

# Physicochemical studies on ZnO-Al<sub>2</sub>O<sub>3</sub> system

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Several mixed ZnO-Al<sub>2</sub>O<sub>3</sub> systems were prepared by the impregnation method and calcined for 5 h at 300, 600 and 1000°C. The crystal structure, surface acidity, surface basicity, surface area, catalytic decomposition of H<sub>2</sub>O<sub>2</sub> and the electrical conductivity of the samples prepared were studied. It was found that the decomposition of H<sub>2</sub>O<sub>2</sub> is catalysed by the acidic sites formed on the catalyst surface at composition less than 50 mol% ZnO and by basic sites for oxides having composition higher than 50 mol% ZnO. ZnAl<sub>2</sub>O<sub>4</sub>-spinel was found to be formed at temperatures  $\geq 600^\circ\text{C}$  and it has a catalytic activity and electrical conductivity lower than each of the pure ZnO and the oxide mixtures. The results obtained were correlated together and discussed.

## 1. Introduction

The binary mixed oxides A<sup>II</sup>O and B<sub>2</sub>O<sub>3</sub> with the spinel structure were found to have many important physical properties such as electrical and catalytic properties [1-5]. Their properties and chemical composition may be affected not only by the type of starting compound, but also by the conditions of their preparation.

Several studies [6-10] on the catalytic and the acidic properties of some inorganic solids showed the presence of a correlation between the acidic and the catalytic properties of many inorganic solids. Also, the acid and basic properties of solid surfaces are interesting aspects of surface structure and important in the fields of ion exchange.

Since the binary oxides are widely used in catalysis [11-13] the present work was designed to measure the acidity and basicity of binary metal oxides, ZnO-Al<sub>2</sub>O<sub>3</sub>, by titration with n-butylamine and benzoic acid respectively, using various indicators of P<sup>K</sup>a = -5.6 to 12.2 in order to test how the catalytic activity correlates with the acid strength of the catalyst. The electrical conductivity and the catalytic decomposition of H<sub>2</sub>O<sub>2</sub> by these catalysts have been also studied.

## 2. Experimental

The binary oxides ZnO-Al<sub>2</sub>O<sub>3</sub>, were prepared in the composition 0, 15, 30, 50, 70, 85 and 100 mol% ZnO from BDH quality chemicals by impregnation technique. The impregnated oxides were dried at 115°C for 5 h. The samples thus obtained were powdered and only such samples collected between 100 and 150 mesh sieves were used. The powders thus obtained were calcined at 300, 600 and 1000°C for 5 h at each one of these temperatures. The samples after calcination were cooled in a desiccator and preserved in covered glass tubes, under vacuum.

X-ray diffraction patterns of the samples investigated were taken by the aid of Phillips unit, type PW 2103/00, using copper target and nickel filter. IR-

absorption spectra of the samples were taken with a Beckman infrared spectrophotometric unit adopting the KBr technique. DTA and TGA experiments were conducted using the TGA, DTA Shimadzu model 30 at a heating rate of 10°C min<sup>-1</sup> in air atmosphere, using a 20 mg sample. The surface area of the binary mixed oxides was determined with a surface area measurer BET micrometer 2200.

The acidity measurement was made using the amine titration method developed by Johnson [14]. For this purpose 0.2 g of the mixed oxide suspended in benzene was titrated with a solution of 0.1 N n-butylamine in benzene using benzylacetophenone (P<sup>K</sup>a = -5.6) Dicinnamalacetone (P<sup>K</sup>a = -3.0), benzene azo diphenylamine (P<sup>K</sup>a = 1.5), p-dimethyl amino azobenzene (P<sup>K</sup>a = 3.3) as indicator. The surface acidity,  $\chi$ , is expressed as m.mol of n-butylamine used in the titration for 1 g of a catalyst. The value given for the surface acidity is the mean of three experiments. The titration method using 0.1 N benzoic acid in benzene was also used for determining the basicity of the oxides investigated. The indicators used for the basicity determination were bromomethylblue (P<sup>K</sup>a = 7.2), phenolphthalein (P<sup>K</sup> = 9.3) and 2, 4, 6-trinitroaniline (P<sup>K</sup>a = 12.2).

The decomposition of H<sub>2</sub>O<sub>2</sub> was selected for the study on the catalytic reactivity of the catalysts and was conducted as described by Keating [15] in a temperature range of 45 to 65°C.

