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Effects of Some Variables on the Point of Zero Charge of TiO_2-ZrO_2 Double Oxides

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Synopsis. Effects of variables such as acid/base reaction temperature, presence of impurities, method of oxide powder preparation, and calcination temperature on the point of zero charge (p.z.c) were investigated for TiO_2-ZrO_2 (79.41—20.59, wt.%) mixed oxides. The visually determined p.z.c. values were also compared with those arrived at by a computational method to obtain an estimate of the error of determination.

Interfacial charge-transfer reactions play a key role in many chemical process industries[1,2] like ceramic, paint, and catalyst industries. The potentiometric investigations of Bolt,[3] and Parks and de Bruyn[4] confirmed that H^+ and OH^- are the potential or charge determining ions for oxides in aqueous medium. They extended the potentiometric titration data to estimate the surface-charge densities as a function of pH and at the same time to detemine the p.z.c. The p.z.c. is determined from the intersecting point of the surface charge density vs. pH curves with the zero surface charge density line. Difficulties arise in determining the exact location of the point of intersection when different ionic concentrations of the supporting inert electrolyte are considered. The p.z.c. values have been found to depend on several factors such as acid/base reaction temperature,[5] impurities,[6] calcination temperature[7] etc.

The present communication intends to show the effects of (i) acid/base reaction temperature, (ii) cationic and anionic impurities, (iii) methods of preparation, and (iv) calcination temperature on the p.z.c. of a TiO_2-ZrO_2 (79.41—20.59, wt.%) double oxide. The visually determined p.z.c. values have also been compared with those arrived at by a computational method to obtain an estimate of the error of determination.

Experimental

Preparation of Double Oxide Powders. Powder samples (Table 1) of TiO_2-ZrO_2 (79.41—20.59, wt%) were prepared in the following way. Sample TZ-1 was prepared by the thermal decomposition of mixed hydroxides which were coprecipitated from a mixture of aqueous $TiCl_4$ (Riedel-de-Haën) and $ZrO(NO_3)_2$ (BDH) solution with aqueous ammonia solution (BDH). Powders having the particle size range of 74—175 μm (obtained by sieving) were used. Sample TZ-2 was prepared from a mixed alkoxide of $Ti(OPr^i)_4$ (Fluka) and $Zr(OPr^n)_4$ (Fluka) by hydrolyzing with doubly distilled deionized water. The average agglomerated particle size was 3.1 μm. This powder sample was impregnated with aqueous H_2SO_4 (Sample TZ-2A, SO_4^{2-} content 0.40 $mmol\,g^{-1}$) and NaOH (Sample TZ-2B, Na^+ content 0.04 $mmol\,g^{-1}$) solution to observe the effects of impurities on the p.z.c. Sample TZ-3 was prepared from high purity TiO_2 (rutile, National Lead Co.) and $Zr(OPr^n)_4$ (Fluka) by hydrolyzing the latter with water. The average agglomerated particle size of the double oxide was 9.1 μm. Sample TZ-4 was prepared from $Ti(OPr^i)_4$ (Fluka) and pure ZrO_2 (monoclinic, Riedel-de-Haën) by hydrolyzing the former with water. The average agglomerated particle size was 4.0 μm. All the samples were calcined at 500 °C for 3 h in static air unless otherwise mentioned.

Method of Study. A potentiometric titration method described previously by Kita et al.,[8] and Karmakar and Ganguli[9] was used. Briefly, aqueous solutions (200 ml) of 0.004 $mol\,dm^{-3}$ HNO_3+KNO_3 (10^{-1}, 10^{-2}, and 10^{-3} mol dm^{-3}) were carefully poured into beakers containing accurately weighed 1.000 g of the sample powder, and the suspension equilibrated overnight; potentiometric titration against 0.1 $mol\,dm^{-3}$ KOH aqueous solution was carried out with the suspension at 40±0.5 °C (some experiments were carried out at 30, 50, and 60±0.5 °C) under a nitrogen stream to avoid CO_2 contamination from air.

