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Surface Chemistry of Nanometric Ceria Particles in Aqueous Dispersions

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The oxide/water interface of nanometric ceria particles has been studied through titration of the surface sites. The adsorption and desorption of protons, hydroxyls, and anions have been measured through potentiometry and chemical analysis. It has been found that these processes cause reactions between surfaces. Conversely, the loss of reactive surfaces which results from chemical treatments changes the charge behavior of the dispersions and reduces it to that of the pure fired oxide. © 1993 Academic Press, Inc.

INTRODUCTION

Oxide minerals have reactive surfaces. In aqueous dispersions this reactivity is expressed in two ways: reactions with ions in the aqueous medium, and reactions between two surfaces when they come in contact with each other. This reactivity is important, since it controls the properties of materials made from these dispersions. However, it causes great problems for the characterization of the surfaces.

The reactivity toward ions is fairly straightforward in the case of potential-determining ions (p.d.i.), i.e., H^+ and OH^-. Adsorption of these ions causes the surface to acquire an electrical charge which is responsible for the colloidal stability of oxide dispersions. Adsorption of other ions complicates the surface chemistry, which no longer reflects the intrinsic properties of the oxide/water interface. So far these problems have been addressed by removing all ions other than p.d.i., either through heat or through chemical treatments. Indeed, nearly all studies of oxides in water have used particles with thoroughly cleaned surfaces; with such dispersions, a consistent description of surface chemistry and colloidal stability has been achieved (1).

In general, these treatments cause irreversible transformations of the particle surfaces. Hence, the chemistry of the final surface does not reflect that of the original one. In this sense, these transformations are the "black box" of surface chemistry. This would not matter too much, if it were not for the fact that colloidal stability and surface area may be lost during such transformations. However, colloidal stability

and surface area are the main criteria for the uses of oxide dispersions; therefore it is important to understand the processes through which they may be lost. These processes are reactions between surfaces; they are driven by the surface energy of the oxide in water. They may be prevented if the surfaces cannot reach each other (steric hindrances or long-range repulsions) or if they cannot react (poisoning—the surface energy is lowered by the binding of ions from the solution). The experimental situation depends on the scale of the dispersion.

(a) Micrometric particles usually have rough surfaces; hence, steric hindrances are important and little surface is lost when cancellation of electrical charges allows them to come in contact. Even this loss may be regained when the particles are charged again because the forces which keep particles together are small compared to the forces which push them apart. Thus it is possible to work with dispersions which have a constant surface area.

(b) On the other hand, for particles which are quite small (e.g., nanometric) the situation is extremely difficult: the particles may be individual crystallites with crystal faces which can stick to each other, the total surface energy is huge, and the particles are extremely mobile; hence, their surfaces will react with each other unless they are kept apart or poisoned.

Verwey and Overbeek had already noticed that nanometric particles cannot be kept apart from each other through electrostatic repulsions, because the interaction potentials are smaller than 15 kT (2). Consequently the predicted behavior is that nanometric particles in water should aggregate and react with each other. Still there are known examples of stable nanometric dispersions of oxide minerals. These dispersions are usually synthesized in special ionic conditions (pH and counterions); if they are brought into different conditions they usually lose stability and reduce their surface area through aggregation of the particles. Thus the main properties of the dispersions, stability and surface area, are conditioned by surface chemistry, and in particular by the concentrations of certain ions at the surfaces. On the other hand, the surface chemistry of the original dispersions cannot be studied by

conventional methods since washing the surfaces will cause irreversible transformations with loss of stability and surface area. This double-bind severely restricts the potential uses of nanometric dispersions; it is unlikely that they will find widespread applications until the underlying processes are properly understood.

In this work nanometric dispersions of ceria have been studied through surface chemistry methods. These aqueous dispersions present both types of problems mentioned above. First, the dispersions contain large concentrations of nitrate ions which originate from the synthesis of the particles; these anions play an important role in the stability of the dispersion (3). Second, the surface area of these ceria dispersions decreases when they are submitted to a treatment designed to clean their surfaces.

We report a systematic investigation of the relation between surface chemistry and colloidal stability during the transformations of the surfaces. Surface chemistry was examined according to reactions of the surfaces with different ionic species, i.e., protons, hydroxyls, and anions. Colloidal stability was examined according to the state of the dispersion, flocculation by salt, and redispersion upon dilution of the salt. The basic observation was that raising pH caused irreversible aggregation and transformations of the surfaces. At pH between 2 and 6 there was a release of strongly bound nitrates; this release was accompanied by aggregation of the dispersion. In the range of pH values between 6 and 10 there were no further transformations: the dispersion retained the same surface area, the surfaces remained free of strongly bound nitrates, and yet their p.z.c. (point of zero charge) differed from that of the pure oxide. At a pH above 10.5 the surfaces underwent further transformation which suppressed the sites responsible for the strong binding of nitrates; beyond this point the surface chemistry was the same as for the pure fired oxide. Thus *the dispersion was obtained in three states depending on the extent of chemical treatment applied to it.*

These different states of the surfaces were analyzed according to predictions based on the structures of the surfaces. For ceria crystallites there are three types of surface hydroxyls, which are monodentate, bidentate, and tridentate. Their respective affinities toward proton adsorption can be calculated according to crystallographic data through the MUlti-Site Complexation (MUSIC) model (4). From these affinities we derived accurate predictions for the acid–base behavior of pure ceria and for dispersions which had undergone complete chemical treatments. However, these predictions did not explain the behavior of surfaces which had undergone less extensive chemical treatments. For such surfaces it was found to be necessary to consider not only the binding of protons but also that of nitrates. Once differences in the binding of nitrates were taken into account, it was possible to account for the behavior of these dispersions: release of strongly bound nitrates, aggregation at pH values well below the p.z.c., and shift in the location of the p.z.c. with respect

to the pure oxide. The analysis of these processes demonstrates a strong relation between the surface chemistry of the dispersion and its colloidal stability.

MATERIALS

Colloidal Dispersions

Nanometric ceria particles can be obtained through the precipitation of $Ce^{4+}(NO_3^-)_4$ salt at very low pH (5). The composition of the precipitate is

$$CeO_2(HNO_3)_{0.5}(H_2O)_4. \tag{1}$$
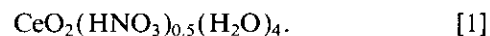
In water it redisperses spontaneously into a colloidal sol which is stable in the pH range 0.5 to 2.5. This sol is transparent with a clear yellow color; examinations through scattering techniques indicate that it is a dispersion of compact, independent particles. The main characteristics of these particles have been determined, i.e., content, size, shape, and internal structure.

