

## The Temperature Dependence of the Point of Zero Charge of $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, and Physical Mixtures

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The temperature dependence of the point of zero charge (pzc) of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, and a physical mixture derived from these oxides has been determined. The pzc of these oxides increases with increasing temperature. The heat and entropy changes associated with the hydrolysis reactions for the individual oxides have been determined and the pzc of the physical mixture at different temperatures is predictable on the basis of a simple model. In this model, the pzc of the physical mixture is considered to be the sum of the surface area weighted values for each of the pure oxides (at that temperature). Agreement between experimentally observed quantities and predicted values is found to be satisfactory. © 1989 Academic Press, Inc.

### INTRODUCTION

The exchange of metal ions with oxide surfaces is controlled by several factors; the point of zero charge (pzc) of the oxide is one of them. Recent publications related to catalyst preparation have suggested two methods for regulating the pzc of oxide surfaces (1, 2). The first method involves doping the oxide with low concentrations of either alkali metals or halides. The second method, which is the subject of this research, is to vary the temperature of the supporting electrolyte. It has been proposed that the adsorption sites for negative or positive species are charged surface groups resulting from the protonation-deprotonation equilibria of the hydroxyl groups present on an oxide surface (1, 3-5). The half-sum of the  $pK$ 's of the surface acidity equilibrium constants is equal to the pH corresponding to the pzc (1). Therefore, the relative concentration of positive and negative surface charge carriers can be controlled through the temperature dependence of the surface acidity equilibrium constants.

Mixed oxides are important in many catalyst systems and their surface properties have been shown to be quite complex (6). Model mixed oxides have been discussed in the literature (7). They are generally prepared by doping a pure oxide with a metal compound, decomposing the compound, and finally fixing the metal onto the pure oxide substrate by high-temperature oxidation. These materials have served as a basis for studies which attempt to remove some of the limitations of using mixed oxides prepared by more conventional methods.

A detailed understanding of the surface properties of these compounds is only now emerging (8-11). For example, the surface-area-weighted pzc associated with each phase of a binary composite oxide has been shown to be related to the pzc of the composite oxide (11). A model of the dispersed oxide which allows for an estimate of its surface area has been presented. The basis for this model was a comparison of the pzc of the composite oxides with those obtained from physical mixtures.

In the case of physical mixtures there is no ambiguity about surface areas exposed to the aqueous phase since they can be determined directly from a knowledge of the

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mass fraction of each component in the physical mixture and its own BET surface area. Thus, physical mixtures appear to serve as a good starting point for evaluating other properties of composite oxides.

In light of the earlier discussion, variation of the temperature of the impregnant along with a knowledge of the temperature dependence of the pzc of composite oxides could be a convenient way of effecting exchange of catalytic precursors selectively with a particular component of the oxide. In order to establish a basis for such an approach, the temperature dependence of the pzc of alumina, titania, and physical mixtures derived from these components has been measured. The results will be analyzed by considering the known surface area of each oxide and the temperature dependence of the pzc of each oxide. The predicted temperature dependence of a physical mixture prepared from these materials will be compared with the experimentally determined pzc of that physical mixture. The heat and entropy changes associated with the hydrolysis of the physical mixture have also been evaluated and compared with the experimentally observed quantities.

#### EXPERIMENTAL

The pure oxides used in these studies were  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (American Cyanamid) and titania (Type P25, Degussa Corp.). The physical properties of these materials are listed in Table 1. The small particle size of the titania prevented preparation of mixtures

with the same physical properties. The  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was ground to 40–80 mesh, a standard procedure in our laboratory (average size = 0.225 mm). The oxides were used as received because variations in the pzc that are dependent on the previous thermal treatment of the oxide have been observed (12).

Procedures for determining the pzc of an oxide exist (13, 14). A simple and easily implemented method is mass titration (15). Mass titration determines the pzc by measuring pH values for different mass fractions of solid in fresh water (distilled water free of CO<sub>2</sub>). The pH of the aqueous suspension of an oxide depends on the amount of oxide in a given volume of water; the suspension pH reaches a steady value after addition of excess solid. It is found that the pH of the solution at "infinite mass" is simply equal to the pzc of the oxide (15).