The surface-charge density as a function of pH was estimated from the difference between the titration curves obtained without and with the sample. The p.z.c. values were determined from the common point of intersection of the surface-charge density vs. pH curves for 10^{-3}, 10^{-2}, and 10^{-1} $mol\,dm^{-3}$ KNO_3.

Results and Discussion

The p.z.c.'s of several TiO_2-ZrO_2 (79.41—20.59, wt%) powders were determined following the above described method by varying different parameters and the results have been listed in Table 1. Effects of specific variables are described below in brief.

Effect of Acid/Base Reaction Temperature. The observed p.z.c. values of the Sample TZ-2 indicated decrease with increase in acid/base reaction temperature (in the range of 30 to 60 °C). Such decrease in p.z.c. was apparently caused by the decrease in the relative affinity of the charge-determining ions (i.e. H^+ and OH^-) for the oxide surface with increasing temperature.[5]

The standard thermodynamic functions (ΔH^*=the standard differential heats of transfer of H^+ and OH^- from the bulk solution to the interfacial region, and ΔS^*=the difference in standard ionic entropy of hydration of H^+ and OH^- at p.z.c.) have been calculated ($\Delta H^*=-92.30$ $kJ\,mol^{-1}$ and $\Delta S^*=-343.88$ $J\,deg^{-1}\,mol^{-1}$) from the slope and intercept of the linear plot of ($1/2\ pK_w-pH_{p.z.c.}$) vs. $1/T$ (Fig. 1) following the equation proposed by Berube and de Bruyn.[5] Here ΔH^* is negative, ΔS^* is also negative and numerically $T\Delta S^*$ (of the Gibbs-Helmholtz equation) is greater than ΔH^* which make ΔG^* positive. The temperature dependent ΔG^* values, therefore, suggest that the transferring reactions of H^+ and OH^- from the bulk solution to the interfacial region were not a spontaneous process. The negative ΔH^* value also suggests that the deprotonation process of the surface MOH_2^+ and MOH groups was exothermic.

Effect of Impurity. Samples TZ-2A and TZ-2B con-

Table 1. Computed and Visually Determined $pH_{p.z.c.}$ Data for Different TiO_2-ZrO_2 (79.41—20.59, wt%) Double Oxides

Sample[a)] (For details, see under "Experimental")	Crystal phase	Acid/base reaction temperature °C	Minimum standard deviation considering all the three surface charge density vs. pH curves at the computed $pH_{p.z.c.}/\mu C\,g^{-1}$	Computed $pH_{p.z.c.}$ m	Visually determined $pH_{p.z.c.}$ p	$(p-m)$ pH unit
TZ-1	Anatase	40	9.30	6.88	6.95	0.07
TZ-1[b)]	Rutile, $ZrTiO_4$	40	0.84	10.03	10.10	0.07
TZ-2	Anatase	30	11.15	5.76	5.90	0.14
TZ-2	Anatase	40	9.62	5.49	5.45	−0.04
TZ-2	Anatase	50	10.42	5.20	5.15	−0.05
TZ-2	Anatase	60	7.83	4.85	4.75	−0.10
TZ-2[b)]	Rutile, $ZrTiO_4$	40	3.97	6.09	6.25	0.16
TZ-2A	Anatase	40	10.62	2.33	2.45	0.12
TZ-2B	Anatase	40	11.02	5.63	5.75	0.12
TZ-3	Rutile	40	5.52	4.54	4.45	−0.09
TZ-4	Anatase, Monoclinic ZrO_2	40	6.09	6.03	6.30	0.27

a) Calcined at 500°C for 3 h unless otherwise stated. b) Calcined at 1000 °C for 3 h.

tained intentionally introduced SO_4^{2-} and Na^+ as typical anionic and cationic impurities respectively. The p.z.c. values of the above samples (Table 1) clearly indicated that on impregnation with (i) SO_4^{2-}, the p.z.c. shifted to the lower pH value, and with (ii), Na^+, the p.z.c. shifted to the higher pH value. Several researchers[6,10)] also reported similar trends on single oxides. The SO_4^{2-} apparently greatly increased the amount of surface Brønsted acid sites (any Lewis acid that might form would be transformed to the Brønsted type in an aqueous medium) of the sample TZ-2A, thereby causing a shift of p.z.c. towards the lower pH value. On the other hand, the Na^+ increased the surface basic sites of the Sample TZ-2B due to the neutralization of the acid sites by NaOH, thereby causing a shift of p.z.c. towards higher pH value.