Content. From the intensity of scattered light and from the increments of refractive index of the dispersions we have obtained the weight average mass per particle, which is $M_w = 2 \times 10^5$ g/mole. From the small angle X-rays scattering by concentrated dispersions we have obtained the average interparticle distance; from this distance and from the concentration it is straightforward to calculate the number average mass per particles, which is $M_n = 1.4 \times 10^5$ g/mole (6). From the small-angle scattering of X-rays by dilute dispersions we have obtained the volume per particle which is excluded to the solvent; its value is $V = 36000$ Å^3. The comparison of mass and volume yields the density within a particle, which is $d = 6.5$ g/cm^3; this is comparable to the density of pure ceria (7.1 g/cm^3).

Size and shape. The average outer diameter of the particles is larger than the diameter of a dense sphere with the same mass. From the curvature of the small angle X-ray scattering curves we obtained diameters between 50 and 60 Å; from the self diffusion of the particles observed through quasi elastic light scattering we obtained a hydrodynamic diameter, which is 70 Å. The discrepancy between size and content is explained by deviations from spherical shape; indeed the small-angle X-ray scattering curves can be fitted by the curves calculated for ellipsoids with an axial ratio of 0.5. Polydispersity in the size of the particles may also contribute, although it is much less than could have been expected from the small particle size (see the electron microscopy below).

The internal structure of these particles has been studied through X-ray diffraction (7). Precipitates and sols yield broad X-ray lines, and the positions of these lines match the lines of ceria. The average size of crystallites was calculated from the width of these lines; it was found to be comparable with the particle size. Hence the particles must be mono-

crystallites of ceria. Electron microscopy confirms this idea and shows well defined crystallites. Figure 1 shows a network of crystallites with individual sizes in the range 40–60 Å and a lattice image for most crystallites. In nearly all cases the planes which cause diffraction are the 111 reticular planes, spaced by 3.12 Å. Each crystallite shows 10 to 15 of the 111 planes. They appear to reach the outer edges of the crystallites; many edges are straight. Hence the surface layers are crystalline as well and it is appropriate to describe them as crystal faces. Most crystallites are oriented with a set of 111 planes along the beam. This preferred orientation may have two possible causes: either the particles are platelets, and they rest on their largest faces, or there is a preferential interaction between the hydrophilic collodion membrane and one of these faces. Since the anisotropy determined by SAXS is not enough to explain a preferential orientation, the second possibility is more likely.

These particles have a very large surface area: from the Porod limit in SAXS we have obtained $A = 400 \ m^2/g$, or 93 nm^2/particle. This surface can be accounted for if the particles are somewhat anisotropic, e.g., shaped as platelets. For a particle of mass 1.4×10^5 g/mole which contains 800 Ce atoms the measured specific surface requires that 400 Ce

atoms must be at the surface; this is possible if the axial ratio of the particle is ≈ 2. At this stage it is important to remark how the very small size of the particles influences their properties: *every other Ce atom is at the surface,* hence the surface layers are just as important as the particle cores. Also, the composition of these surface layers differs from the cores: indeed, the ratio of nitrates to surface ceriums equals 1, hence *the surfaces are completely loaded with nitrate ions.*

For surface chemistry it is important to know whether these surface layers are crystalline or amorphous. Information on the structure of these layers has been provided by neutron diffraction patterns of precipitates where some of the hydration water was replaced with D_2O (8). It was found that the intensities of diffraction lines vary with the D_2O content of the surface water; hence, the water molecules contribute to the diffraction peaks of the ceria structure. This contribution arises because water molecules are in locations which are coherent with the lattice; consequently there must be lattice sites on the outer surface of the particle. This rules out the existence of amorphous layers on the particle surfaces.

Thus the particles can be described as very small monocrystallites with surfaces which are hydrated and loaded with nitrate ions.
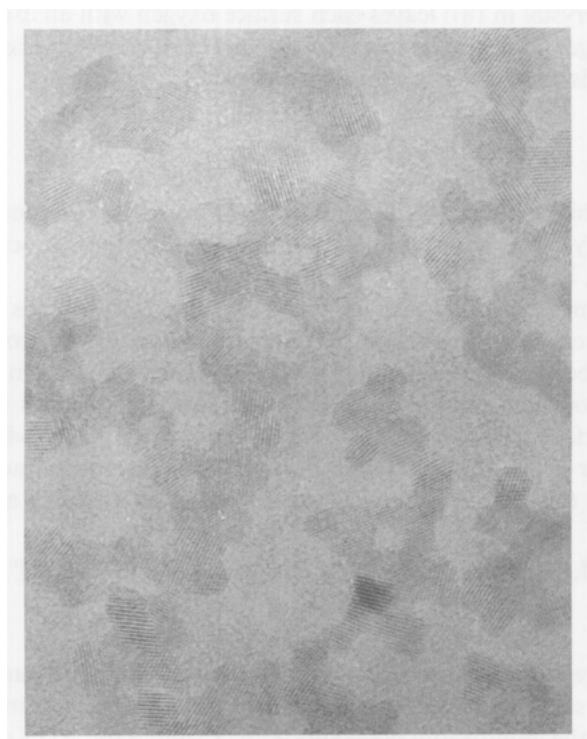

FIG. 1. High-resolution TEM micrograph of a ceria dispersion spread on a membrane and dried in air. Individual crystallites give a lattice image through diffraction from the 111 reticular planes, spaced by 3.12 Å. The crystallite sizes are 4–7 nm; they match the particle sizes obtained through scattering techniques. The crystallites appear aggregated in the micrograph; this is a result of increased concentration during drying; in the original dispersion they are separated.

Ionic Solutions

In the sols the dispersed particles are in equilibrium with ionic species. Most of these are H^+ or NO_3^- ions which originate from the nitric acid which was present during the synthesis of the particles (see [1]).

On the other hand there may also be other ions, in particular Ce^{III} cations or polycations. Indeed, when the original precipitate is dispersed in water, 2% of the cerium is present as Ce^{III} ions. These ions can undergo hydrolysis and obscure or modify the surface chemistry of the dispersions. In order to eliminate them, the dispersions were dialyzed against nitric acid at low pH until the concentration of Ce^{III} ions was below 0.1% of the total cerium, or less than one Ce^{III} per particle. Subsequently the dispersions were titrated to higher pH values; analyses of the supernatants showed that no other free Ce^{III} ions were released during the titrations. Still, it was considered good practice to use the dispersions within a few days of the dialysis; at much longer times (4 months) we noticed that Ce^{III} ions were again present in the supernatants. These ions may originate from a slow dissolution of Ce^{IV} and then reduction.

The standard sol used was a dispersion which had been washed according to these procedures, first with nitric acid and then with water. The final pH of the sol was 3.4, indicating that most of the original H^+ and NO_3^- ions had been removed. The remaining H^+ and NO_3^- ions control the value of the surface charge and the interaction between surfaces; the surface equilibria involving these ions are the main object of this work.