On the basis of the BET surface areas reported, physical mixtures were prepared with approximately equivalent surface areas contributed by each compound. To provide enough sample of a physical mixture for mass titration experiments, approximately 16 g of TiO<sub>2</sub> was thoroughly mixed with 4 g of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

Deionized and distilled water was stripped of CO<sub>2</sub> by heating it (Thermolyne Type 1000 Stir Plate) in a glovebox under a nitrogen atmosphere at 363 K for 2 h. This water was used to prepare seven samples of different oxide to water ratios for each oxide and the physical mixture. The samples prepared in the glovebox were sealed tightly, agitated, and then placed in a constant temperature bath. They were kept in the constant temperature bath for 24 h to equilibrate the oxide/water suspensions. Previous experiments have shown 24 h to be sufficient. The pH of the equilibrated suspension was measured by a Corning Model 145 temperature-compensated pH meter (accuracy  $\pm 0.01$  ph) calibrated by standard buffers at pH values of 4 and 10.

Gravimetric experiments were conducted to evaluate the homogeneity of sam-

TABLE 1  
Properties of Oxide Samples

	TiO <sub>2</sub>	$\gamma$ -Al <sub>2</sub> O <sub>3</sub>
Supplier	Degussa	American Cyanamid
BET area (m <sup>2</sup> /g)	50	190
Specific gravity	3.8	2.9
Average particle size (nm)	30	$0.225 \times 10^6$
Solubility	Negligible	Negligible

ples extracted from the physical mixture. The mass ratio of  $\text{TiO}_2/\gamma\text{-Al}_2\text{O}_3$  of the prepared mixture was approximately 4; it was expected that due to the extreme difference in particle size of the two oxides, when small amounts of this mixture were selected for mass titration, the actual mass ratio would be different from 4. Truly representative samples of the physical mixture were expected at higher values of total mass. Simple filtering/weighing experiments confirmed this hypothesis. Increasing amounts were drawn from the homogenized physical mixture and placed on a series of 40–80 mesh screens, and the fines were collected and weighed. The results are shown in Table 2. There is a significant deviation from the desired mass ratio at low total-sample weights, but this divergence decreases as the sample size increases.

### RESULTS

The mass titration results are presented in Figs. 1–3 for  $\gamma\text{-Al}_2\text{O}_3$ ,  $\text{TiO}_2$ , and the physical mixture at each of the temperatures studied, respectively. The pH values increase with increasing mass percent of  $\gamma\text{-Al}_2\text{O}_3$  and decrease with increasing mass percent of  $\text{TiO}_2$ , and in both cases the pH values reach a plateau at  $\sim 20\%$ , oxide/water. The pH values at the plateau, designated  $\text{pH}_\infty$ , increase for both pure oxides as the temperature of the supporting electrolyte increases.

TABLE 2  
Results of Sampling of Physical Mixture

Sample size (g)	% of $\text{Al}_2\text{O}_3$ and $\text{TiO}_2$ in the sample	
	Trial No. 1	Trial No. 2
0.015	4% $\gamma\text{-Al}_2\text{O}_3$ 96% $\text{TiO}_2$	8% $\gamma\text{-Al}_2\text{O}_3$ 92% $\text{TiO}_2$
0.15	13% $\gamma\text{-Al}_2\text{O}_3$ 87% $\text{TiO}_2$	14.7% $\gamma\text{-Al}_2\text{O}_3$ 85.3% $\text{TiO}_2$
1.0	16.5% $\gamma\text{-Al}_2\text{O}_3$ 83.5% $\text{TiO}_2$	17.3% $\gamma\text{-Al}_2\text{O}_3$ 82.7% $\text{TiO}_2$

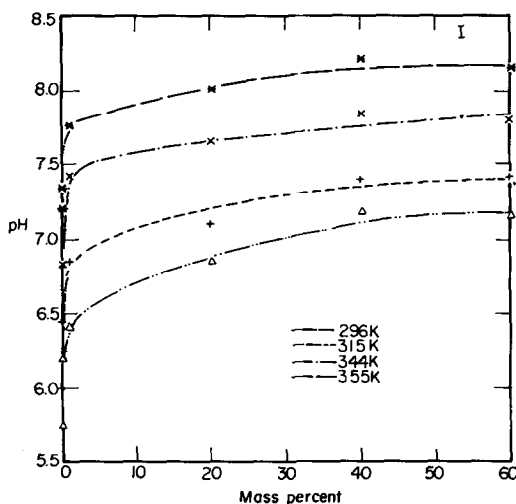


FIG. 1. Mass titration curves for  $\gamma\text{-Al}_2\text{O}_3$  at four different temperatures. The cursor length represents the standard deviation in measured pH values.

