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Monoclinic ZrO₂ Powders. Some Features of the Interfacial Electrostatic Behaviour*

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The paper reports results of both surface charge *vs* pH measurements and of electrokinetic determinations performed on suspension of monoclinic zirconia. The time length of the pre-conditioning of the oxide in the electrolyte (KNO₃) appears to affect the value both of the c.i.p. and of the i.e.p. and to modify the pattern of charge curves. The transition from »fast« to »slow« titrations also introduces remarkable differences in the degree of hysteresis and in the overall trend of charge curves. A common interpretation of these phenomena is proposed considering the high temperature of preparation of the samples and the possible consequent removal of the surface chemisorbed water.

INTRODUCTION

The paper reports some results concerning the interfacial characterization of samples of monoclinic ZrO₂. Zirconia has received much attention as a high temperature solid electrolyte, while results of surface and interfacial characterizations, in room temperature conditions, are limited and concern mainly, the hydrous oxide or the hydroxide¹⁻⁵. This occurs notwithstanding the relevance these aspects may bear to different low temperature applications of zirconia, *i.e.* in the production of ceramics⁶, in catalysis⁷, in corrosion processes⁸. The monoclinic phase is the only stable crystallographic form of the Zr^{IV} oxide up to *c.a.* 1200 °C. Metastable tetragonal and cubic phases happen to form however, in the lower temperature region (from the initial formation of crystalline phases up to *c.a.* 800 °C) together with the monoclinic phase⁹⁻¹¹. High temperatures (900—1000 °C) have therefore to be reached in order to obtain zirconia a pure monoclinic phase.

EXPERIMENTAL

Two different ZrO₂ samples have been used in this work, both high purity commercial samples obtained by calcination of Zr^{IV} compounds in the high temperature region: Sample A, ZrO₂ 99.99% by Aldrich and Sample B, ZrO₂ 99.9% by Ventron.

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All chemicals were of reagent grade quality and used without further purification. Water was purified by means of a Milli-Q apparatus and nitrogen (SIO N 50) was used as the de-aerating means. Charge *vs* pH curves have been determined with the usual »fast« potentiometric titration procedure (save when stated differently) in KNO_3 as the base electrolyte. The first titrations obtained at the lowest KNO_3 concentration (in the alkaline direction and then backwards in the acid direction or *vice versa*) were always discarded and results in the following pertain to subsequent sets of titrations.

Error bars of common intersection points of charge curves (c.i.p.) (Fig. 3) represent the maximum pH distance (averaged on independent experiments) which occurs between the different intersections of the curves obtained at the three ionic strengths (both in the alkaline and in the acid direction).

Isoelectric points (i. e. p.) have been obtained from the point of zero mobility of microelectroforetic mobilities *vs* pH curves. Microelectroforetic mobilities have been determined by means of a Rank Brothers Mark II apparatus. The accuracy of these determinations may not be very high due to different reasons: a) the high polydispersity of the powders, b) possible pH drifts ensuing the transference of the suspension from the outgassed reservoir to the measuring cell, c) possible inaccuracies in the optical determinations of both stationary levels and of the mobilities themselves. Error bars of i. e. p. values (Fig. 3) are based on the reproducibility of independent mobility *vs* pH curves.

Before performing both titrations and electrokinetic determinations, the samples were subjected to conditionings in KNO_3 of variable time lengths. Different values of the pH of the conditioning solution were tested: acid, neutral and alkaline. No effect appeared to be introduced by the different pH values either on the pattern of charge curves or on the electrophoretic mobilities. The following procedure was adopted: the samples were conditioned at spontaneous pH (pH = 7.5) for the first part of the conditioning and then left at pH = 4.5 for the 16 h immediately preceding the test.