Pure Ceria

Pure ceria was obtained from the colloidal dispersions in the following way. The precipitate was washed with an excess of ammonia (3 mol/liter) and then dried. This treatment cleaned the surfaces of the nitrate ions which were bound to them. Then the powder was heated to 800°C over 2 h. After these treatments the powder was made of larger crystallites and its composition was exactly CeO_2. Its specific surface was 40 m²/g.

METHODS

Potentiometry

Acid–base equilibria at the surfaces of the particles were investigated through titration of the surface groups with either base (NaOH 0.1 mol/liter) or acid ($HClO_4$ 0.1 mol/liter). $HClO_4$ is the natural choice when one is looking for a passive anion. For a base, TMA OH would have been a better choice, but TMA ClO_4 is not a very soluble salt. The instrument was a Metrohm Dosimat "Titroprocessor" where the sample was kept at a temperature of 25°C. The initial conditions for a titration were as follows. The concentration of ceria dispersion was such that its total surface area was 50 m². The ionic strength was fixed with $NaClO_4$, and carbonate ions were removed by bubbling argon gas through the sample for 1 h. After this preparation a flow of argon gas over the surface of the sample was enough to keep the dispersion free of carbonate ions.

At each step of the titration the resulting pH was measured with a combined electrode calibrated at pH 4, 7, and 9. It was important to keep the time scale of the measurement slow compared with the response time of the electrode and with the kinetics of ion exchange near the surfaces. We found that for a large addition of base or acid the response of the system through protonation or deprotonation reactions was completed in less than 5 min; for the titrations we used small additions (80 μl of 0.1 M NaOH or $HClO_4$), and then a waiting time of 2 min was sufficient to ensure a good overlap of the up and down titration curves. Kinetic effects were observed for the reactions occurring at a pH above 10.5; for these reactions the waiting times were increased until the pH of the dispersions had stabilized.

The concentration of free nitrate ions was also measured with a specific electrode. However, this measurement could only be performed in dispersions which did not contain perchlorate ions, because the electrode did not distinguish between ClO_4^- and NO_3^- ions.

Chemical Analysis

The total amounts of Ce^{IV} and NO_3^- ions were measured through specific chemical reactions. Ce^{IV} were titrated by conversion into Ce^{III} and then back into Ce^{IV} through a redox method; NO_3^- ions were transformed to ammonia and then titrated through an acid–base reaction (Kjeldahl reaction).

THEORETICAL CONSIDERATIONS

"MUSIC" Model

The acid–base behavior of surface hydroxyls in aqueous dispersions can be predicted according to the "MUSIC" model developed by Van Riemsdijk and co-workers (4). This model calculates the charge carried by surface hydroxyls through Pauling's definition of formal valence charge. According to this definition, an atom in an ionic crystal gives each of its neighbors a number of electrons equal to $v = Z/CN$, where Z is the valency of the atom and CN its coordination number. The charge of the resulting ion is $Z = nv$, and in a bulk ionic crystal it is exactly compensated by the charges of the neighboring ions.

A free surface may be created by splitting the crystal into two parts; then the coordination of surface atoms will no longer be satisfied. For surfaces in water, the coordination of metal atoms will be completed by oxygens from adsorbed water. However, the coordination of oxygens will be incomplete; if oxygens in the bulk are bound to CN metal ions, and oxygens at the surface to n metals only, then splitting the crystal in two leaves each surface oxygen with an excess charge which is determined by the number CN $- n$ of missing bonds and by the bond valence v:

$$\delta = (-CN + n)v = -2 + nv. \qquad [2]$$

This excess charge is not necessarily an integer because in many crystals the coordination is larger than the valency of ions, hence $v < 1$.

Since the bond valence v of the metal ion includes the influence of other atoms on the particle, the surface groups can be treated as individual surface species isolated from the rest of the particle. At this point the model recognizes that a surface may carry more than one type of hydroxyls, which differ according to the number n of metal atoms bound to each one. The equilibria for each site are then written as

$$M_n-O^{nv-2} + H^+ \leftrightarrow M_n-OH^{nv-1} + H^+ \leftrightarrow M_n-OH_2^{nv},$$
$$[3]$$
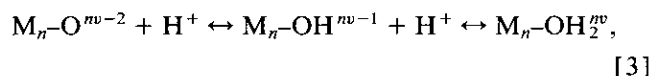
where M_n represents the n metal atoms to which this particular surface oxygen is bound. Here the important point is that the equilibrium constants $K(n, 1)$ and $K(n, 2)$ of sites with different values of n will not be the same.

The next step is to estimate the values of the equilibrium constants $K(n, 1)$ and $K(n, 2)$. For this purpose the free energy of proton adsorption is split into a local electrostatic contribution and a chemical contribution. It is assumed that the chemical contribution is the same for all surface hy-

droxyls in a given dispersion. Then differences between surface sites can originate only from different electrostatic contributions. In the Pauling model the electrostatic term depends only on the formal charge carried by each atom: it contains an attraction between the oxygen and the proton and a repulsion between the metal atoms to which the oxygen is attached. Accordingly the expression for $K(n, 1)$ and $K(n, 2)$ has the form:

$$\log K_{n,1} = A_1^s - B\frac{nv}{L} \quad \log K_{n,2} = A_2^s - B\frac{nv}{L}, \quad [4]$$

where the constants A_1^s and A_2^s contain the chemical terms for the first and second acidity of an hydroxyl at the surface, B is the coefficient of the electrostatic term, and L is the distance between the metal and the proton.

The general validity of such expressions is checked against literature data for the acidity constants of monomers in solution (9). One important feature is that the two successive protonation constants differ by 14 pH units. Because of this difference, only one protonation reaction can occur in aqueous solutions.

Then surface equilibria are considered, and it is assumed that the acidity constants have the same expressions as in solution, but with different values for the chemical term and with values of n which may be higher than unity. The values for A_1^s and A_2^s and B are deduced from measured acidity constants for gibbsite, and L from crystallographic data. Acidity constants for other materials may then be predicted; the important feature is that hydroxyls which are coordinated to more metal ions (higher n) are more acidic.

Application of "Music" to Ceria

The bulk structure of ceria is made of Ce^{IV} ions which are each coordinated to eight oxygens, while each oxygen is coordinated to four ceriums. Thus each cerium distributes its charge ($+4$) over eight oxygens, and the formal bond valence is $v = +0.5$. Now we examine the coordination of cerium and oxygen atoms which are at the surface of a ceria particle. It is assumed that the particle is a single crystal, and that its surface is made of simple crystallographic planes. The planes with the highest atomic density have indices 111, 110, and 100; we assume that these are the only planes present as crystal faces. This choice is confirmed by images of the particles taken through high-resolution electron microscopy. For each one of these faces we define the nature of the sites and calculate the equilibrium constant for proton adsorption.