The electrical conductivity has been measured by a method reported elsewhere [16].

## 3. Results and discussion

The DTA and TGA diagrams of ZnO, Fig. 1, show an endothermic peak at 200 to 300°C with a decreasing in the weight (10%) due to the elimination of H<sub>2</sub>O molecules adsorbed on the surface. This loss in the weight decreases with increasing the calcination temperatures. The diagram of Al<sub>2</sub>O<sub>3</sub>, Fig. 1, shows also an

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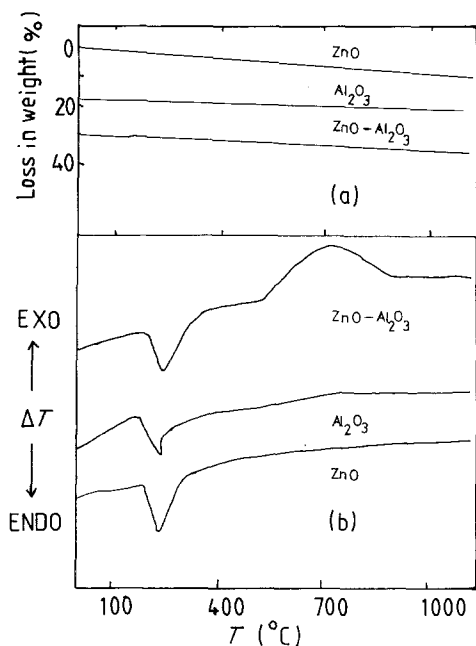


Figure 1 (a) TG and (b) DTA of ZnO, Al<sub>2</sub>O<sub>3</sub> and ZnO-Al<sub>2</sub>O<sub>3</sub> mixture (1:1 mole ratio).

endothermic peak at 250°C and a decrease in the weight by about 3% in the temperature range 250 to 1100°C.

The DTA and TGA results of ZnO-Al<sub>2</sub>O<sub>3</sub> (1:1 molar ratio) show an endothermic peak at 250°C due to the elimination of loosely bonded water molecules and a broad exothermic peak between 550 and 900°C which may be attributed to the solid state reaction between ZnO and Al<sub>2</sub>O<sub>3</sub> to form ZnAl<sub>2</sub>O<sub>4</sub> spinel.

Fig. 2 illustrates the X-ray diffraction patterns of the pure and the products of thermal treatment of ZnO and Al<sub>2</sub>O<sub>3</sub> at different calcination temperatures. It can be seen that at a calcination temperature of 1000°C only the intensive lines of ZnAl<sub>2</sub>O<sub>4</sub> (*d*-values of 0.143, 0.247 and 0.282 nm) could be detected, which refers to the formation of the spinel at 1000°C.

Fig. 3 shows the IR spectra of ZnO, Al<sub>2</sub>O<sub>3</sub> and their mixtures (1:1 molar ratio). The figure shows for each sample a band at 3500 cm<sup>-1</sup> which its intensity

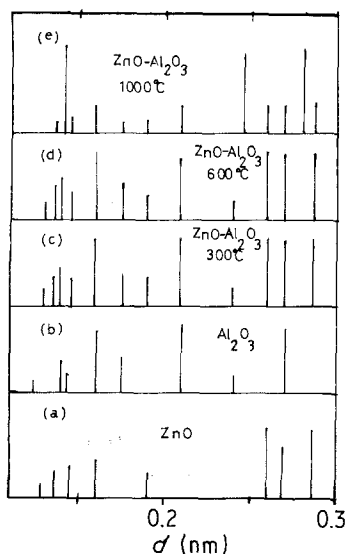


Figure 2 X-ray diffraction pattern of ZnO, Al<sub>2</sub>O<sub>3</sub> and ZnO-Al<sub>2</sub>O<sub>3</sub> mixture (1:1 mole ratio) calcined at different temperatures.

