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Determination of the Point of Zero Charge of Composite Oxides

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The variation of the point of zero charge (pzc) as a function of dopant concentration in a composite oxide system has been examined. For the model system, titania–alumina, the surface charge development of the composite material varies systematically in accordance with the relative proportion of each of the pure phases in the composite. The pzc of these composites as well as physical mixtures of TiO_2 and Al_2O_3 were determined by mass titration. A model is proposed to explain the results obtained on the basis of a highly dispersed dopant phase. The cluster size estimated from this model is consistent with those estimated by X-ray diffraction analysis. The surface area contributed by each of the individual oxides forming the composite determines the pzc for this composite oxide system. © 1988 Academic Press, Inc.

INTRODUCTION

Metal oxide catalysts are of importance for a number of industrial processes, such as catalytic cracking, dehydration, and partial oxidation (*1–3*). The acidic properties of these oxides are generally thought to play an important role in determining their catalytic properties. As carriers, mixed metal oxides are of particular interest since the number, strength, and type of acid sites can be controlled by varying their composition (*4–6*). Generally, these materials are prepared by coprecipitation procedures and the resulting chemical and physical structures are complex. Recently, Connell and Dumesic reported on the properties of a series of model binary oxides formed by doping a metal oxide at low concentrations onto the surface of a second metal oxide (*7–9*). In an elegant series of papers they used Mössbauer spectroscopy, gaseous base adsorption, and IR spectroscopy to study the relationship between their acidic and structural properties.

In addition to the acid site properties of oxides, it is now well established that certain ceramic carriers can induce strong interactions with a supported metal phase. Systems exhibiting strong metal–support interactions have been designated SMSI catalysts (*10, 11*). Although SMSI carriers have demonstrated beneficial effects, they suffer limitations. Chief among them is that they lose surface area under typical reaction conditions. In an attempt to stabilize the surface area, McVicker and Ziemiak (*12*) prepared composite oxides of TiO_2/Al_2O_3 by procedures similar to those used by Dumesic. They studied the relative oxidation sintering stabilities of Pt and Ir on these mixed oxide systems.

Our interest in composite oxides is their potential use as a class of novel supports for designing metal-supported catalysts with unique properties. A critical step in the preparation of supported catalysts is the deposition of an active ion onto the support. The hydrated surface of an oxide exhibits ion exchange properties and there is a correlation between ion exchange capacity and the net surface charge carried by the oxide (*13, 14*). Oxides exchange cations in environments which result in a net negative surface charge and exchange anions in environments which produce a net positive surface charge. An index of the propensity of a surface to become either positively or

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negatively charged as a function of pH is the value of the pH required to give zero net surface charge. This value is designated the point of zero charge (pzc). It has been reported recently that the adsorption sites for anions and cations are charged surface groups resulting from the protonation–deprotonation equilibria of the surface hydroxy groups of the oxide (*15–17*). Therefore, if the pH of the pzc is known for an oxide, in principle, one can direct preferentially the ion exchange to a specific component of the oxide system.

Dumesic *et al.* suggested that in the limit of dilute binary oxides the major component controls the oxide structure and the dopant surface concentration controls the number of new acid sites. It is tempting to examine if this apparent independent operation of the two phases occurs when the composite oxide is placed in an aqueous environment. A number of years ago Parks suggested that the pzc of a mixed oxide should be related to the values of the pure phases of the two end members (*18*). More recently, Schwarz *et al.* (*19*) demonstrated that, for a series of silica–alumina supports prepared by coprecipitation, indeed, this was the case. The objective of this study is to examine the changes in the pzc of a series of composite oxides as a function of dopant concentration. The hypothesis that the surface charge development of the composite material varies in accordance with the pzc of each of the pure phases, as proposed by Parks and examined independently by Schwarz and Dumesic, is tested. The titania–alumina system has been investigated.