The mass titration results for the physical mixture (Fig. 3) show a behavior that is not consistent with theory (15). Regardless of the temperature, they show an initial decrease at low mass fractions, followed by a steady increase, and finally saturation at higher mass fractions. Recall that sampling errors at low mass fractions of oxide were expected to occur in this system. The data

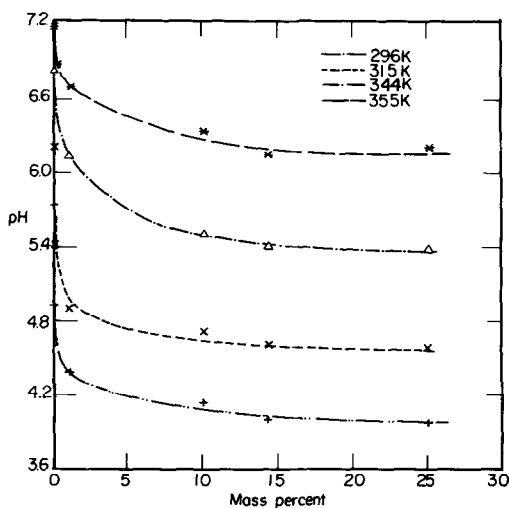


FIG. 2. Mass titration curves for  $\text{TiO}_2$  at four different temperatures.

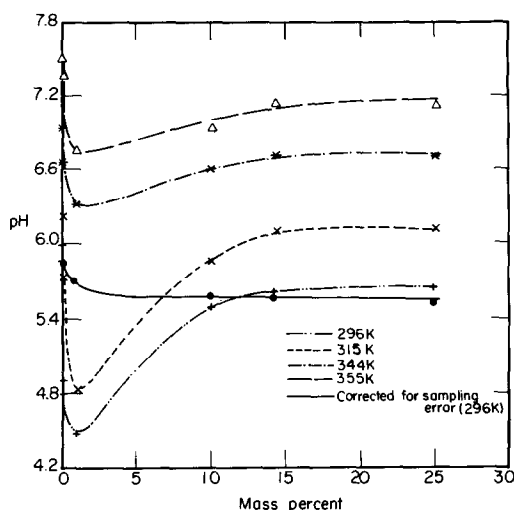


FIG. 3. Mass titration curves for the physical mixture at four different temperatures. Solid line drawn for data at 296 K corrects for sampling errors due to differences in particle sizes of oxides. See text for details.

at 296 K were corrected using the results presented in Table 2. The basis for this correction was that it was previously shown that the pzc of a physical mixture at 296 K is well represented as the sum of the contributions from each oxide weighted by its BET surface area (11). When this was done the results align themselves with a more expected behavior as shown by the solid line in Fig. 3. It was assumed that similar proce-

dures applied at the other temperatures would correct for the sampling errors.

The values of  $\text{pH}_\infty$  for each temperature are the pzc at that temperature. These values are summarized in Table 3 for each of the samples at all the temperatures; pzc values determined by potentiometric titration at 296 K are also presented in Table 3 to establish the reliability of the mass titration results.

#### DISCUSSION

The temperature dependences of the pzc of several oxides and hydroxides have been reported in the past (2). In some cases a slight decrease of the pzc with increasing temperature has been observed (2, 16). These discrepancies have been explained on the basis of the models used for calculation of the thermodynamic parameters for the transfer of  $\text{H}^+$  and  $\text{OH}^-$  from the bulk solution to the interfacial region (2). The mass titration method makes no assumptions about the structure of the interfacial layer and thus should be free from these complications.