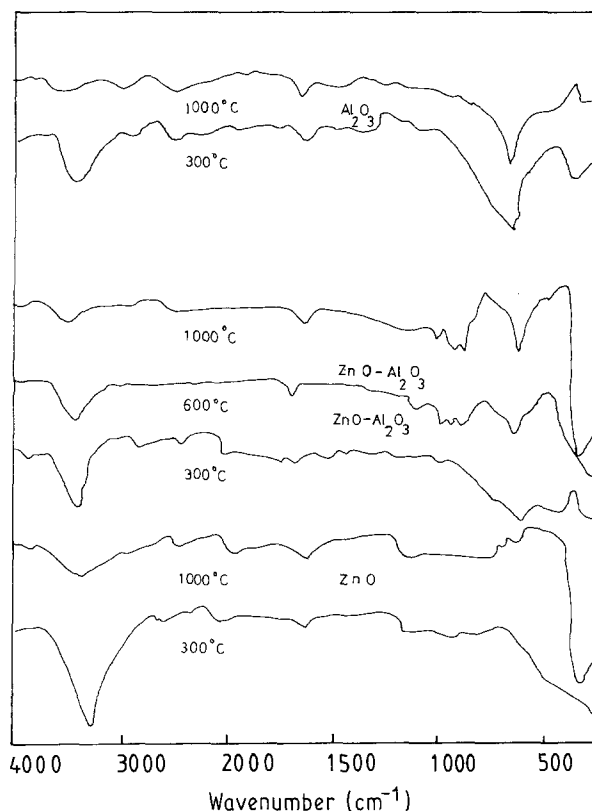


Figure 3 IR absorption spectra of ZnO, Al<sub>2</sub>O<sub>3</sub> and ZnO-Al<sub>2</sub>O<sub>3</sub> mixture (1:1 mole ratio) calcined at different temperatures.

decreases with increasing the calcination temperature. This band was assigned to -OH groups [17] present in the hydrated ZnO, Al<sub>2</sub>O<sub>3</sub> and their mixture. The infrared spectra of the calcined mixed oxides, at 600 and at 1000°C, show the appearance of new bands in the range 880 to 940 cm<sup>-1</sup>. These new bands can be attributed to the formation of ZnAl<sub>2</sub>O<sub>4</sub> spinel [18]. The results of X-ray and IR spectra of the calcined mixture at 600°C show some contrast. The IR spectra refers to the formation of ZnAl<sub>2</sub>O<sub>4</sub> spinel, but X-ray analysis could not detect its formation. If the spinel is formed in lower concentration at 600°C, then this contrast can be explained on the basis of the higher sensitivity of IR method for detecting the spinel formation compared with X-ray analysis [19].

The results of surface acidity,  $\chi$ , of the oxides investigated are shown in Fig. 4. A non-linear behaviour between the acidity and the composition of the oxides can be observed. The acidity shows maxima at 15 mol % ZnO. Moreover, the acidity was found to be decreasing with increasing the calcination temperature for all the samples investigated. This may be attributed to the decrease in the concentration of the water molecules adsorbed on the surface of the oxides with increasing the calcination temperature, as shown in the results of infrared.

Assuming that the acidic sites owe their formation to the inclusion of Zn<sup>2+</sup> ions into the Al<sub>2</sub>O<sub>3</sub> network, the number of acidic sites on the ZnO-Al<sub>2</sub>O<sub>3</sub> surface will increase with the ZnO content in the binary oxides because that promotes the substitution of Zn<sup>2+</sup> ion into the Al<sup>3+</sup> place. When, however, a certain ZnO concentration, corresponding to the maximum Zn<sup>2+</sup> allowed to become a part of the Al<sub>2</sub>O<sub>3</sub> network, is