100 face. Along this face cerium atoms are below the surface, still fully coordinated, but the oxygens are above, each coordinated to two ceriums only. Thus the surface site is Ce_2-O, and according to the definition of formal valence charge this is not a neutral species: if the particle is split
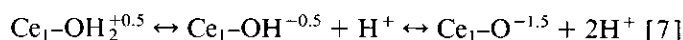
along a 100 face the surface oxygens are left with a charge of -1. They can adsorb protons, and the corresponding equilibria are written:

$$Ce_2-OH_2^{+1} \leftrightarrow Ce_2-OH^0 + H^+ \leftrightarrow Ce_2-O^{-1} + 2H^+ \quad [5]$$
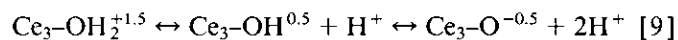
$$pK_{2,2} = 1.0 \qquad pK_{2,1} = 14.8. \qquad [6]$$

This face is almost uncharged in the accessible range of pH; nevertheless, a p.z.c. can be defined as the average of both pK values, and its value is 7.9. The density of surface sites is 6.8 per nm^2.

111 face. The unit cell of this face contains one heptacoordinated cerium and one tricoordinated oxygen. An adsorbed water molecule may split with the hydroxyl binding to a cerium and the proton to a surface oxygen. This process generates two types of surface hydroxyls, with coordinations Ce_3-OH and Ce_1-OH. The surface density of each site is $7.9/nm^2$. The equilibria for each site are:

$$Ce_1-OH_2^{+0.5} \leftrightarrow Ce_1-OH^{-0.5} + H^+ \leftrightarrow Ce_1-O^{-1.5} + 2H^+ \quad [7]$$

$$pK_{1,2} = 10.4 \qquad pK_{1,1} = 24.2 \qquad [8]$$

$$Ce_3-OH_2^{+1.5} \leftrightarrow Ce_3-OH^{0.5} + H^+ \leftrightarrow Ce_3-O^{-0.5} + 2H^+ \quad [9]$$

$$pK_{3,2} = -8.3 \qquad pK_{3,1} = 5.5. \qquad [10]$$

Accordingly, this face is positively charged below pH 5.5, zwitterionic between 5.5 and 10.4, and negatively charged above 10.4. Its p.z.c. is again 7.9.

110 face. The unit cell of this face contains one hexacoordinated cerium and two tricoordinated oxygens. Each cerium can take two hydroxyls from water, giving two Ce_1-OH groups. Each oxygen can take one proton from water, giving one Ce_3-OH site. The surface density of each site is $9.6/nm^2$. The protonation reactions of these sites are the same as for similar sites on the 111 face; the only difference is that the density of sites is higher.

Thus the predicted p.z.c. for every type of face is 7.92, remarkably close to the value measured by Ray et al. (10). However, this average value is not very meaningful because it masks a strong heterogeneity of the surface: one face is cationic at low pH, and zwitterionic at neutral pH, with a very high density of charges; another one has the same behavior but with a lower charge density; finally, the last type of face would be uncharged.

RESULTS

At the origin of this work there was an attempt to measure the surface charge of the nanometric particles through titration of the surface groups with either base or acid. It was found that titrations in the pH range where charge reversal
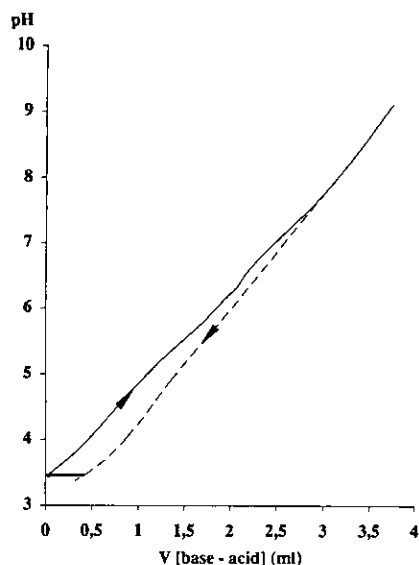
FIG. 2. Raw data from the first cycle of a potentiometric titration. Horizontal axis shows the amount of base or acid used at each step; vertical axis, measured value of the pH after each step. Solid line is the titration with base of a sol initially at pH 3.4; dotted line, return part of the cycle, titration with acid of the basic dispersion. The horizontal distance between both curves corresponds to an excess consumption of hydroxyls during the first leg of the cycle.

was expected could not be performed as cycles, because the colloidal dispersion did not return to its original state. Indeed, the dispersion adsorbed less protons on the way down than hydroxyls on the way up (Fig. 2). This was contrary to the behavior of the pure oxide, for which we found that titration cycles were reversible.

This lack of reversibility may have three possible origins. First, some protonated sites may be lost through a condensation reaction between two surfaces. In this case the difference between the up and down parts of the cycle corresponds to a loss of active sites (charges and coordination are not specified here):

$$Ce-OH + HO-Ce \rightarrow Ce-O-Ce + HOH. \quad [11]$$
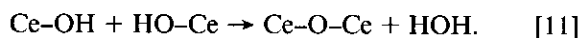
The second possibility is an additional hydroxylation of the surfaces by which an hydroxyl replaces a covalently bound nitrate:

$$Ce-O-NO_2 + OH^- \rightarrow Ce-OH + NO_3^-. \quad [12]$$

The last possibility is a reorganization of some surface sites, for instance a replacement of sites which are uncharged by others which are negatively charged in the same pH range.

We have found that these three processes do occur in specific conditions for the colloidal dispersions. They are related to the nature of the surfaces of nanometric particles. In order

to understand them, a systematic study of surface reactions was performed.

Release of Protons and Hydroxyls

Surface reactions which result in the release of OH^- or H^+ gave different results depending on the range of pH where the titration was performed. In order to analyze this phenomenon, we have decomposed the titration curves by performing cycles which extend to different pH values and comparing them. In each cycle the initial dispersion was at pH 3.4, then it was titrated up to an uppermost pH which was chosen between 4 and 12, and finally it was returned to pH 3.4. For each experiment we recorded the excess use of hydroxyls at the end of the cycle and the lack of readsorption of nitrate ions.

