for the specimens including those already presented in Fig. 2. For clarity in the figure, the results of other specimens have been omitted. These plots show a linear relationship between log σ and $1/T$ for all specimens. At each temperature the conductivity increases with alumina content up to 2.06 mol % (sample S5) and decreases thereafter. The conductivity of sample S6 almost coincides with that of "pure" iron oxide (sample S1). Samples containing high alumina show lower conductivity than "pure" Fe_2O_3. The activation energies for various specimens as measured from the slope of the straight lines are: S1, 0.30 eV; S5, 0.25 eV; S6, 0.30 eV; S7, 0.30 eV; S9, 0.35 eV; S11, 0.38 eV, and S12, 0.35 eV.

To observe the effect of oxygen partial pressure on the conductivity values of these specimens, measurements were also carried out in dry nitrogen gas which has a lower oxygen partial pressure than air. The results of these measurements are shown in Fig. 4. The behaviour is very similar to that obtained in air. However, the conductivity of sample S1 is found to be lower in nitrogen than in air and the maximum conductivity is observed at 3.43 mol % alumina compared to the earlier value of 2.06 mol %. The activation energies for the different specimens are: S1, 0.27 eV; S3, 0.27 eV; S5, 0.26 eV; S6, 0.26 eV; S7, 0.27 eV; S9, 0.29 eV; and S11, 0.29 eV.

The effect of alumina content on the conductivity of various specimens at a fixed temperature (180° C) may be observed in Fig. 5. Addition of alumina initially increases the conductivity of ferric oxide both in air and nitrogen atmospheres, followed by a decrease at higher concentrations. However, the maximum is obtained at different concentrations depending upon the gaseous atmosphere. It may be noted that at low alumina contents, the conductivity in air is higher than that in nitrogen, while at higher concentrations, the situation is reversed.

The observed conductivity behaviour may satisfactorily be explained if one considers the following conduction mechanism in these materials.

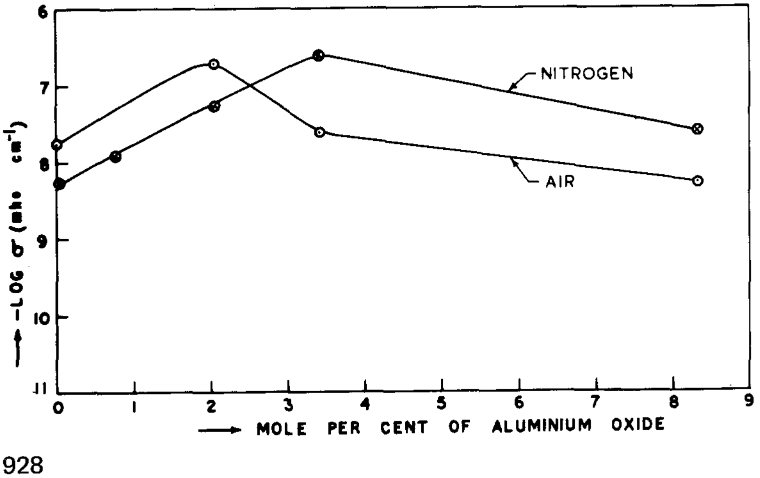

Figure 5 Variation of electrical conductivity with alumina content at 180° C.

Pure ferric oxide has generally been referred to as oxygen deficient *n*-type conductor when sintered at high temperatures. However, it has also been reported by several investigators as a *p*-type semiconductor. All the electrical measurements in the present investigation were taken within 400° C which is a rather low temperature for conductivity study of these materials. Furthermore, the specimens were powders pressed in the form of pellets and were not sintered at elevated temperatures. Therefore, it may be assumed that the results of the present investigation represent mainly the surface properties of the powders rather than the behaviour of the bulk. The generation of electron holes in ferric oxide may take place by the adsorption of oxygen molecules on the surface of the specimens producing electron holes and metal vacancies. The reaction may be represented as:

$$3/2\mathrm{O}_2 \rightleftharpoons 3\mathrm{O}_0 + 6\oplus + 2\mathrm{V}_{\mathrm{Fe}}''' , \qquad (1)$$

in which usual defect notations have been used, i.e. $\oplus$ represents electron hole, O_0 is the oxygen in usual lattice site, V_{Fe} is a vacant iron site and primes represent effective negative charges.