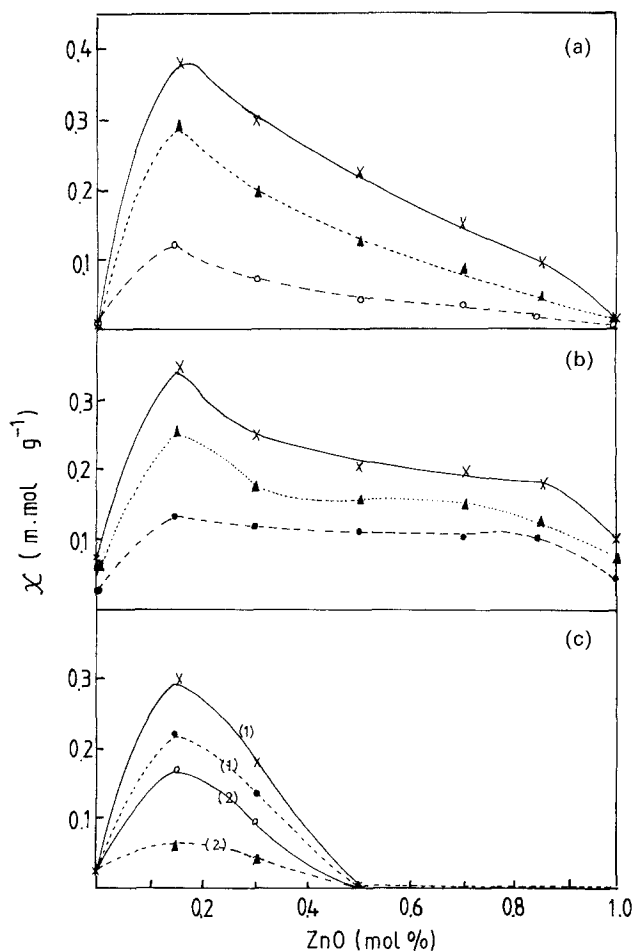


Figure 4 The variation of acidity (expressed as m.mol of n-butylamine per gram of catalyst) with the composition and calcination temperature. (a)  $P^{K_a} = 3.3$  ( $\times$  300°C,  $\blacktriangle$  600°C,  $\circ$  1000°C) (b)  $P^{K_a} = 1.5$  ( $\times$  300°C,  $\blacktriangle$  600°C,  $\bullet$  1000°C) (c) (1)  $P^{K_a} = -3.0$  ( $\times$  300°C,  $\bullet$  600°C) (2)  $P^{K_a} = -5.6$  ( $\circ$  300°C,  $\blacktriangle$  600°C).

reached the excess will precipitate as ZnO, as an independent layer with a lower acidic character than the one of ZnO–Al<sub>2</sub>O<sub>3</sub>. This precipitate of ZnO could even block some acidic sites already formed and make the surface acidity decrease with increasing ZnO content as shown in our results.

The results of surface area measurements, Table I, show a change in the surface area with changing the oxide composition in a manner similar to that obtained in the results of the surface acidity. The surface area shows a maximum value at a composition of 15 mol % ZnO.

Fig. 5 shows the change in the basicity,  $\beta$ , with the composition of the oxides investigated, for  $P^{K_a} = 7.2$ ,

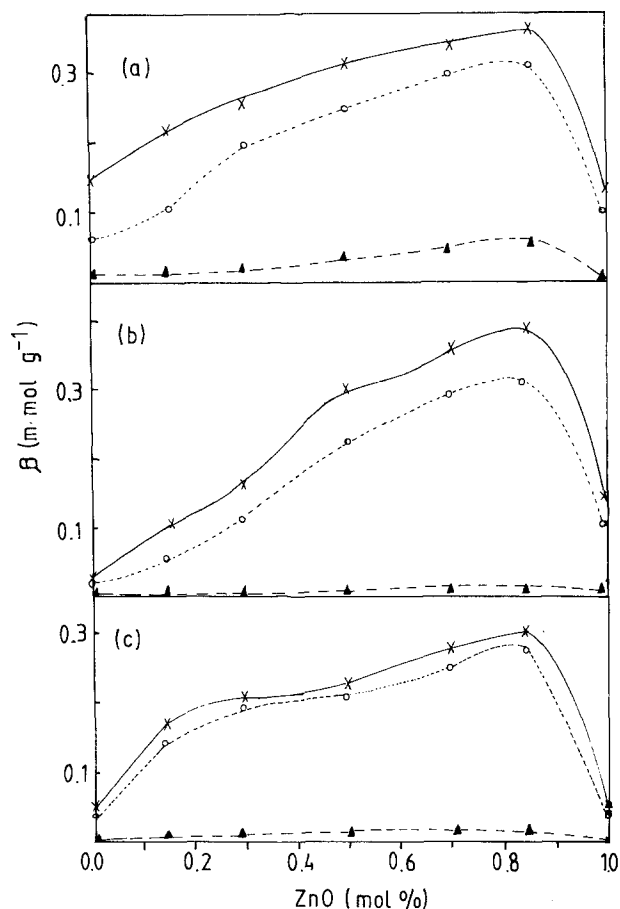


Figure 5 The variation of basicity (expressed as m.mol of benzoic acid per gram of catalyst) with the composition and calcination temperature. (a)  $P^{K_a} = 12.2$ , (b)  $P^{K_a} = 9.3$ , (c)  $P^{K_a} = 7.1$ . ( $\times$  300°C,  $\circ$  600°C,  $\blacktriangle$  1000°C)

9.3 and 12.2. For all indicators used maxima in the intensity of basic sites is shown at 85 mol % ZnO. A decrease in the basicity of the oxides investigated with increasing the calcination temperature can also be seen.

