Surface charges at the interface oxydic semiconductor/electrolyte solution

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SURFACE CHARGES AT THE INTERFACE OXYDIC SEMICONDUCTOR / ELECTROLYTE SOLUTION

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Different pretreatments of ZnO or TiO₂ leading to significant differences in donor concentrations, do not cause distinct differences in the colloid chemical properties of suspensions of these solids in aqueous electrolyte solutions.

1. INTRODUCTION

The present investigation aims at answering the question, whether changes in the solid state parameters of oxidic semiconductors influence the colloid chemical properties of dispersions of these solids in aqueous solutions.

This question has a two-fold significance:

a. Dispersions of oxidic solids are used a.o. in ceramics. The flow behaviour of such systems is influenced profoundly by the occurrence or absence of coagulation. If the colloid chemical properties of oxides could be influenced by changing the dope concentration, e.g. by pretreatment under reducing or oxidizing conditions, a possibility might be found to affect the flow behaviour of suspensions or pastes of these solids.

b. In colloid chemistry, research has been focused on dispersions containing model solids such as AgI or polystyrene latices. With dispersions of oxides one meets the difficulty, that the low conductivity of oxides frequently prevents the measurement of changes in the overall potential difference over the oxide / electrolyte solution interface. This parameter can be measured for semiconducting oxides, as a shift in the flatband potential.

However, the use of results obtained with semiconducting oxides for interpreting data for the same oxides when isolating, raises the question whether changes in solid state character influence colloid chemical phenomena.

In the present investigation, ZnO and TiO₂ were used as solids. Their solid state characteristics were changed by heating in oxidizing or reducing atmospheres.

2. EXPERIMENTAL materials

ZnO: ex Merck p.a., BET surface area 3.66 m² g⁻¹. It was pretreated by heating in a continuous stream of oxygen (1 atm) at 450 °C for 4 hrs; samples cooled in an O₂ stream are indicated by ZnO/O₂. Treatment with H₂ was restricted to cooling in a H₂ stream in order to avoid pronounced sintering; such samples are indicated by ZnO/H₂. Interstitial Zn, as determined by Norman's method¹⁾, amounted to 6 ppm (= 3 × 10²³ Zn atoms per m³) in ZnO/O₂, and to 75 ppm (= 4 × 10²⁴ Zn atoms per m³) in ZnO/H₂. ESR indicates a significant increase upon cooling in H₂, of the signals at g = 1.965 and at g = 2.003, ascribed to interstitial Zn and O⁻, respectively²⁾.

TiO₂ :

a. ex Merck p.a. (referred to as M808);
 b. ex Degussa p.a. (referred to as DP 25).
 The TiO_2 was pretreated by Soxhlet extraction with water (72 hrs), followed by heating. Pretreatment under oxidizing conditions leading to TiO_2/H_2 , consisted of heating for 20 hrs at 600 °C in a continuous stream of O_2 , and cooling in O_2 ; pretreatment under reducing conditions, leading to TiO_2/H_2 , consisted of heating for 19½ hrs. at 600 °C in a stream of O_2 , followed by 30 minutes heating in a N_2 stream, and by passing finally H_2 during 15 at 600 °C and cooling in a H_2 stream. ESR data confirmed the presence of Ti^{3+} ions in TiO_2/H_2 , by a broad signal at $g = 1.96$ absent in TiO_2/O_2 .

3. METHODS

The methods employed are described in more detail elsewhere ^{3) - 7)}. In short, they consisted of :

a. Measurement of the adsorption of potential determining ions (H^+ or OH^-) at various pH values, by following the amount of HCl or KOH necessary for maintaining the pH at a present value. The net amount of H^+ adsorbed is expressed as surface charge (σ_0 , C.m^{-2}). In those cases where a fast adsorption was followed by a slow process ⁴⁾, values extrapolated to time = 0 were employed.

b. Electrophoresis. Zeta potentials were calculated from the electrophoretic mobilities by the Wiersema-Loeb-Overbeek method ⁸⁾. As particle radius we took the average radius of the primary particles as calculated from the BET surface area for spherical particles.

c. Coagulation kinetics were investigated for ZnO in a stirred cylindrical vessel ^{3, 5)} (diameter 15 mm) containing a magne-

tic stirrer, in 10 ml of the suspension.

At a stirrer speed of 700 rpm, light extinction ($\lambda = 486 \text{ nm}$) was followed as a function of time. Directly before the coagulation experiment, the ZnO was dispersed by ultrasonic treatment;

$$-\frac{1}{E_0} \left(\frac{dE}{dt} \right)_{t \rightarrow 0},$$

with E = extinction, was taken as a measure for the coagulation rate.

For TiO_2 , a simpler method giving comparative data only was employed ^{4) 7)}: in a suspension at rest, light extinction ($\lambda = 440 \text{ nm}$) was measured directly after ultrasonic treatment (E_0) and two hours later (E_2). The ratio E_2/E_0 was taken as a measure of the stability of the suspension.

4. RESULTS

Fig. 1 shows the surface charge (σ_0) vs. pH for ZnO/O_2 and ZnO/H_2 in 10^{-2} M KCl solutions.

Fig. 1.
 Surface charge vs. pH for ZnO/O_2 (X) and ZnO/H_2 (O) in 10^{-2} M KCl.

Differences in pretreatment do not lead to noticeable differences in surface charge: neither the point of zero charge (pzc) nor the slope $d\sigma_0/dpH$ is changed significantly.