As mentioned above, the results show different behavior depending on the value of the uppermost pH which was reached in the cycle. There was a first range, up to pH 5, where the cycle was fully reversible. Then, for cycles extending to pH values between 5 and 8, the return curve did not coincide with the curve obtained on the way up, because the dispersion adsorbed less protons on the way down than hydroxyls on the way up. Moreover, this excess use of hydroxyls was stabilized, i.e., all the return curves coincided with each other (but of course not with the up curve). Again, for cycles extending to pH values between 10.5 and 11.5, there was another range where the return curves differed from each other, and the excess use of hydroxyls increased abruptly with the value of the uppermost pH. Finally, for cycles extending beyond pH 11 all cycles gave the same return curves, and therefore the excess use of hydroxyls was stabilized.

A neat way to summarize these results is to plot the excess use of hydroxyls (or lag in the use of protons on the return curve) as a function of the uppermost pH reached during the titration cycle. This was done for a dispersion at ionic strength 0.01 M and for another one at 0.1 M. The results obtained in either case are nearly identical; they show a remarkable step-like behavior, where each step occurred in a narrow pH range. Accordingly we define three ranges of pH where the behavior of the dispersion in a titration is stable (Fig. 3).

(1) Range A extends up to pH $\approx$ 5. In this range the titration cycles were reversible: there was no excess use of hydroxyls. Also the dispersion remained stable in this range, hence the amount of accessible surface did not change. Flocculation could be induced by the addition of salt (Na NO_3 0.55 M, but not $NaClO_4$) and reversed through dialysis of the salt. Hence, in this range only weak nonspecific bonds between surfaces may be formed, e.g., Van der Waals bonds.

(2) Range B extends from pH 7 to 10. Dispersions which were titrated from pH 3.4 to a pH in this range and then returned to pH 3.4 showed a difference of 40 hydroxyls per
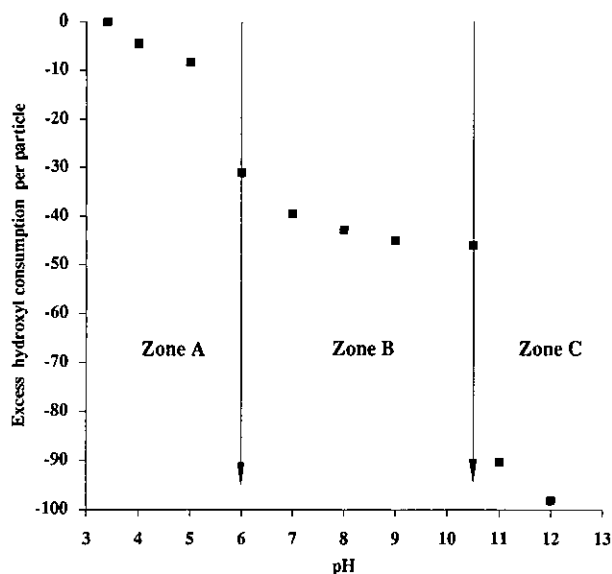
FIG. 3. Loss of surface sites during the first cycle of a titration of a dispersion with 0.1 M salt. Horizontal axis shows the value of the uppermost pH reached in the titration cycle. Vertical axis shows the excess consumption of hydroxyls during the titration to high pH, as compared with the consumption of protons during the return titration to low pH.

particle between both legs of the cycle. Visual observation of the dispersion showed that it flocculated as it entered region B; when it was returned to low pH it did not redisperse in the time scale of the titration experiments (a few hours). Hence, in this range strong surface to surface bonds may be formed.

Successive titration cycles in this range did not show any further hysteresis, hence the number of sites accessible to hydroxyls had stabilized. Also, the dispersions remained flocculated over the time scale of titration cycles.

(3) Range C extends beyond pH 10. The first titration cycle in this range resulted in an excess use of 50 hydroxyls. The step at pH 10 was quite sharp if the titrations were slow; it was much reduced and blurred for fast titrations. Hence the excess use of hydroxyls in this range is associated with the kinetics of a slow reaction.

These results on the release of OH⁻ or H⁺ indicate that there are different surface states and different surface reactions in these three ranges of pH. However, they do not specify whether the sites accessible to hydroxyls are lost or modified through reaction [11] or [12], or still another one. Some of this information is provided by measurements of the release of nitrates, which are presented below.

Release of Nitrates

The original dispersions contain high concentrations of nitrate ions. Most of these nitrates are there as counterions, which compensate the surface charge of the particles; they

must be released during a titration because the charge is progressively cancelled by the release of protons. Some of the nitrates may be more strongly bound; such nitrates, if they exist, would be released by an exchange reaction of type [12]. In a first stage we measured the release of all nitrates with a specific nitrate electrode, and in a second stage we measured the release of strongly bound nitrates through ion exchange and chemical analysis.

Release of all nitrates. The measurements with the specific nitrate electrode were performed during the first run of a titration in the absence of ClO_4^- ions (see "Methods"). Figure 4 presents the evolution of pNO_3 ($= -\log NO_3$) with pH during the first run of a potentiometric titration done in previous conditions. According to these measurements, nitrates are continuously released by raising the pH to 9.5, and then this release stops.

It is instructive to compare quantitatively the amount of released nitrates and the number of protons released from the surfaces. This comparison is presented in Fig. 5. Throughout range A, the fraction of hydroxyls which release a nitrate is 0.76. The slope rises upon entering range B, where each hydroxyl releases one nitrate. Finally, beyond pH 10, the release of nitrates stops; at this point the number of measured free nitrates equals the total amount of nitrates in the dispersion.

The results in range B are in agreement with a simple electrostatic model where a particle of p.z.c. 10 is surrounded by NO_3^- counterions, and these counterions are released or captured according to the surface charge of the particle. On the other hand, the mechanism of nitrate binding in region A cannot be electrostatics alone, since each OH⁻ releases
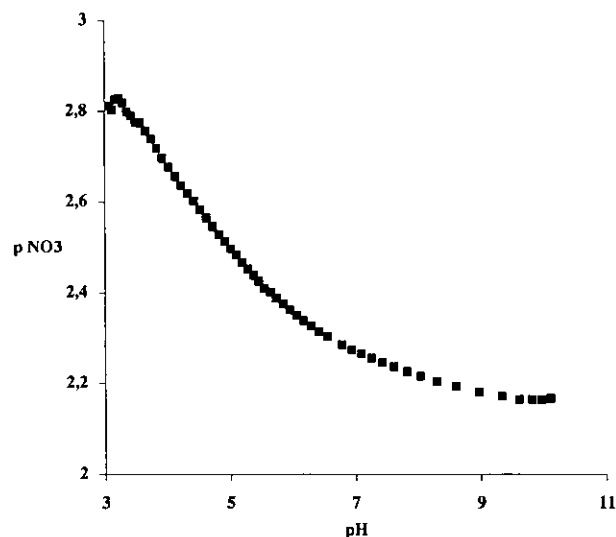