The sample calcined at 1000°C shows a slight change in each of the acidic and basic sites with a change in the composition. This indicates that the addition of ZnO or Al<sub>2</sub>O<sub>3</sub> to the ZnAl<sub>2</sub>O<sub>4</sub> spinel, which is formed at this temperature, does not alter the acidic and basic character of the spinel. Furthermore, it can be said that the acidity and basicity of the spinel and the pure oxides are not greatly different and they are affected by the presence of adsorbed water molecules.

The specific rate constants,  $k$ , determined in the

TABLE I Surface area and kinetic data (at 45°C) of the catalytic decomposition of H<sub>2</sub>O<sub>2</sub> over different composition of ZnO–Al<sub>2</sub>O<sub>3</sub> system.

Calcination temperature (°C)	300		600		1000		600
	$k \times 10^6$ (sec <sup>-1</sup> )	$E$ (kcal mol <sup>-1</sup> )	$k \times 10^6$ (sec <sup>-1</sup> )	$E$ (kcal mol <sup>-1</sup> )	$k \times 10^6$ (sec <sup>-1</sup> )	$E$ (kcal mol <sup>-1</sup> )	
Composition (ZnO mol %)							Surface area (m <sup>2</sup> g <sup>-1</sup> )
0	3.5	7.1	2.3	10.6	1.5	9.8	210
15	5.3	6.0	4.0	6.1	3.0	7.2	270
30	5.5	4.8	5.2	3.7	3.8	4.2	215
50	4.5	5.1	2.7	8.1	2.5	5.1	190
70	5.0	6.0	4.6	7.8	3.6	5.4	176
85	5.5	6.0	4.8	7.8	3.9	6.3	65
100	5.1	7.9	4.2	10.0	3.5	6.3	2.2

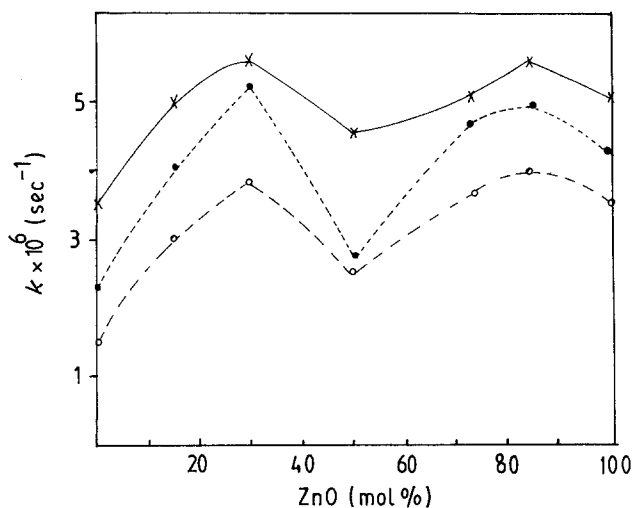


Figure 6 Effect of composition and calcination temperature on the decomposition rate of  $\text{H}_2\text{O}_2$ . ( $\times$  300°C,  $\bullet$  600°C,  $\circ$  1000°C).

experiments carried out on the decomposition of  $\text{H}_2\text{O}_2$  are shown in Table I from which it can be seen that the rate of the decomposition of  $\text{H}_2\text{O}_2$  changes with the composition of oxides; a typical plot is given in Fig. 6. Similar behaviours were observed for each of the calcination temperatures. The  $k$ -values decrease with increasing calcination temperature in the order  $k_{300} > k_{600} > k_{1000}$ . The effect of the calcination temperature on the reactivity of the oxides follows the same trend observed for the acidity and basicity results, where the number of acidic and basic sites on the oxides at 1000°C are lower than those obtained at lower calcination temperatures. From Fig. 6 it can be also seen that the rate of  $\text{H}_2\text{O}_2$  decomposition increases first with increasing the concentration of ZnO to a maximum at 30 mol % ZnO, then decreases to a minimum at 50 mol % ZnO before it increases again to a maximum at 85 mol % ZnO. By comparing the reactivity results with those obtained for acidity (maximum at 15 mol % ZnO), basicity (maximum at 85 mol % ZnO), and surface area (maximum at 15 mol % ZnO) it can be seen that the decomposition of  $\text{H}_2\text{O}_2$  over the oxides with concentration greater than 50 mol % ZnO is attributed to the basic sites present on the surfaces. On the other hand, the reactivity of the oxides containing lower concentration of ZnO (less than 50 mol % ZnO) can be attributed to the increase in their acidity and/or to the increase in their surface area.