NMR measurements have been performed on zirconia (A samples) with the following procedure: the samples have been prepared by cooling the dry powder under vacuum and then diffusing a known amount of D_2O over the sample bed. Changes in the water content were prevented by sealing the hydrated ZrO_2 in glass tubes. Deuterium NMR spectra were recorded on a Bruker WM 300 spectrometer, at a resonance frequency of 46.07 MHz. The use of the quadrupolar echo technique was necessary, as a consequence of the large spectral width required, with two 90 pulses spaced by 30 μs . The relaxation delay was 1 s. Given the small amount of absorbed water and the large width of the spectra, between 50,000 and 100,000 scans were needed to assure a good signal to noise ratio. All measurements were conducted at 20 °C and the temperature was controlled by a BUT-1000 unit with an accuracy of ± 1 °C.

RESULTS

X-ray diffraction proved both A and B samples to be pure monoclinic phases with crystallites dimensions of about 1000 Å. The specific surface area of the samples was obtained by B.E.T. measurements and found to be: sample A = 1.4 m²/g, sample B = 0.66 m²/g.

Fig. 1 reports charge *vs* pH curves of sample A subjected to an overnight (16 h) conditioning in KNO_3 10⁻³ at acid pH (pH = 4.5). The titrations were performed with the usual »fast« procedure with waiting times of 5 minutes between successive additions of acid or base. The alkaline end of the pH range was fixed at pH = 9.8 in order to prevent any possible alkaline dissolution of the oxide and to minimize alkaline errors of the glass electrode. The curves in Fig. 1 are representative of titrations performed both in the acid and in the alkaline direction for each ionic strength. Due to the low degree of hysteresis, points pertaining to alkaline and to acid going runs have been, in fact, interpolated, with a good approximation, by a single curve at each ionic strength. No intersection is apparent between the curves relative to the three

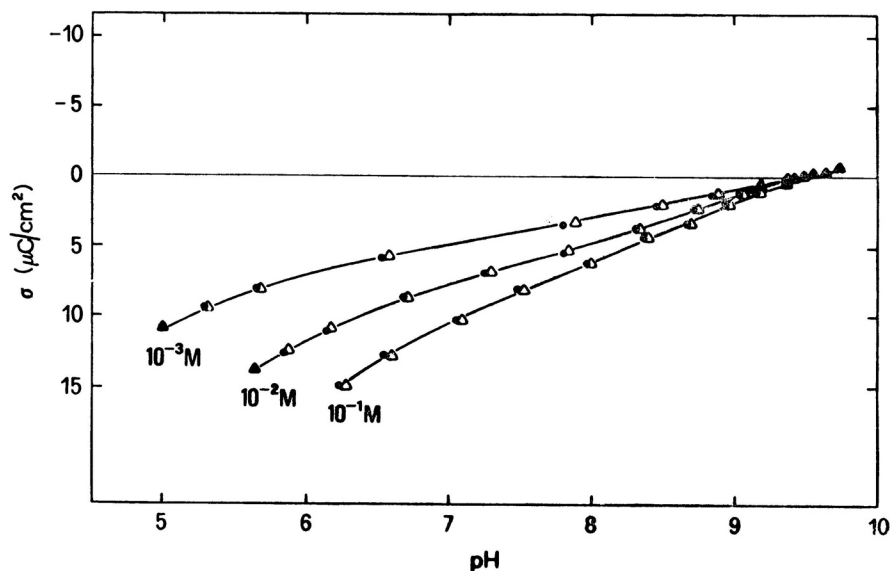


Figure 1. Charge vs pH curves of sample A subjected to an overnight (16 h) conditioning in KNO₃, 10⁻³ M. ● and ▲ refer to titrations performed, respectively, in the acid and in the alkaline direction.

KNO₃ concentrations, the curves merging one into the others for pH > 9.4. Also sample B subjected to 16 h conditioning in the electrolyte shows a picture very similar to the one reported in Fig. 1 the curves merging for pH > 8.8. When the time of equilibration of the oxide in the electrolyte is increased, the pattern of charge curves undergoes significant modifications. As an example Fig. 2 reports charge vs pH curves obtained for sample A subjected to 53 h conditioning in KNO₃, 10⁻³ M. In this case some degree of hysteresis is present at each ionic strength and charge curves, although not showing a common intersection point, definitely cross each other with intersections occurring in a neutral pH range. The pattern of charge curves reported in Fig. 2 is common to all determinations performed on both A and B samples equilibrated in solution for times longer than 16–20 h:

- i) an un-avoidable degree of hysteresis is in any case present between curves obtained in the acid and in the alkaline direction at the same ionic strength.
- ii) the curves obtained at the three KNO₃ concentrations never intersect in a single point and the cross-overs are spread in rather broad pH ranges.
- iii) the pH range of the intersections, although never narrow, apparently undergoes a transition from alkaline to neutral pH values with increasing the time of conditioning of the sample.