Effect of Methods of Preparation. On comparison of the p.z.c. values among the Samples TZ-1, TZ-2 (40 °C), TZ-3, and TZ-4, it was observed that the p.z.c. depended on the method of preparation and varied in the pH range of 4.45—6.95. The p.z.c. of the anatase containing Samples TZ-1, TZ-2 (40 °C), and TZ-4 remained in a higher pH range than that of the rutile-containing Sample TZ-3. Here the degree of intermixing of the reacting constituents, product homogeneity and the sources of starting materials of samples TZ-3 and TZ-4 were completely different from each other, due to the difference in their methods of preparation (see "Experimental"). Further, the Samples TZ-3 and TZ-4 were obviously less homogeneous than the Samples TZ-1 and TZ-2 (40 °C).

Again, both the Samples TZ-1 and TZ-2 (40 °C) contained the anatase crystal phase, although they were prepared from inorganic salts and metal alkoxides respectively. The excellent chemical homogeneity in mixed oxide systems prepared via mixed alkoxides is well-known.[11)] Samples prepared via inorganic salt solutions, though much more homogeneous than those prepared via solid-solid reactions, are less so than alkoxide-derived ones. They are also less pure because of the presence of dissolved ionic impurities etc. Thus, the differences in the origin of starting materials and mode of preparation are amply reflected in the p.z.c. values.

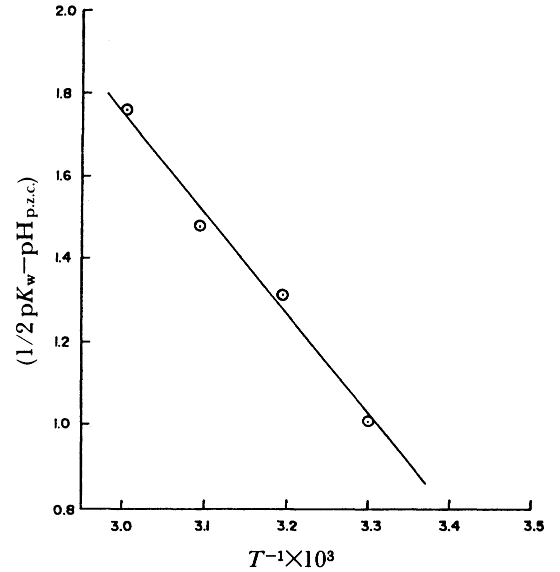

Fig. 1 Plot of $(1/2\,pK_w-pH_{p.z.c.})$ vs. T^{-1} (reciprocal of temperature in Kelvin) for Sample TZ-2.

Effect of Calcination Temperature. The p.z.c. values of TZ-1 and TZ-2 (Table 1) indicated that the p.z.c. of TiO_2-ZrO_2 double oxides shifted to higher pH on calcination at 1000 °C. Important factors responsible for changing p.z.c. with calcination temperature are, e.g. change in crystal structure,[7)] change in the nature of atomic arrangements (i.e. amorphous to crystalline, or separate components to compound formation), dehydration and dehydroxylation etc. In the present case the formation of $ZrTiO_4$ in addition to anatase-rutile conversion should be considered as a