The equilibrium constant of this equation is given by

$$K_1 = \frac{p^6\,[\mathrm{V}_{\mathrm{Fe}}''']^2}{P_{\mathrm{O}_2}^{3/2}}, \qquad (2)$$

where ρ represents the concentration of holes.

According to Equation 1

$$[\mathrm{V}_{\mathrm{Fe}}'''] = 1/3p$$

and therefore Equation 2 may be written as

$$K_1 = p^8/9P_{\mathrm{O}_2}^{3/2}.$$

Thus,

$$p = (9K_1)^{1/8}P_{\mathrm{O}_2}^{3/16}. \qquad (3)$$

Equation 3 suggests that the hole concentration and, consequently, the conductivity is proportional to $P_{\mathrm{O}_2}^{3/16}$. Therefore, the conductivity will decrease with decreasing oxygen partial pressure as has been observed in the present investigation for samples containing small quantities of alumina. Since at lower concentrations alumina forms an interstitial solid solution, the defect reaction may be given by

$$\mathrm{Al}_2\mathrm{O}_3 \rightarrow 2\mathrm{Al}_\mathrm{i} + 3\mathrm{O}_0 + 2\mathrm{V}_{\mathrm{Fe}} \qquad (4)$$

in which Al_i represents an interstitial aluminium ion. The neutral metal vacancies may be ionized by any of the following three mechanisms producing excess holes with a resultant increase in conductivity:

$$\mathrm{V}_{\mathrm{Fe}} \rightarrow \mathrm{V}_{\mathrm{Fe}}' + \oplus \qquad (5)$$

$$\mathrm{V}_{\mathrm{Fe}} \rightarrow \mathrm{V}_{\mathrm{Fe}}'' + 2\oplus \qquad (6)$$

$$\mathrm{V}_{\mathrm{Fe}} \rightarrow \mathrm{V}_{\mathrm{Fe}}''' + 3\oplus. \qquad (7)$$

On the other hand, at higher alumina contents where the aluminium ions occupy the vacant cation sites instead of interstitial positions, there is a reduction in the concentration of iron vacancies with a consequent decrease in hole concentration. This leads to the observed drop in conductivity at high alumina contents. It is possible that the change-over from the interstitial to substitutional type of solid solution takes place at a particular concentration of iron vacancy. At lower oxygen partial pressures the concentration of iron vacancies in "pure" ferric oxide is also lower than that at higher oxygen partial pressure and, therefore, larger quantities of alumina can be added before the solid solution is changed from an interstitial type to a substitutional one. As a result, the conductivity maxima is observed at higher alumina content in the case of nitrogen than that in air.

The activation energies observed in the present investigation vary between 0.25 and 0.38 eV. These values are rather low compared to those generally obtained with sintered specimens (around 1.0 eV). This is also indicative of the fact that the electrical conduction in these materials, under the present experimental conditions, takes place mainly through the surface of the particles for which the formation energy of the defects are rather low. It is the migration energy which mainly contributes to the activation energy value.

4. Conclusions

(1) Co-precipitated iron–aluminium mixed oxides form solid solutions on calcination at 420° C. At lower concentrations of alumina (< 1.5 mol %) they form an interstitial type of solid solution, while at higher alumina contents it changes to a substitutional one.

(2) Below 400° C the electrical conduction in these materials takes place mainly through the surface of the particles and is influenced by the surrounding atmosphere. The effect of moisture becomes more significant with increasing alumina content.

(3) The conducting species are predominantly

the electron holes produced as a result of oxygen adsorption on the surface of the specimens.

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