In the sections to follow, we present the experimental findings of this study. A model has been proposed to explain the results obtained; its basis is a highly dispersed second phase on a primary component. The cluster size of the former, estimated from this model, is consistent with those estimated from X-ray diffraction analysis. To determine the pzc of each of the supports, a method we have designated mass titration was used. This method is briefly outlined first.

CONCEPT OF MASS TITRATION

We have observed that when an oxide is placed in solution, the pH of the solution changes in response to the amount of oxide added. In solutions of pH > pzc [the same reasoning applies for pH < pzc], the solid surface will be negatively charged. The surface can be charged negatively either by adsorbing OH^- ions or by desorbing H^+ ions. As a consequence, the pH will decrease on addition of oxide into the solution if the pH of the fresh solution is higher than the pzc. If more oxide is added sequentially, the pH will decrease further in a manner to reduce the difference between the solution pH and the pzc. This difference is, in fact, a driving force for the pH change. The concept of mass titration is illustrated in Fig. 1. Once the pH becomes close to the pzc, where the coverage of H^+ equals the coverage of OH^-, no change in pH will occur because water molecules are dissociated into H^+ and OH^- ions by equal amounts, only to maintain the balance in their equilibrium concentrations on the surface without causing an increase or decrease in the solution pH. Therefore, titrations of water by oxide mass will reach a steady value of pH asymptotically.

The aforementioned considerations can

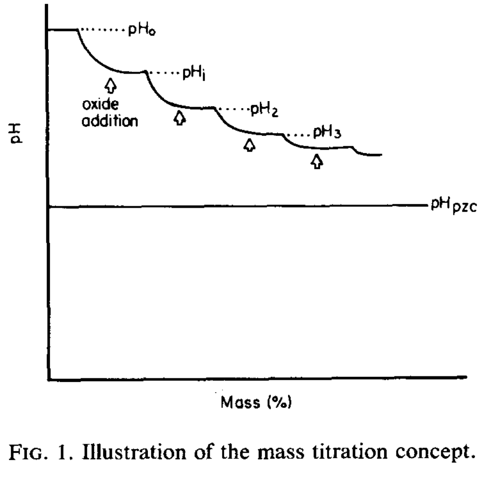

FIG. 1. Illustration of the mass titration concept.

be quantified by considering the surface ionization reactions at the oxide/water interface. The detailed results are reported elsewhere (*20*). It is found that the pH of the solution at "infinite mass" is simply equal to the pzc of the oxide.

EXPERIMENTAL

Two types of composite oxide supports were prepared in addition to physical mixtures of oxides. The physical mixtures were prepared by mixing desired amounts of γ-alumina (American Cyanamid, BET area 195 m^2/g, pore volume 0.484 cc/g) with titania (Degussa Corp., Type P25, BET area 50 m^2/g). Titania on alumina supports was prepared by dry impregnation of γ-alumina with titanium isopropoxide (Alfa Chemicals). The desired weight loadings were obtained by diluting the isopropoxide in toluene. Based on void volume considerations, TiO_2 weight loadings higher than 11.4% could not be obtained. To prepare alumina on titania supports, aluminum isopropoxide (Alfa Chemicals) was dissolved in a desired amount of toluene. In this case, 20 cc of impregnation solution were contacted with 5 g of TiO_2. Here, the solubility of aluminum isopropoxide in toluene limits the Al_2O_3 weight loading to less than approximately 10%. The isopropoxides in both cases were oxidized slowly by drying the composites overnight. The surface areas of the composite supports were stabilized by calcining them for 16 h in air at 823 K. The degree of hydration in general affects the pzc of oxides. Hence, the physical mixtures were also subjected to identical thermal treatment. Bulk TiO_2 transforms from anatase to the rutile structure at temperatures higher than 973 K (*21*).