Our results show also that the lowest decomposition of  $\text{H}_2\text{O}_2$  occurs for a sample containing 50 mol % ZnO and calcined at 1000°C. It indicates that the  $\text{ZnAl}_2\text{O}_4$  spinel, which is formed in higher concentrations at this temperature and composition, has lower catalytic activity than each of the pure ZnO and the mixed oxides.

The activation energies,  $E_a$ , for the oxides investigated were calculated from the Arrhenus plots of  $\log k$  against  $1/T$ . The  $E_a$  values obtained are given in Table I from which it can be seen that the lowest activation energies for the decomposition of  $\text{H}_2\text{O}_2$  occur at a composition of 30 mol % ZnO. This indicates that the acidic sites present on the oxides surfaces accelerate the decomposition rate of  $\text{H}_2\text{O}_2$  more than

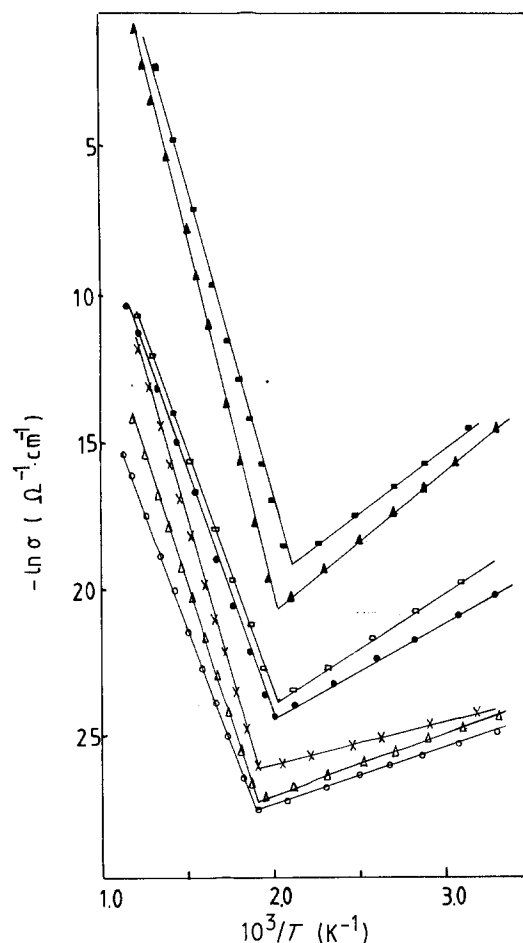
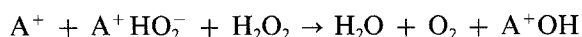
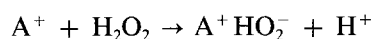


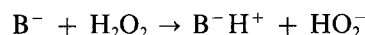
Figure 7 The effect of temperature on the electrical conductivity of the mixed oxides  $\text{ZnO-Al}_2\text{O}_3$  calcined at 300°C. ( $\circ$  0 mol % ZnO,  $\triangle$  15 mol % ZnO,  $\times$  30 mol % ZnO,  $\bullet$  50 mol % ZnO,  $\square$  70 mol %,  $\blacktriangle$  85 mol % ZnO,  $\blacksquare$  100 mol %).

the basic sites. However, the results obtained indicate that the oxides investigated behave an acid-base bifunctional catalysts. According to this concept the following mechanism can be proposed

For acidic sites



For basic sites



where  $\text{A}^+$  are the acidic sites and  $\text{B}^-$  the basic sites present on the surface.