FIG. 4. Release of all nitrates during a titration to high pH. Horizontal axis shows the uppermost pH value reached at the end of the titration. Vertical axis shows the concentration of nitrate ions, from reading of a nitrate specific electrode. The decrease in p NO₃ indicates a continuous rise in the concentration of free nitrates between pH 3 and pH 9.
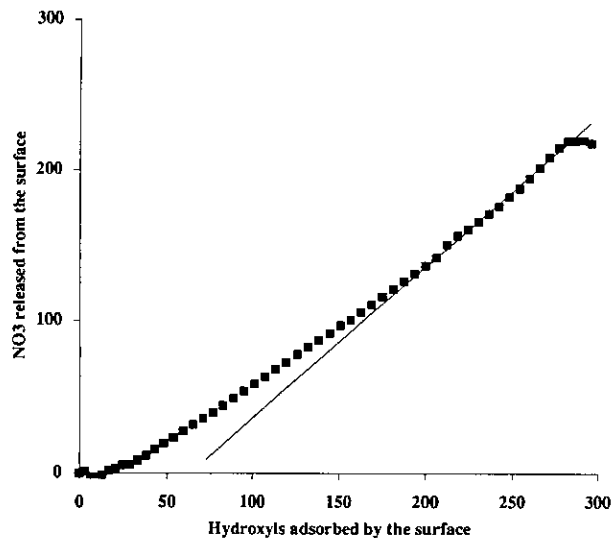
FIG. 5. Effect of the consumption of hydroxyls on the release of nitrates. Horizontal scale shows the number of hydroxyls adsorbed by the surface of one particle, according to the amount of base used during each step of a titration. Vertical scale shows the number of nitrates which have been released at this stage of the titration.

less than one nitrate. This balance suggests a specific interaction between some surface sites and NO_3^- ions.

Release of strongly bound nitrates. The amount of nitrates which are strongly bound to the particles at each pH was determined as follows. First the dispersion was brought to the desired pH. Then all electrostatically bound nitrates were exchanged with ClO_4^- ions: $NaClO_4$ was added until the ClO_4/NO_3 ratio was 100, and the dispersion was filtered

and washed at constant pH. Finally, the amount of remaining nitrates was measured through chemical analysis. The results are presented in Fig. 6. They show that there are, at low pH, about 70 nitrates strongly bound to each particle. Moreover, these nitrates are all released between pH 4 and 7, i.e., at the end of range A. They coexist with electrostatically bound nitrates, of which there are about 200 per particle at pH 2 (see below for the determination of surface charge).

Reversibility of the Equilibria

During titration three processes were observed which were not reversed in the return part of the cycles: Flocculation of the dispersion, excess consumption of hydroxyls, and release of strongly bound nitrates. The absence of the reverse processes over the time scale of titration cycles suggests the formation of strong bonds or a reorganization within the surfaces. In this section the possibility of reverse processes is examined.

Readsorption of strongly bound nitrates. In this experiment the strongly bound nitrates were first desorbed from the surfaces by keeping the dispersion at high pH for 24 h. Then the dispersion was brought back to pH 3.4 and the original nitrates were kept in contact with the surfaces for 24 h. Finally, all nitrates which were not strongly bound to the surfaces were eliminated by washing with perchlorate ions. The resulting dispersion was dried and its nitrate content was analyzed chemically as above. The results are shown in Fig. 6. Again they depend on the range of pH where the experiments have been made.

(i) For cycles performed between pH 3.4 and 11 the nitrates released on the way up were completely readsorbed on the way down after the equilibration time of 24 h.
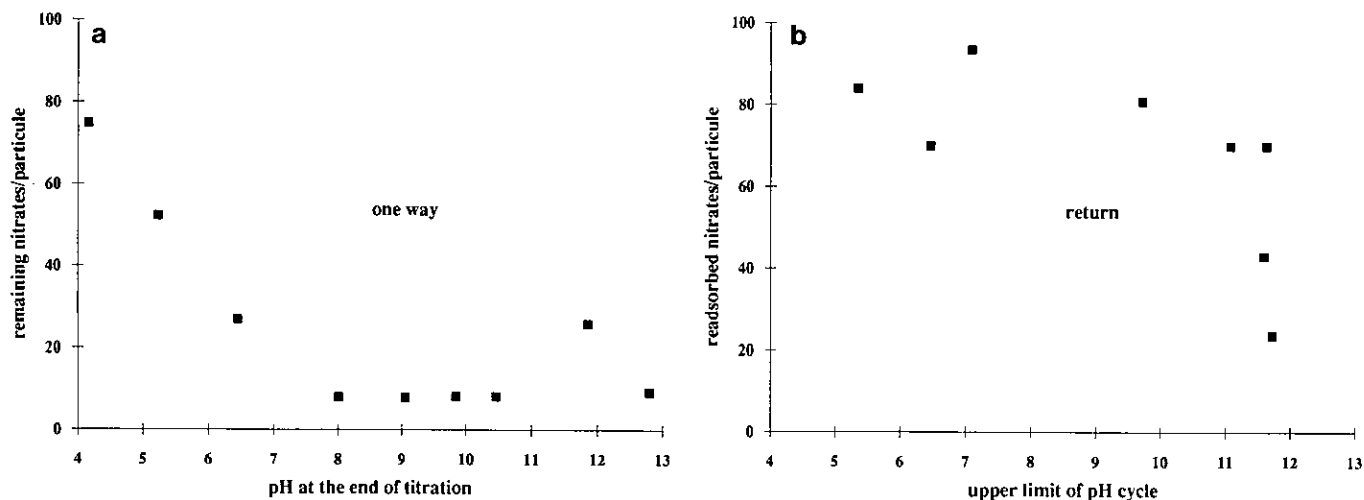

FIG. 6. (a) Release of nitrates which were strongly bound to the surface. Horizontal scale shows the value of the uppermost pH reached during the titration. Vertical scale shows the number of nitrates which remain strongly bound to a particle, after completing the titration and washing with perchlorate ions. (b) Readsorption of nitrates upon return to low pH. Horizontal scale shows the value of the uppermost pH reached during the titration. Vertical scale shows the number of nitrates which remain strongly bound to a particle after titration to the pH indicated on the horizontal axis, returning to pH 3.4, and washing with perchlorate ions.

(ii) If the uppermost value of the pH was beyond 10, then the 70 strongly bound nitrates released on the way up were not readsorbed after 24 h of equilibration at pH 3.4.

(iii) If the return cycle was continued to a pH below 2, then the kinetics for readsorption was significant regardless of the uppermost value of the pH in the cycle.

Release of excess hydroxyls. The titration cycles were performed in a few hours; after this time the excess consumption of hydroxyls was irreversible. At longer times, however, this was no longer true. An experiment was performed in which a dispersion at pH 3 was titrated up to pH 9 and then brought back to pH 3; subsequently the value of the pH was followed over time. After 40 days the apparent excess consumption of hydroxyls had been reduced by a factor of 2.