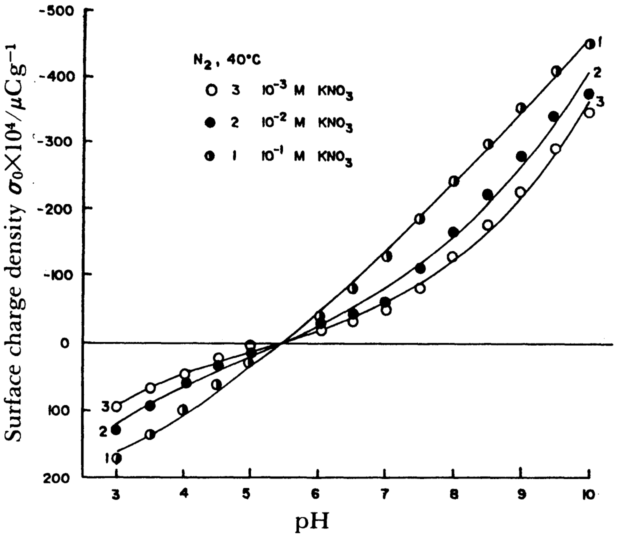

Fig. 2. Experimental and computed surface-charge density as a function of pH for Sample TZ-2 (40 °C). Solid lines are calculated by fitting cubic equations at the minimum standard deviation considering all the three curves; the experimental data points (circles) are shown for comparison.

determining factor.

It is evident from the above discussion that p.z.c. values can be sensitive to various preparative and experimental parameters. However, all such comparisons must ensure a minimum of relative errors in the experimental measurements. To check on this in the present case, where p.z.c. values were determined from the visually estimated cut points of three titration curves at different electrolyte concentrations, cubic equations for the titration curves were set up. The process is described below.

Cubic Equations for Surface-Charge Density vs. pH Curves and Determination of p.z.c. A careful examination of the nature of the experimental surface-charge density vs. pH curve (Fig. 2) showed that this curve having a single inflection point should correspond to cubic (third degree) polynomials.[12,13] For this reason, cubic regression analyses were performed on the experimental points of surface-charge density vs. pH curves and p.z.c. values were determined. The cubic equation (y=surface charge density, x=pH) could be written as:

$$y = A_0 + A_1x + A_2x^2 + A_3x^3 \cdots \quad (1)$$

The values of A_0, A_1, A_2, and A_3, (dependent on both the concentration of supporting electrolyte and the nature of oxide powder considered) were obtained by using a computer program in the following way. Following the theory of p.z.c. two conditions were applied:

(i) At p.z.c., according to the equation[8,14]

$$\sigma_0 = F(\Gamma_{H^+} - \Gamma_{OH^-}),$$

where F is the Faraday constant (C/equiv. wt.), Γ_{H^+} and Γ_{OH^-} are the net adsorption densities of H^+ and OH^- respectively, $y=0$ and x must have a real and positive value.

(ii) All the three curves (of 10^{-3}, 10^{-2}, and 10^{-1} mol dm^{-3} KNO_3) should pass through the point having coordinates of $y=0$, x=single fixed value mentioned in (i).

Standard deviations were computed for all the three curves of σ_0 vs. pH in each set of data, considering a large number of points on the line $y=0$ to be their possible points of intersection. Mean standard deviations were then computed for all such points. The point corresponding to the minimum standard deviation was selected as the point of intersection of the three curves, i.e. the p.z.c. The eleven sets of experimental data on TiO_2-ZrO_2 powders were processed following the above-mentioned procedure and the results have been listed in Table 1. The curves of Sample TZ-2 (40 °C) indicating the difference between the experimental (circles) and the computed (solid lines) points of σ_0 at the corresponding pH values, have been shown in Fig. 2 as an example.

The above diagram indicates the goodness of fit of cubic equations with the experimental points. The differences between the visually determined and the computed p.z.c.'s for the eleven sets of experimental data were found to vary in the range of −0.10 to +0.27 pH unit. These differences arose possibly due to the fact that for visually determined p.z.c., weightage was given to only some experimental points near the p.z.c., whereas for computed p.z.c., uniform importance was given also to the points very much away from the p.z.c. The above differences of p.z.c.'s were, however, not too large in the present case and remained within the errors of measurement.

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