Concerning this last item Fig. 3 collectively reports results of common intersection points of charge curves and of isoelectric points (from microelectrophoresis determinations) of both sample A and sample B, subjected to increasing times of conditioning in KNO₃ before beginning the experiments. Although with some scatter and with large error bars, the figure clearly

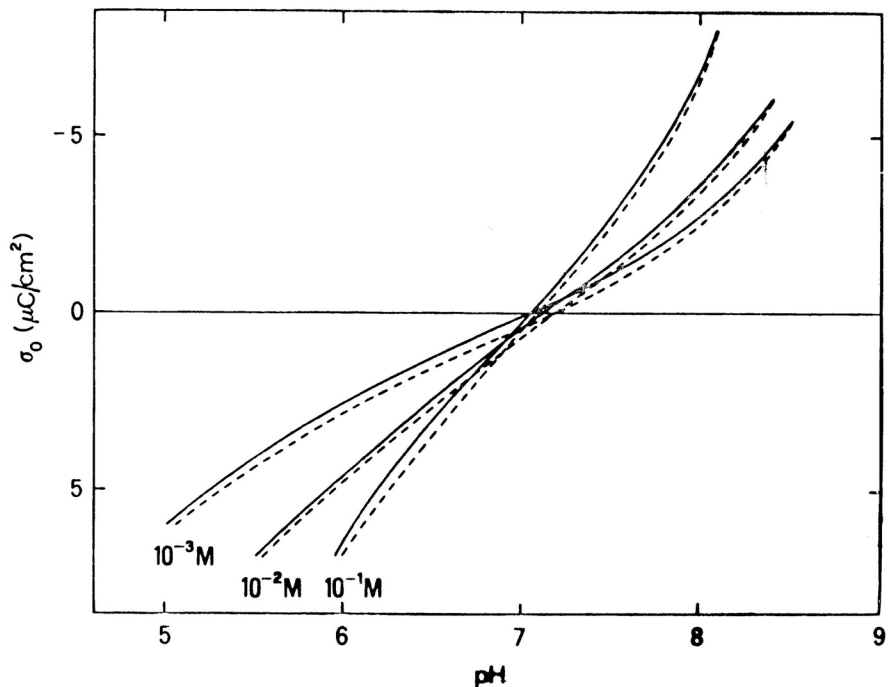


Figure 2. Charge vs pH curves of sample A subjected to 53 h conditioning in KNO_3 10^{-3} M. Titrations have been performed with fast additions (5 min.). Full and dotted curves refer, respectively, to acid and to alkaline going titrations.