The point of zero charge of all the oxides was determined by mass titration. This procedure has been described by Noh and Schwarz (*20*). Varying amounts of oxide solids (typical values of oxide/water by weight were 0.01, 0.1, 1, 5, 10, and 20%) were added to water and the resulting pH values were measured after 1 day of equilibration. A Burrel Wrist (Model 75) action shaker was used for this purpose. A Corning (Model 145) pH meter calibrated using pH 4 and 10 buffers was used to measure the pH. The buffer solutions were obtained from Fisher Scientific. All measurements were carried out using air-saturated distilled–deionized water. An open system approach was preferred because of its convenience. It has been shown by Noh and Schwarz (*20*) that the measured pzc (by mass titration) is only slightly affected by the presence of weakly adsorbing ions like CO_3^{-2} and HCO_3^-.

A Debye–Scherrer X-ray powder camera with nickel Cu*K*α radiation (1.542 Å) was used for X-ray diffraction studies. A Kodak direct exposure film was used in all these studies. The studies were conducted on pure Al_2O_3 and TiO_2, as well as selected samples of Al_2O_3 on TiO_2 and TiO_2 on Al_2O_3 composites.

RESULTS

Figure 2 shows a typical plot of pH versus mass percentage of oxide for the pure supports and a physical mixture. The plateau in the mass titration curve is the pH corresponding to the pzc. The values for the pure oxides are in agreement with those

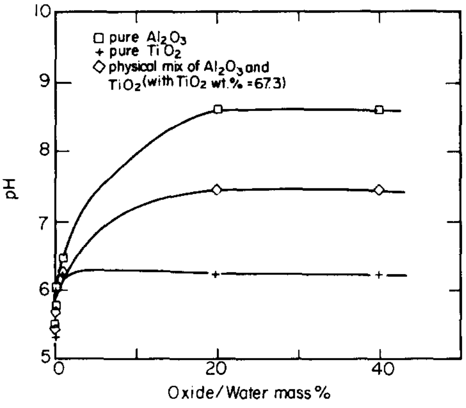

FIG. 2. Plot of pH versus oxide/water mass percentage for (□) alumina, (+) titania, and (◇) physical mixture of alumina and titania [titania mass fraction = 0.673].

TABLE 1

Point of Zero Charge for a Range of Physical Mixtures and Composite Oxides (Al_2O_3 and TiO_2)

% Of area contributed by TiO_2	0	8.1	20.9	34.5	51.1	70.0	90.0	100.0
Mass % of TiO_2	0	25.6	50.7	67.3	80.3	90.1	97.2	100.0
pH_{pzc}	8.30	8.04	7.90	7.46	7.11	6.80	6.40	6.20
pH_{pzc}[a]	6.9–9.5							3.8–7.2
	TiO_2 on Al_2O_3 composite							
TiO_2 weight loading (%)		2.0		5.0		8.0		11.4
pH_{pzc}		8.14		7.91		7.66		7.29
	Al_2O_3 on TiO_2 composite							
Al_2O_3 weight loading (%)	0.5	0.9		1.4	2.7		5.3	7.8
pH_{pzc}	6.90	7.28		7.67	7.72		7.91	8.06

[a] From (*13, 18, 19, 22–25*).

reported in the literature (*13, 18, 19, 22–25*). Table 1 shows the point of zero charge for a range of physical mixture compositions. Also shown are the corresponding mass fractions as well as the surface area contributed by the pure phases.

The results presented in Table 1 demonstrate that the physical mixtures have pzc values between the values for the pure phases. The hypothesis presented earlier was tested at two levels. The pzc values for the physical mixtures were plotted against the mass percentage of the oxide; values were also plotted against the percentage of total surface area contributed by each oxide in the physical mixture. The former showed no simple relationship; the latter results are shown in Fig. 3. A linear relationship (correlation coefficient = −0.99) results when the data are analyzed on an area basis.