Fig. 2 shows similar results in 10^{-3} M KCl solution. The peak near $pH = 8.6$ is related to impurities in the ZnO, notably to foreign cations desorbed from the ZnO leading to saturation of the solution towards the hydroxides of these cations (when the ZnO is added in two portions, the peak values are observed on addition of the first portion). Again, no change is effected by pretreatment of the ZnO under reducing conditions. The pzc in 10^{-3} M KCl is shifted towards lower pH values when compared with the pzc in 10^{-2} M KCl, indicating chemisorption of chloride ions. But this pzc shift is not affected by pretreatment under reducing conditions; thus, Cl^- chemisorption is not noticeably influenced by reducing pretreatment.

Fig. 2.
Surface charge vs. pH for ZnO/O₂ (X) and ZnO/H₂ (O) in 10^{-3} M KCl.

Similar observations were made about the coagulation rate (in 10^{-2} M KCl solutions): the coagulation rate is determined by the zeta potential irrespective of the pretreatment (fig. 3).

Fig. 3.
The initial coagulation rate as a function of the zeta potential in 10^{-2} M KCl, for ZnO/O₂ (O) and for ZnO/H₂ (X).

Thus, the Hamaker constant describing the attraction between particles in suspension⁹⁾ is not influenced to a noticeable degree by changes in the pretreatment procedure.

For TiO₂, however, under some circumstances an influence of pretreatment is found: for TiO₂ M808, a systematic shift of σ_0 at a given pH, towards more positive values is found for TiO₂/H₂ as compared with TiO₂/O₂ (fig. 4). The zeta potential is not influenced (fig. 5); thus all differences effected by a reducing pretreatment are compensated behind the electrokinetic slipping plane, by additional adsorption of counterions or desorption of cations.

Fig. 4.

Surface charge vs. pH for TiO_2/O_2 (O) and TiO_2/H_2 (X) in 10^{-2} M KNO_3

On closer inspection, the shift of σ_0 on reduction towards more positive values appears not to be a property of the TiO_2 itself: for TiO_2 DP 25, practically identical σ_0 (pH) relationships are found with TiO_2/O_2 and TiO_2/H_2 (fig. 6).

From analysis of the wash-water obtained during Soxhlet extraction, it appeared that TiO_2 M808 is contaminated by SO_4^{2-} ions while no such contamination was found in TiO_2 DP 25. If on reduction, sulfide ions are formed and if these are strongly chemisorbed, they will promote H^+ adsorption and counteract OH^- adsorption. This results in the observed shift of σ_0 towards more positive values.

Fig. 5.

Zeta potential vs. pH for TiO_2/O_2 (O) and TiO_2/H_2 (X) in 10^{-2} M KNO_3 (TiO_2 : M 808).

Fig. 6

Surface charge vs. pH for TiO_2/O_2 (●) and TiO_2/H_2 (○) in KNO_3 solutions (TiO_2 : DP 25).

Alternatively one could think of Fe^{3+} as a contamination in TiO_2 M808; on reduction Fe^{2+} or Fe will be formed.

A stronger desorption of Fe^{3+} than of Fe^{2+} could explain the σ_0 shift; however, no iron could be detected in the wash water by Atomic Adsorption Spectroscopy (detection limit 2×10^{-6} mol/l).

The observations with regard to the stability of the TiO_2 DP 25 dispersions are summarized in fig. 7.:

no difference between $\text{TiO}_2 / \text{O}_2$ and $\text{TiO}_2 / \text{H}_2$ is found.

Fig. 7.

Stability of TiO_2 dispersions vs. pH
 TiO_2 : DP 25. (X) $\text{TiO}_2 / \text{O}_2$; (O) $\text{TiO}_2 / \text{H}_2$.

5. DISCUSSION

Taken at their face value, the data obtained in the present investigation indicate that the colloid chemical parameters concerned (surface charge, net charge behind the electrokinetic slipping plane and Hamaker constant) are rather insensitive towards the donor concentration.

The possibility cannot be excluded, that during cooling after the reduction, a surface layer is reoxidized by a contaminant

in the H_2 employed (e.g., H_2O). This should make us cautious to draw the conclusion mentioned with regard to the surface charge and the net charge behind the electrokinetic slipping plane: these parameters are expected to be determined predominantly by local conditions near the interface.

An indication against superficial reoxidation of $\text{TiO}_2 / \text{H}_2$ during cooling is, that a significant difference between the surfaces of $\text{TiO}_2 / \text{O}_2$ and $\text{TiO}_2 / \text{H}_2$ was found with regard to the number of hydroxyl groups per unit surface area. This was determined by active hydrogen analysis¹⁰⁾. The values found were : $\text{TiO}_2 / \text{O}_2$: 5.1 ± 0.3 OH groups per nm^2 ; $\text{TiO}_2 / \text{H}_2$: 9.3 ± 0.8 OH groups per nm^2 .

For ZnO , however, no distinct difference was found between ZnO / O_2 (8.3 ± 0.4 OH nm^{-2}) and ZnO / H_2 (8.5 ± 0.2 OH nm^{-2}).

In the case of the Hamaker constant, no significant influence of any surface layer is expected, because the attraction between two particles is made up additively from contributions by the various parts of the particles. Thus the experimental result, that ZnO / O_2 and ZnO / H_2 have, at a given zeta potential, similar coagulation rates (fig. 3) leads to the conclusion, that an increase in interstitial Zn by a factor 10 does not result in a change of the Hamaker constant large enough to cause a distinct change in coagulation rates. A similar conclusion holds for TiO_2 (Fig. 7).

6. CONCLUSIONS

Pretreatment with H_2 at high temperatures, although increasing the donor concentrations in ZnO and TiO_2 significantly, does not lead to changes in the colloid

chemical parameters investigated: surface charge, chemisorption of counterions, net charge behind the electrokinetic slipping plane, and Hamaker constant.

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