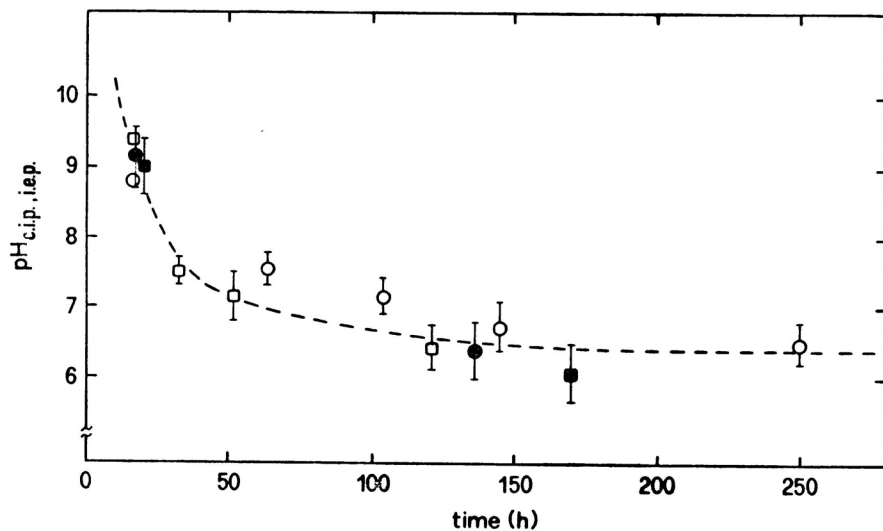


Figure 3. Common intersection points of charge curves and isoelectric points of sample A and B subjected to conditionings of increasing time length
 □ ○ c.i.p. values, sample A and sample B, respectively
 ■ ● i.e.p. values, sample A and sample B, respectively

indicates that the parameters of zero charge progressively shift from alkaline to neutral-acid pH values with increasing the time length of the oxide conditioning in the solution.

The trend of variation of the electrical parameters is not accompanied by a parallel variation of other parameters. NMR spectra obtained on A samples do not show, in fact, any significant variation upon increasing the time length of the contact of the sample with the diffusing D₂O.

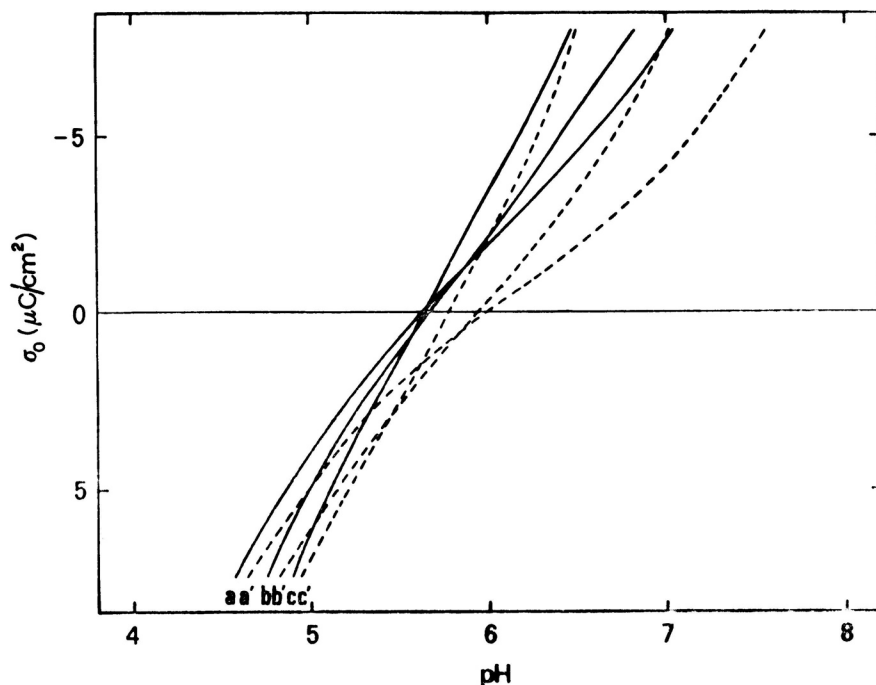


Figure 4. Charge vs pH curves of sample A subjected to 53 h conditioning in KNO₃, 10⁻³ M. Titrations have been performed with slow additions (20 min.). Full and dotted curves as in Fig. 2; a, a' = 10⁻³ M; b, b' = 10⁻² M; c, c' = 10⁻¹ M. For reasons of space the figure does not contain the alkaline end of titrations.

Going back to consider point i), an attempt was made to try to reduce the extent of the hysteresis loops. Instead of performing titrations with fast additions, which might result in non complete equilibrium for the surface reactions, several sets of titrations have been obtained adopting longer waiting times (20 min.) between subsequent additions of acid or base. Fig. 4 reports the case of sample A conditioned 53 h, in order to allow a direct comparison with results in Fig. 2. It can be seen that in the case of »slow« titrations the degree of hysteresis, in contrast with what could have been expected, increases dramatically even at the highest ionic strength, the extent of hysteresis largely exceeding the variation in charge due to the increase in ionic strength. Besides hysteresis other aspects of charge curves in Fig. 4 appear to be anomalous when compared with the trend in Fig. 2. In the case of slow titrations the charge and the slope of charge curves becomes, in fact, much higher than

in the case of fast additions, while the charge variation upon increasing the salt concentration is much smaller (especially at positive charges).