Electrical conductivity measurements may give us information about the type of charge carriers and the phases formed for the different calcination temperatures. Therefore, the electrical conductivity,  $\sigma$ , of calcined samples ZnO,  $\text{Al}_2\text{O}_3$  and their mixtures was measured as a function of temperature in the range 25 to 600°C. The results obtained are represented by plotting  $\ln \sigma$  against  $1/T$ ; a typical plot is shown in Fig. 7 and all the conductivity data are summarized in Table II. The plots of all calcined samples investigated show the same trend. Each plot consists of two straight lines with different slopes. In the lower temperature range the conductivity decreases with increasing temperature due to the elimination of adsorbed water

TABLE II Electrical conductivity data of ZnO–Al<sub>2</sub>O<sub>3</sub> system.

Calcination temperature (°C)	300			600			1000		
	T <sub>b</sub> (°C)	σ*	E#	T <sub>b</sub> (°C)	σ*	E#	T <sub>b</sub> (°C)	σ*	E#
0	260	1.1 × 10 <sup>-11</sup>	27.2	180	9.2 × 10 <sup>-9</sup>	23.8	180	3.7 × 10 <sup>-8</sup>	23.1
15	260	1.4 × 10 <sup>-11</sup>	21.9	180	9.4 × 10 <sup>-9</sup>	19.6	180	1.2 × 10 <sup>-8</sup>	23.5
30	250	4.6 × 10 <sup>-11</sup>	29.3	180	3.4 × 10 <sup>-8</sup>	24.9	180	1.0 × 10 <sup>-7</sup>	23.3
50	220	1.5 × 10 <sup>-9</sup>	30.9	210	5.1 × 10 <sup>-8</sup>	23.4	190	2.5 × 10 <sup>-9</sup>	34.8
70	220	1.8 × 10 <sup>-9</sup>	24.9	180	1.4 × 10 <sup>-6</sup>	21.2	140	6.1 × 10 <sup>-6</sup>	12.9
85	220	1.8 × 10 <sup>-7</sup>	39.2	220	5.0 × 10 <sup>-4</sup>	29.3	120	1.2 × 10 <sup>-8</sup>	18.9
100	210	1.2 × 10 <sup>-6</sup>	32.3	190	5.5 × 10 <sup>-4</sup>	25.1	120	3.7 × 10 <sup>-3</sup>	16.1

E# = activation energy in kcal mol<sup>-1</sup>.

σ\* = electrical conductivity at 400°C in Ω<sup>-1</sup> cm<sup>-1</sup>.

T<sub>b</sub> = temperature at which the break in conductivity occurs.

molecules [20]. On the other hand, in the higher temperature range the conductivity increases with increasing the temperature in an exponential manner, as shown in the semiconducting behaviour. The temperature T<sub>b</sub>, at which the break in σ values appears, shifts to a lower temperature with increasing calcination temperature. This can be attributed to the decrease in the concentration of adsorbed water molecules on the surfaces of the oxides with increasing the calcination temperature. The conductivity data of the pure oxides calcined at 1000°C was found to coincide closely with those reported in the literature [21, 22]. Table II shows that the σ values decrease with increasing concentration of ZnO to minimum at 50 mol % ZnO for the sample calcined at 1000°C. This minimum can be attributed to the lower conduction in ZnAl<sub>2</sub>O<sub>4</sub> spinel, which can be formed in higher concentration at this composition and temperature. The results of the calcined samples at lower temperatures, where ZnAl<sub>2</sub>O<sub>4</sub> is not formed, show that the addition of ZnO to Al<sub>2</sub>O<sub>3</sub> causes an increase in the conductivity values. The substitution of Zn<sup>2+</sup> ions on Al<sup>3+</sup> sublattice gives rise to the formation of the effectively negative defects: Zn<sub>Al</sub><sup>-</sup> and Al<sub>i</sub><sup>3+</sup> (i is the interstitial position). Kröger [22] reported that Al<sub>i</sub><sup>3+</sup> is the principal charge carrier in Al<sub>2</sub>O<sub>3</sub>. Thus, the addition of Zn<sup>2+</sup> ions to Al<sub>2</sub>O<sub>3</sub> causes an increase in the concentration of Al<sub>i</sub><sup>3+</sup> charge carriers and in turn an increase in the conductivity. At the same time, the higher conductivity values observed for the samples containing higher concentration of ZnO can be attributed to the higher mobility of the excess electrons (zinc atoms) present in ZnO lattice [21].

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