Other factors could account for deviations observed between laboratories. For example, Lycourghiotis and co-workers (2) determined the temperature dependence of the pzc of an alumina sample by potentiometric titration. The alumina used in their study was a Houdry alumina with a specific

TABLE 3  
pzc of Oxides at Different Temperatures

Oxide	pzc at different temperatures (determined by mass titration) <sup>a</sup>				pzc at 296 K <sup>a</sup> determined by potentiometric titration
	296 K	315 K	344 K	355 K	
$\text{Al}_2\text{O}_3$	7.2	7.4	7.8	8.2	7.8
$\text{TiO}_2$	4.0	4.6	5.4	6.2	4.4
Physical mixture of $\text{Al}_2\text{O}_3$ and $\text{TiO}_2$	5.7	6.1	6.7	7.1	—

<sup>a</sup> pH values reported to one significant figure.

surface area of  $\sim 125 \text{ m}^2/\text{g}$ . Prior to measurement they calcined their alumina at 873 K for 12 h. Due to the use of a different source material and the extensive thermal pretreatment, it was expected that the results presented here would agree only qualitatively with those reported earlier. Indeed this is the case. They observed that the pzc varied from 5.3 at 296 K to 9.0 at

323 K, while the results of this work show that the pzc changes from 7.2 to 7.6.

Figure 4 shows the variation in pzc with temperature for  $\gamma\text{-Al}_2\text{O}_3$ ,  $\text{TiO}_2$ , and a physical mixture prepared to have equivalent BET surface areas of each oxide in contact with water. The solid line has been drawn assuming that the pzc at each temperature is given by

$$\frac{\text{pzc of physical mixture}}{\text{pzc of mixture}} = \frac{\left(\text{amt. of Al}_2\text{O}_3\right) \left(\frac{\text{surface area of Al}_2\text{O}_3}{\text{Al}_2\text{O}_3 \text{ per gram}}\right) \left(\frac{\text{pzc of Al}_2\text{O}_3}{\text{Al}_2\text{O}_3}\right) + \left(\frac{\text{amt. of TiO}_2}{\text{of TiO}_2}\right) \left(\frac{\text{surface area of TiO}_2}{\text{TiO}_2 \text{ per gram}}\right) \left(\frac{\text{pzc of TiO}_2}{\text{TiO}_2}\right)}{\left(\text{amt. of Al}_2\text{O}_3\right) \left(\frac{\text{surface area of Al}_2\text{O}_3}{\text{Al}_2\text{O}_3 \text{ per gram}}\right) + \left(\frac{\text{amt. of TiO}_2}{\text{of TiO}_2}\right) \left(\frac{\text{surface area of TiO}_2}{\text{TiO}_2 \text{ per gram}}\right)} \quad (1)$$

The experimental results and those predicted by this simple model are in excellent agreement over the entire temperature range. This suggests that in the case of a physical mixture, the area exposed to the aqueous phase by each component of the oxide controls the equilibrium bulk proton concentration. This occurs in a simple additive fashion determined only by the acidity constants of their amphoteric surface hydroxyl groups.

The  $\text{pH}_\infty$  is equal to the half-sum of the  $\text{p}K$ 's of the surface acidity equilibrium constants,

$$\text{pH}_\infty = \frac{1}{2}[\text{p}K_1 + \text{p}K_2] \quad (2)$$

Using the principles of chemical thermodynamics (2), Eq. (2) can be rewritten as

$$\text{pH}_\infty = 1/4.606R(\Delta H^\circ/T - \Delta S^\circ), \quad (3)$$

where  $\Delta H^\circ = \Delta H_1 + \Delta H_2$  is the sum of the enthalpy changes associated with the hydrolysis reactions and  $\Delta S^\circ = \Delta S_1^\circ + \Delta S_2^\circ$  is the sum of the entropy changes associated with the hydrolysis reactions.

van't Hoff plots were constructed for the different oxides and  $\Delta H^\circ$  and  $\Delta S^\circ$  values obtained from the slope and intercept are shown in Table 4. Since the pzc of the physical mixture follows an area-weighted sum of the values of the pure components (Eq. (1)), and the pzc of the pure component is also equal to the half-sum of the surface acidity equilibrium constants (Eq. (2)), it is reasonable to expect the thermodynamic properties of the physical mixture,  $\Delta H^\circ$  and  $\Delta S^\circ$ , to be the area-weighted sum of the corresponding thermodynamic properties of the pure oxides,