DISCUSSION

Different evidences have to be considered and possibly interpreted within a common frame:

- 1) The c.i.p.'s of charge curves and the i.e.p.'s change from alkaline to neutral in passing from short to long conditionings of the oxide in the solution.
- 2) Hysteresis between acid and alkaline runs is never completely absent.
- 3) In passing from »fast« titrations (5 min. waiting times between subsequent additions) to »slower« titrations (20 waiting time) a definite increase of the degree of hysteresis takes place and the pattern of charge curves is deeply modified.

The possibility to attribute hysteresis and the pH shift of the zero charge parameters to phenomena related to adsorption/release of impurities and/or of specifically adsorbing ions, is to be excluded.

It is in fact well known that specific effects would determine shifts of the c.i.p. of charge curves and of the i.e.p. in opposite pH directions, while in the present case the two parameters move conformingly (although with low accuracies) from alkaline to neutral pH upon increasing the time of conditioning. Incidentally, on the apparent absence of specific adsorption effects, the c.i.p.'s of charge curves are all to be given the meaning of points of zero charge of the zirconia surface¹².

As specific adsorption/desorption effects can be excluded, other factors determining the trend in Fig. 3 are to be considered.

The present samples, in order to be obtained as pure monoclinic phases, had to be prepared by calcination at very high temperatures ($T > 800^\circ\text{C}$) (as a consequence of the formation of metastable polymorphs at lower temperatures). Heat treatments, even at low temperatures, may significantly affect the state of oxide surfaces: more specifically calcinations of oxides at temperatures higher than 800°C are reported¹³ to partially remove the water chemisorbed at the oxide surface, thus rendering the surface less hydrophilic. It could, therefore, be expected that the surface of the present ZrO_2 samples is partially dehydrated by the high temperature of preparation and progressively re-hydrates with increasing the time of conditioning in solution. The trend shown in Fig. 3 is, however, opposite to that expected on a simple transition from an anhydrous surface to the same hydrated surface. An anhydrous oxide surface is in fact expected to show p.z.c. (and i.e.p.) values shifted in the acid direction in comparison with the p.z.c. of the same hydrated oxide. In Park's correlation (2) an »anhydrous« oxide presents a point of zero charge 2 pH units lower than the corresponding »hydrated« oxide. Also more recent results from Morimoto *et. al.* (13) indicate a trend congruent with this expectation: the i.e.p.'s of $\alpha\text{-Fe}_2\text{O}_3$ samples treated at temperatures higher than 800°C shift from acid to neutral pH upon increasing the time of conditioning in the solution, that is upon increasing the hydration of the external layer. The trend shown in Fig. 3 can not, therefore, find a direct explanation on the basis of a simple progressive hydration of the monoclinic ZrO_2 surface. The fact that a process of different nature takes place during the conditioning may be suppor-

ted also by the invariance of the NMR spectra which would, otherwise, appear modified by an increased interaction of the ZrO₂ surface with water.

Penners *et al*¹⁴ suggest that when the surface of an oxide is strongly de-hydrated by a high temperature treatment, the ensuing re-hydration might occur through the formation of an external amorphous or gel-like layer different from the internal crystalline core of the oxide.