Deflocculation. Similarly, the flocculation of a dispersion which had been titrated up into region B may be reversed if it is kept at a lower pH. At pH 3.4 significant redispersion was observed after 40 days; at pH 2 it took a few days, and at pH 0.5 it was immediate. This kinetics is identical with that for the release of excess hydroxyls, indicating that the sites which had been lost in titration experiments were lost through condensation of opposing surfaces. Both kinetics are much slower than that for the readsorption of nitrates; however, they occur in the same pH range (2 to 6).

Point of Zero Charge

In the previous section it was shown that the nanometric dispersion is stable within certain ranges of pH; i.e., it is possible to perform titration cycles and keep the same surface sites for the adsorption of protons and hydroxyls. In these ranges, the state of the surfaces may also be characterized by the number of charged sites carried by the surfaces and by the location on the pH scale of the p.z.c. For this purpose, titration cycles were performed across the p.z.c. and back, and the curves at different ionic strengths were expected to intersect at the p.z.c. Indeed, titration curves made at higher ionic strengths are steeper because the surface can acquire a higher charge, and all curves should intersect at the p.z.c. where the effect of ionic strength on the surface must vanish.

These experiments could not be performed on the original dispersion (region A) because its p.z.c. lies outside region A where the behavior of the dispersion is reversible. They were performed for dispersions which had been brought into region B, and then also for dispersions which had been brought into region C. Finally, the results were compared with the behavior of the pure oxide, which showed the classical behavior with a p.z.c. close to that predicted according to the MUSIC model.

P.Z.C. in region B. For these experiments the dispersion was cycled once into region B and back. After this treatment the surface area of the dispersion was stable, and the strongly bound nitrates had been released (see the previous section).

Dispersions were prepared in this way with different backgrounds of salt, respectively 0.1, 0.5, and 1 mol/liter $NaClO_4$. These dispersions were titrated again from pH 3 to pH 10.5, and the amount of base used was recorded as a function of pH. The results of this second titration are presented in Fig. 7. The ordinate is the charge per particle instead of the usual charge/nm^2 because the surface area per particle is not known accurately (some surface was lost during the first cycle).

The total variation of the charge per particle from pH 3 to pH 10.5 was 200 charges. Assuming that all positive sites had been titrated at pH 10.5 this variation is also the number of charges carried by a particle at pH 3. This number is lower than the total number of surface hydroxyls, which is 500. In terms of surface densities, the numbers are 7 hydroxyls per nm^2 and 2.8 electron charges per nm^2 at pH 3.

The three titration curves have a common intersection point (c.i.p.) located at pH 10. This point must be the p.z.c. of the surfaces in region B. However, it is surprisingly high compared with the p.z.c. of pure ceria (see the measurements presented below). In other systems, changes in the location of the p.z.c. have been explained by the presence of adsorbed counterions. This effect does not appear to apply here. Indeed the shift in p.z.c. cannot be explained by specifically adsorbed nitrates (it is in the wrong direction) nor by complexation of nitrates as in reaction [12] (all the strongly bound nitrates have been released). Thus it is more likely that the shift results from a modification of surface hydroxyls. This point is taken up again in the Discussion.
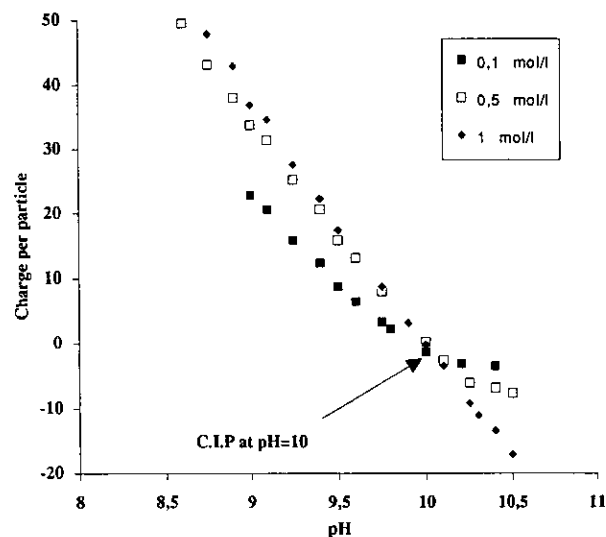

FIG. 7. Titration curves of a dispersion which had already been cycled once into region B of Fig. 2. Horizontal scale shows the measured pH; vertical scale shows the charge per particle, calculated from the amount of base or acid used in the titration. At each ionic strength the measured titration curves are exactly reversible in the pH range from 3.5 to 11. The common intersection point of the three curves corresponds to a cancellation of the surface charge of the particles.

P.Z.C. in region C. For these experiments the dispersion was flooded with hydroxyls and kept at pH 12 for 3 h; then it was brought back to pH 6 with $HClO_4$ and the ionic strength was adjusted to either 0.1, 0.3, or 0.5 mole/liter. From these three starting points titration cycles were performed up to pH 10.5; in each the return curve did match the first part of the cycle (Fig. 8). The curves at the three ionic strengths have a c.i.p. at pH 8.6; this point must be the p.z.c. of the surfaces obtained in region C; it is much lower than the p.z.c. of surfaces kept in region B.

It is interesting to compare the numbers of hydroxyls required to titrate surfaces which have been prepared either in region B or in region C. For titrations performed in the same range of pH and at the same ionic strength we found that the number of hydroxyls used was comparable for both surface states. According to this observation the surface area of dispersions in both regions must be similar.

P.Z.C. of pure ceria. We also measured the surface charge of a fired oxide obtained from the colloidal dispersion through thermal processes as described in the "Materials" section. It is important to realize that this fired oxide had a much smaller surface area ($40\ m^2/g$) than the dispersion ($400\ m^2/g$) and that it was made of porous grains wetted by the aqueous solution. We made sure that all surface sites had been hydroxylated by using suspensions which had been
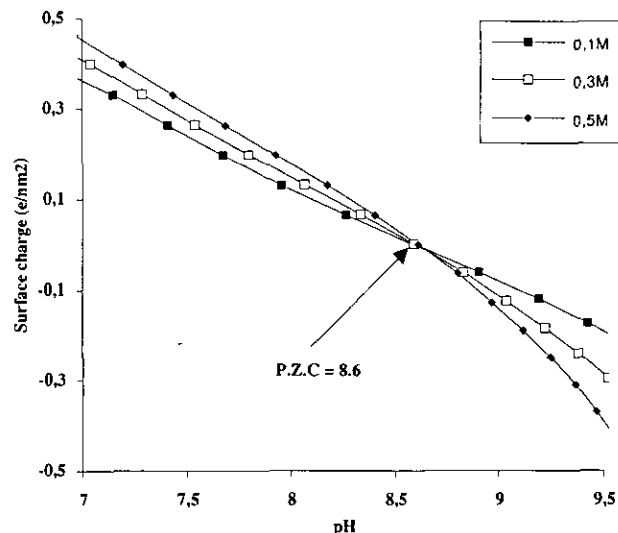
FIG. 9. Titration curves of a pure ceria. Horizontal scale shows the measured pH; vertical scale the surface charge, calculated from the amount of base or acid used in the titration. At each ionic strength the measured titration curves are exactly reversible in the pH range from 3.5 to 11. The common intersection point of the three curves corresponds to a cancellation of the surface charge of the particles.

