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Potentiometric mass titrations: a quick scan for determining the point of zero charge

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A novel technique for determining the point of zero charge (pzc), called 'potentiometric mass titrations technique', has been developed and used for determining the pzc of several industrially used catalytic supports (SiO_2, TiO_2, γ-Al_2O_3 and MgO).

The pzc is a very important surface parameter characterizing the acid–base behaviour of the solids, mainly of mineral oxides, in electrolytic suspensions. It is defined as the pH value at which the charge of the solid surface is zero, which means that at this pH the charge of the positive surface sites is equal to that of the negative ones.

Since the pzc is a very useful parameter for many applications, for instance in cases where oxides are used as supports for preparing supported catalysts, a few methods have been developed so far for its experimental determination. The potentiometric titrations technique (PT), the mass titration technique (MT) and the immersion technique (IT) are widely used.[1–5] Each of the above-mentioned methodologies presents several weaknesses. By applying the immersion technique usually low accuracy is achieved (±1 pH unit).[4] On the other hand the mass titration technique demands quite a large amount of the solid, which is not always available, whereas in some cases the polymerization of the solid particles renders the determination quite difficult. Finally, following the most familiar potentiometric titrations technique, the change of the ionic strength presumably, in some cases, influences the surface solubility of the oxide particles and thus their surface characteristics.

In this short communication we present a new technique for determining the pzc. We call this methodology 'potentiometric mass titrations technique' (PMT). This is quite similar to the PT technique. The main difference is that in the PMT technique, the potentiometric curves are determined for three different values of the mass of the oxide immersed in the electrolyte solution, keeping constant the ionic strength of the solution.

In Fig. 1–4 the experimental curves corresponding to the novel PMT technique are illustrated. Four different oxides used in industrial catalysis as catalytic supports with pzc values ranging from 3 to 10.5 have been selected. It may be observed that in all cases the potentiometric mass titrations technique provides a common intersection point at a pH value almost

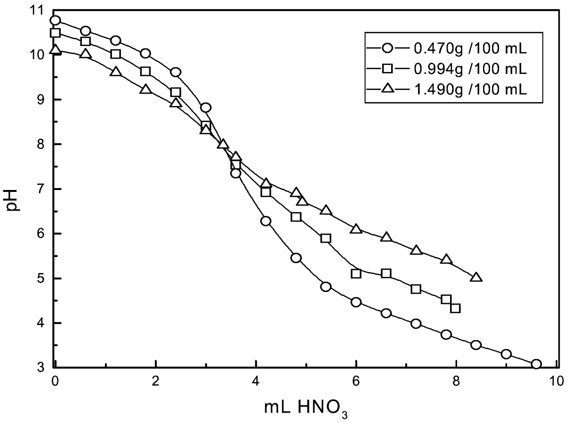

Fig. 1 Experimental curves corresponding to the proposed potentiometric mass titrations technique for the determination of the pzc of γ-Al_2O_3.

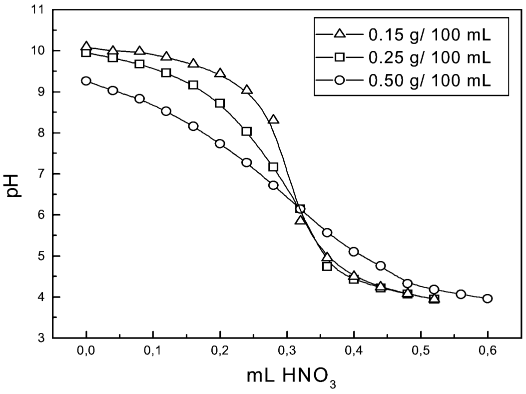

Fig. 2 Experimental curves corresponding to the proposed potentiometric mass titrations technique for the determination of the pzc of TiO_2.

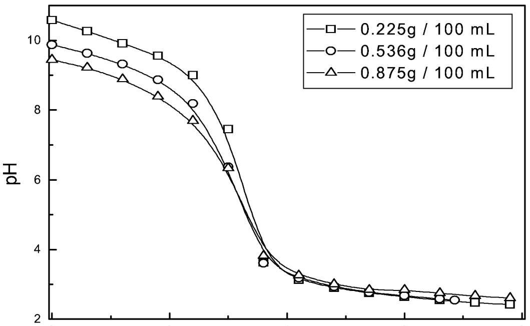

Fig. 3 Experimental curves corresponding to the proposed potentiometric mass titrations technique for the determination of the pzc of SiO_2.

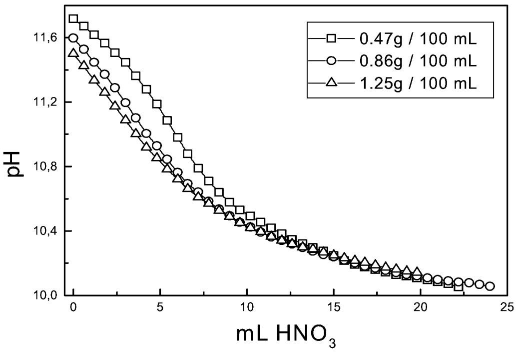

Fig. 4 Experimental curves corresponding to the proposed potentiometric mass titrations technique for the determination of the pzc of MgO.