It is proposed that the same happens in the present case and that during the time of conditioning the »phase composition« of the surface undergoes a continuous transition; at very short equilibration times (16 h, Fig. 1) the response of the oxide might reflect the behaviour of the crystalline monoclinic zirconia, although, possibly, with surface reactions not fully equilibrated; with increasing the conditioning length, Zr(OH)₄, might form, progressively at the surface, giving rise to a continuous layer shielding the internal oxide core. The i.e.p. and p.z.c. values determined on samples subjected to long conditioning times (pH = 6.5—6.0) agree well with this hypothesis: literature data reported for the i.e.p. and p.z.c. of zirconium hydroxide or of the amorphous oxide are, in fact, all around pH = 6.5(3—5). Zr(OH)₄ is a bulk ion-exchanger (1); if Zr(OH)₄ forms, progressively, at the surface of the samples, its properties might be responsible for the un-avoidable presence of hysteresis between titrations performed in the acid and in the alkaline direction; together with surface ion adsorption/desorption reactions, bulk ion-exchange reactions would, in fact, occur, these latter reactions being intrinsically slower and not reversible on a short time scale. The presence of a slower, not ready reversible reaction is clearly evidenced also by the dramatic effects introduced by increasing the waiting time between successive additions of acid or base (see Fig. 4). The formation, for long equilibration times, of a layer of hydroxide covering the internal oxide core seems therefore quite reasonable; the attribution of the more alkaline p.z.c. (and i.e.p.) values, which occur for short conditioning times, to the intrinsic surface of monoclinic zirconia is instead more difficult to assess. The only literature result concerning a crystalline ZrO₂ with the baddelyite structure (8), indicates pH = 6.5 as the p.z.c. value. These results, however, do not, necessarily, contrast with the present i.e.p./p.z.c. values obtained for short conditionings; the authors in (8), in fact, do not report any detail concerning either conditioning or equilibration times, of the samples before the titrations; a value of p.z.c. = 6.5 may in fact reflect the conditions of a monoclinic zirconia undergone a conditioning comparable to the one of the present, longer equilibrated, samples. Results in (8), therefore, can not bring either positive or negative support to the present results relative to short equilibrations. Following a different approach, a value of point of zero charge for monoclinic zirconia can be obtained by inserting the structural parameters of the heptacoordinated Zr^{IV} in the Yoon equation¹⁵:

$$\text{pH}_{\text{p.z.c.}} = 18.43 - 53.12 (\nu/L) - 1/2 \log \left[\frac{2 - \nu}{\nu} \right]$$

where, $\nu = z/\text{CN}$, is the effective charge on the cation per Me—O bond, z is the cation charge, CN is the coordination number of the cation and $L = r(\text{Me—O}) + r(\text{OH})$.

The value calculated with $L = 3.17 \text{ \AA}$ is $\text{pH}_{\text{p.z.c.}} = 8.65$.

By comparison with the calculated value the attribution of the alkaline i.e.p., p.z.c. values relative to short-conditioned samples (average p.z.c, i.e.p. value = 9.1) to the monoclinic ZrO_2 surface seems not to be unreasonable.

If this were the case, results obtained for short conditionings might be very interesting as they would represent the first data relative to the intrinsic crystalline ZrO_2 surface not modified by the presence of the amorphous hydroxide. As the direct consequence of the short equilibration in water, the values of i.e.p. and p.z.c. obtained after 16 h conditionings, may be expected however, to represent a non completely equilibrated surface still affected by Lewis acid and basic behaviour.

Work is in progress in this laboratory in order to obtain monoclinic ZrO_2 by different procedures not involving a high temperature calcination step.

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SAŽETAK

Monoklinski ZrO_2 prah. Neke osobitosti međufaznog elektrostatskog ponašanja

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Prikazani su rezultati mjerenja površinskog naboja u odnosu na pH, te elektrokinetičkih mjerenja na vodenim suspenzijama monoklinskog ZrO_2 . Dokazuje se da vrijeme predobrade oksida u vodenoj suspenziji utječe na vrijednost kako presjecišta krivulja naboja, tako i izoelektrične točke. Primjenom »brze« (koraci do-dataka od 5 minuta) i »spore« (20 minuta) titracije ukazuje se na postojanje histereze i na promjenu oblika krivulja naboja. Uzrok ovim pojavama nalazi se u načinu pripreve uzoraka kod visokih temperatura (800 °C, kojom se s površine uklanja kemisorbirana voda i površina čini manje hidrofilnom. Proces rehidratacije nakon takve pripreve teče sporo i to putem vanjskog površinskog gel-sloja, različitog od kristalinične strukture u masi oksida.