$$X_{\text{physical mix}} = \frac{\left(\frac{\text{amt. of Al}_2\text{O}_3}{\text{Al}_2\text{O}_3}\right) \left(\frac{\text{surface area of Al}_2\text{O}_3}{\text{Al}_2\text{O}_3 \text{ per gram}}\right) (X_{\text{Al}_2\text{O}_3}) + \left(\frac{\text{amt. of TiO}_2}{\text{of TiO}_2}\right) \left(\frac{\text{surface area of TiO}_2}{\text{TiO}_2 \text{ per gram}}\right) (X_{\text{TiO}_2})}{\left(\frac{\text{amt. of Al}_2\text{O}_3}{\text{Al}_2\text{O}_3}\right) \left(\frac{\text{surface area of Al}_2\text{O}_3}{\text{Al}_2\text{O}_3 \text{ per gram}}\right) + \left(\frac{\text{amt. of TiO}_2}{\text{of TiO}_2}\right) \left(\frac{\text{surface area of TiO}_2}{\text{TiO}_2 \text{ per gram}}\right)}, \quad (4)$$

where  $X$  is the thermodynamic property ( $\Delta H^\circ$  or  $\Delta S^\circ$ ). The values of  $\Delta H^\circ$  and  $\Delta S^\circ$  estimated by Eq. (4) are shown in columns

3 and 4 of Table 4. The experimental results and those predicted by this simple model are in excellent agreement.

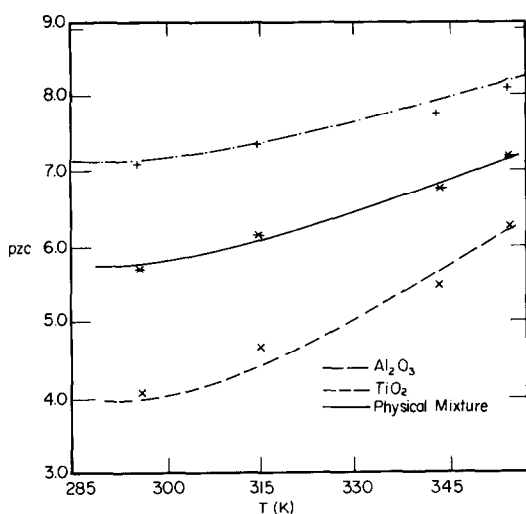


FIG. 4. pzc vs  $T$  (K) curves for alumina, titania, and the physical mixture. Calculated pzc vs  $T$  (K) for physical mixture based on model (see text) shown as solid line.

In the case of a composite oxide it has already been shown (11) that the surface area of the dopant phase can be evaluated by measuring the pzc of composite oxide samples of varying composition. Thus, the temperature dependence of a composite oxide of a specific composition can be evaluated from the corresponding values of the pure oxides, the BET surface area of the substrate, and the surface area of the dopant.

A final comment is warranted regarding the observed increase in pzc with increasing temperature for all oxide samples. The van't Hoff plots of the pzc data demonstrate that the sum of the standard-state enthalpies of the surface deprotonations of  $\text{MOH}_2^+$  and  $\text{MOH}$  groups ( $M = \text{Al}$  or  $\text{Ti}$ ) is negative. Thus, the concentration of  $\text{MOH}_2^+$  increases while the concentration of  $\text{MO}^-$  decreases with an increase in electrolyte temperature. The mass titration results do not permit us to say anything about the relative changes in the surface protonation-deprotonation equilibrium constants since the pzc is equal to the  $\text{pK}$ 's of their half-sum.

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TABLE 4

Enthalpy and Entropy Changes Associated with Hydrolysis Reactions

Sample	Experimental results		Estimated from Eq. (4)	
	$\Delta H^\circ$ <sup>a</sup> (kcal/mol)	$\Delta S^\circ$ (cal/mol · K)	$\Delta H^\circ$ (kcal/mol)	$\Delta S^\circ$ (cal/mol · K)
Al <sub>2</sub> O <sub>3</sub>	-16 (0.98)	-119	—	—
TiO <sub>2</sub>	-34 (0.99)	-150	—	—
Physical mixture of Al <sub>2</sub> O <sub>3</sub> and TiO <sub>2</sub>	-23 (0.99)	-129	-25	-134

<sup>a</sup> Correlation coefficient reported in parentheses.

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