In the case of physical mixtures, the BET surface areas of the bulk oxides were used to calculate the percentage of total surface area contributed by each oxide. In the case of composite oxides, the BET surface area of the substrate is known, but a value for the surface area of the dopant is not known. If the area weighting of the pzc values of the pure phases is valid for the intermediate compositions then the results presented in Fig. 3 allow us to determine the surface area of the dispersed phase directly. The results of this analysis are shown in column 3 of Tables 2 and 3. However, the surface area of the dopant in a composite oxide system has not been reported and therefore these values cannot be confirmed. On the other hand, our X-ray diffraction data can be used in conjunction with a model for the dispersed phase to further test the hypothe-

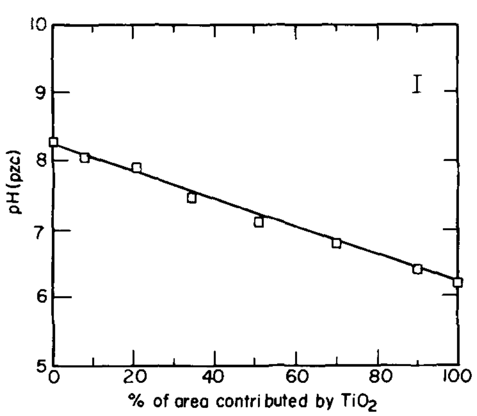

FIG. 3. Plot of pH_{pzc} versus percentage of area covered by TiO_2 for physical mixtures of TiO_2 and Al_2O_3. The cursor length represents the standard deviation in measured pzc values (calculated from replicate pzc measurements of selected oxides).

TABLE 2

Values of *d*, *N*, and *c* for TiO_2 on Al_2O_3 Composites

TiO_2 weight loading (%)	pH_{zpc}	c_f (%)[a] (Fig. 3)	d (Å)	$N \times 10^{-19}$	c_m (%) (model)
2.0	8.14	5.2	7.80	4.24	7.62
5.0	7.91	16.3	12.69	2.46	18.57
8.0	7.66	28.4	14.46	2.66	30.48
11.4	7.29	46.2	13.88	4.29	48.10

[a] c_f = [surface area of TiO_2/(surface area of TiO_2 + surface area of Al_2O_3)] * 100 = % of area contributed by TiO_2.

sis of an area averaged value of the pzc for intermediate compositions of the composite oxides. Specifically, X-ray diffraction analysis carried out on composite supports indicates the impregnated oxide to be very well dispersed even at higher weight loadings (viz., 11.4% TiO_2 on Al_2O_3 and 7.8% Al_2O_3 on TiO_2). McVicker and Ziemiak (*12*) have conducted X-ray diffraction and TEM analysis of TiO_2 on Al_2O_3 composites. On the basis of their X-ray diffraction results they have indicated the crystallite size of the dispersed TiO_2 to be less than 50 Å. The TEM results indicate the TiO_2 surface phase to be very well dispersed. McVicker and Ziemiak suggest that the crystallite size could be less than 10 Å based on TEM measurements. A model is used to estimate the surface area of the dopant. This model depicts a specific geometry for the dispersed phase; qualitatively, it should yield values for the dopant particle size that are consistent with experimental X-ray diffraction results. The model is described in the following section.

DISCUSSION

The pzc for the composite oxide is considered to be the weighted sum (by surface area) of the pure oxide pzcs. Mathematically this can be expressed as

$$\begin{aligned}&\mathrm{pH_{obs}}\ (\text{exposed surface area of substrate} \\ &+ \text{surface area of dopant}) \\ &= \mathrm{pH_{alumina}}\ (\text{exposed surface area of substrate}) \\ &+ \mathrm{pH_{titania}}\ (\text{surface area of dopant}). \qquad (1)\end{aligned}$$

Equation (1) reduces to the limiting conditions in the case of pure oxides; we assume the fraction of the substrate surface covered by the dopant to be inaccessible to the water molecules.

In the following analysis we have considered the titania on alumina composite in detail. A similar analysis can be extended to alumina on titania composites. We assume the dopant to be dispersed as uniformly sized hemispherical clusters. Equation (1) can be written as

$$\begin{aligned}&\mathrm{pH_{obs}}\ [\text{surface area of alumina} + \pi N(d/2)^2] \\ &= \mathrm{pH_{alumina}}\ [\text{surface area of alumina} \\ &- \pi N(d/2)^2] + \mathrm{pH_{titania}}\ [2\pi N(d/2)^2]. \qquad (2)\end{aligned}$$

Here d is the diameter of the TiO_2 cluster and N is the number of such clusters on the alumina surface. It is noted that the bulk surface area of the dopant oxide is not used when it is the dispersed phase on the substrate.