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identical to that determined in the present study as the pzc, for each oxide, using the traditional techniques (see Table 1). This is the first evidence that the novel methodology may be used for determining pzc.

However, the observation that the PMT technique provides a common intersection point corresponding to the pzc is not sufficient to demonstrate that this technique indeed results in the determination of this parameter. We need, at least, a qualitative interpretation. In order to do this it is necessary to describe briefly the potentiometric titration experiment, taking as an example one of the above studied oxides (see Fig. 5).

Let us start with the solution of the indifferent electrolyte (KNO_3 0.03 M), which we shall call the blank solution. First we regulate the pH of the blank solution at a high value using a given volume of a solution of a base (NaOH 1 M) and then we titrate the blank solution using an acidic solution (HNO_3 0.10 M) which causes the progressive decrease in the pH value (Fig. 5(a)). Repeating this procedure in a suspension containing a fixed amount of γ-Al_2O_3 in the blank solution (Fig. 5(b)), it is necessary to note the following observations.

First, we observed an increase in the solution pH from 5.5 to 7.7 after the immersion of the fixed mass of the oxide and equilibration, under N_2 atmosphere, of the suspension for 24 h. This is expectable because, as the pzc of γ-Al_2O_3 is near to 8, hydrogen ions are moved from the solution and absorbed on the γ-Al_2O_3 surface protonating basic surface sites.

When, in the second step of the procedure, we added to the suspension the same volume of base solution as that added to the blank solution, we observed that, after equilibration, the pH of the suspension was lower than that of the blank solution (compare the starting point of Fig. 5(a) with the corresponding one of Fig. 5(b)). This is because in the case of the suspension the hydroxyls of the base solution have to neutralize the hydrogen ions in the solution, the protonated surface sites created in the first step and in addition to remove hydrogen ions from the surface sites creating basic sites on the γ-Al_2O_3 surface. It is plausible to expect that the difference in the pHs obtained after the addition of the same amount base solution in the blank solution and the suspension should be almost proportional to the number of surface sites (because it depends also on the ratio between the buffering capacities of the oxide surface and bulk solution) and thus to the amount of the oxide in the suspension. This is, in effect, the case; as one may observe in Fig. 1–4. In the third step of the procedure we added small amounts of the acidic solution and measured the resulting pH. It may be seen that the decrease in the pH corresponding to the same amount of the acidic solution added is smaller, for the same pH range, in the suspension (compare Fig. 5(a) with Fig. 5(b)). This is expectable in the pH range above the pzc because the hydrogen ions added in the suspension are consumed not only to neutralize the hydroxyl ions in the solution but in addition, to neutralize the basic surface sites of the γ-Al_2O_3, which predominate in this pH range. Therefore, Fig. 5(a) and 5(b) approach each other and they are intersected at a given pH value. At this point we have to note that the amount of the acidic solution necessary for the given pH value to be achieved is not affected by the presence of the oxide in the suspension. This is strong evidence that this pH value corresponds to the pzc. Beyond this value it is observed that the pH values of the suspension are higher than the corresponding ones of the solution (compare Fig. 5(a) with Fig. 5(b)). This would be expected provided that the above-mentioned intersection point corresponds to the pzc. In fact, at pH values lower than the pzc acidic surface groups are created on the alumina surface consuming thus a part of hydrogen ions added during titration of the suspension. The difference in the corresponding pH values observed between the suspension and the blank solution at pHs lower than the pzc should be almost proportional to the number of the surface acidic groups created and thus to the amount of the oxide contained in the suspension. This is, in effect, the case; as one may observe in Fig. 1–4. The intersection point of Fig. 5 should appear at the same pH value irrespective of the amount of the oxide contained in the suspension. Therefore, it is expected to appear at the same pH value with the common intersection point of Fig 1. Consequently the latter corresponds indeed to the pzc.

From the above it is clear that for a fast determination one may use a methodology corresponding to Fig. 5 instead of the PMT technique corresponding to Fig. 1–4. However, it is obvious that the latter technique offers more accuracy than the former in pzc determination.

Table 1 The pzc values of several oxides measured using various techniques

	pzc values[a] measured by			
Oxide	PT	MT	IT	PMT
Al_2O_3	8.6	8.2	8	8.2
TiO_2	6.3	6.4	6	6.2
SiO_2	3.1	3.3	3	3.1
MgO	10.0	10.8	11	10.2

[a] All pzc values are measured using aliquots from the same sample of each oxide.

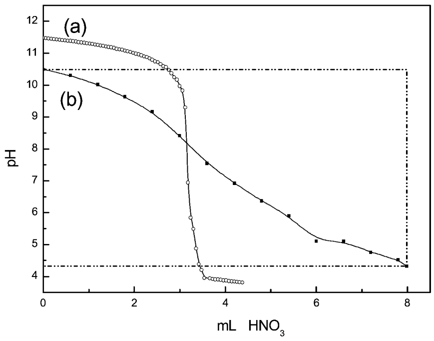

Fig. 5 Potentiometric curves of the blank solution (a) and one (b) taken from Fig 1.

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