The weight loading can be related to d and N by the equation

$$Q = (2/3) * \pi N(d/2)^3\ \Sigma_{\mathrm{titania}}, \qquad (3)$$

where Q is grams of titania per gram of composite and $\Sigma_{\mathrm{titania}}$ is the density of TiO_2 (anatase) = 3.8 g/cc ($\Sigma_{\mathrm{alumina}}$ = 3.2 g/cc).

Equations (2) and (3) can be solved simultaneously to determine N and d. These quantities can be used to calculate the percentage of area contributed by TiO_2, c de-

TABLE 3

Values of *d*, *N*, and *c* for Al_2O_3 on TiO_2 Composites

Al_2O_3 weight loading (%)	pH_{zpc}	c_f (%)[a] (Fig. 3)	d (Å)	$N \times 10^{-19}$	c_m (%) (model)
0.5	6.90	35.1	5.52	3.55	33.33
0.9	7.28	53.4	5.87	5.32	51.43
1.4	7.67	72.1	6.03	7.62	70.00
2.7	7.72	74.6	11.23	2.28	72.38
5.3	7.91	83.7	18.96	0.93	81.43
7.8	8.06	90.9	25.07	0.59	88.57

[a] c_f = [surface area of Al_2O_3/(surface area of TiO_2 + surface area of Al_2O_3)] * 100 = 100 − % of area contributed by TiO_2.

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$$c_{f,m} = 2\pi N(d/2)^2/\{\text{surface area of } Al_2O_3 + \pi N(d/2)^2\}, \quad (4)$$

where subscript f refers to c calculated from Fig. 3 and subscript m refers to c calculated from Eq. (4). The values of d, N, c_f, and c_m for TiO_2 on Al_2O_3 composites are listed in Table 2. Similar values for Al_2O_3 on TiO_2 supports are listed in Table 3. The agreement between c_f and c_m is satisfactory. The least-squares fit in Fig. 3 uses all the data points obtained from physical mixtures to estimate c_f; c_m is calculated from experimentally determined pzc values of the pure oxides. This explains the slight discrepancy between c_f and c_m.

Bulk titania is a nonporous material; its surface area of approximately 50 m^2/g is a consequence of its relatively small particle size (average particle size is 300 Å). The values for the surface area of TiO_2, calculated from the above model, exceed the value of 50 m^2/g because titania on TiO_2–Al_2O_3 composites is highly dispersed. The values of d are consistently less than 25 Å. X-ray diffraction analysis carried out on composite supports indicates the impregnated oxide to be very well dispersed even at higher weight loadings. This is in agreement with the results of McVicker and Ziemiak (*12*). One may modify Eq. (1) to assume the dopant layer to be transparent to the water molecules; i.e., the dopant does not exclude surface area of the primary phase. This would result in a different set of numerical values for d and N. The value of c obtained in this case would be identical to that obtained from the previous case. This can be explained by the fact that this linear model (Eq. (1)) fits the experimental results to a straight line.

CONCLUSION

In this study, the surface chemistry of composite oxides in contact with water has been examined. The data result in an intensive property of the oxide system. This property value, the pzc, is determined by the surface ionization equilibrium constants of the amphoteric functionalities on the oxide surface. The results suggest that the total number of ionizable sites can be treated as the independent contribution from each of the components and the thermodynamic properties of the dispersed phases retain the same identity as their counterparts in the bulk phases. These assumptions are supported by the fact that the pzcs of both physical mixtures and composites have values that lie between the values for the two pure phases. If these findings can be considered to be applicable to other mixed oxide systems then the method of mass titration and the procedures outlined herein can be viewed as a simple and new technique for surface area determination of supported oxides.

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