equilibrated with acid ($HClO_4$, pH 4) or base (NaOH, pH 12.7) for 3 weeks. From either starting point a titration cycle was performed; the cycle was free of hysteresis if the overall titration time was at least 4 h. With faster titrations the curve for base addition was the same but the return curve lagged behind, presumably because the diffusion of ClO_4^- ions through the porous material was slow.

The value of the surface charge was calculated from the amount of base used for the titration and from the known surface area of the dispersion. The titrations were performed at three different ionic strengths; the results are presented in Fig. 9. For the curve at ionic strength 0.1 mol/liter the overall variation of surface charge between pH 7 and 10 amounts to 1 electron charge per nm^2, or 0.33 charge per nm^2 for one pH unit. This value is comparable to the values of the surface charges for other oxide surfaces (1). It is lower than the density of hydroxyls on the surface (7 sites per nm^2) because the repulsions between electrostatic charges limit their surface density.

The titration curves at the three ionic strengths have a common intersection point located at pH 8.6. This point must be the p.z.c. of the surfaces of the fired oxide. It is somewhat higher than the classical value for ceria, which is 7.6 (10). The discrepancy presumably may originate from the poisoning of some surface sites by residual nitrates which were not eliminated by the firing process, or it may be caused by other rare earths present as impurities in the cerium oxide.

In summary, the characteristics of the three types of surfaces are as follows.
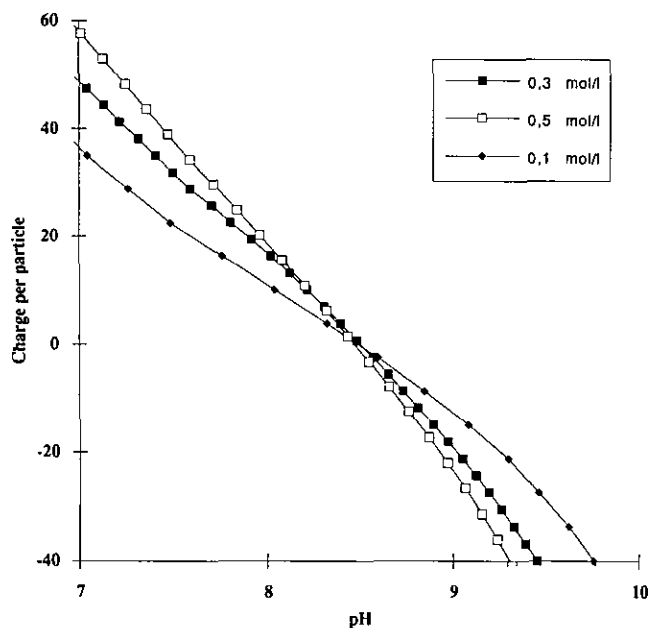

FIG. 8. Titration curves of a dispersion which had already been cycled once into region C of Fig. 2. Horizontal scale shows the measured pH; vertical scale the charge per particle, calculated from the amount of base or acid used in the titration. At each ionic strength the measured titration curves are exactly reversible in the pH range from 3.5 to 11. The common intersection point of the three curves corresponds to a cancellation of the surface charge of the particles.

—Surfaces of colloidal dispersions brought into regions B and C have a very large surface area ($400\ m^2/g$), whereas that of the fired oxide is much lower ($40\ m^2/g$).

—Surfaces of colloidal dispersions brought into regions B and C have the same surface density of positive charges (2.8 charges per nm^2 at pH 3).

—Surfaces of colloidal dispersions brought into region C have the same p.z.c. as pure ceria, whereas surfaces which have remained in region B have a much higher p.z.c.

DISCUSSION

Our aim was to understand why nanometric oxide dispersions behave so differently from classical micrometric dispersions. The main observation was that *changes of ionic conditions in the aqueous medium cause irreversible transformations for the dispersion.* These transformations affect the surface chemistry of the dispersion (different reactions of the surfaces with ionic species), its stability (the surfaces may bind to each other), and its surface area; after they are completed the dispersion has the same behavior as the classical micrometric cerium oxide. We also found that these transformations may be decomposed into definite stages, separated by regions of stable behavior. Thus a good approach to the problem is to start from the final stage; i.e., the calcinated oxide, which is well understood, and work our way back through each transformation and each intermediated stage until we can describe the original nanometric dispersion.

Calcination

The last transformation in the process for making a regular oxide was the calcination of the dispersion. The effect of this transformation may be analyzed by examining the stage which precedes it immediately. This stage is the dispersion washed with base at pH 12. We found that this dispersion has the same p.z.c. as the calcinated oxide, at pH 8.6; however, its specific surface ($400\ m^2/g$) is much larger than that of the calcinated oxide ($40\ m^2/g$). Accordingly, in a process where individual steps are well separated, *the effect of calcination is only to reduce the surface area; the surface chemistry is changed in the wet stages which precede it.*

Washing at pH > 10.5

The previous transformation is the washing of the dispersion by a base at pH > 10.5. The effect of this transformation may be analyzed by examining the stage which precedes it immediately. This stage is the dispersion washed with base at pH < 10.5. We found that this dispersion has a p.z.c. at pH 10. This is much higher than the p.z.c. of the calcinated oxide. The difference may be explained in two ways. Either the surfaces in this dispersion are the same as for a regular oxide, but they are complexed with nitrates and this binding of anions causes the shift in p.z.c., or the surfaces differ from those obtained after washing at pH > 10.5. The first option is excluded by the results from chemical analysis: at this pH there are no longer any covalently bound anions. Hence, the second option is the correct one.

Another important effect of this transformation is that it affects the binding of nitrates by surfaces which are brought back to low pH. Surfaces which have been kept at pH < 10.5 bind nitrates covalently when they are equilibrated with nitrates at pH 3. Surfaces which have been brought to pH > 10.5 lose this ability to bind nitrates. Consequently the process of washing the surfaces at pH > 10.5 has eliminated the sites which bind the nitrates covalently.

Taken together, these results indicate that *there are specific sites which, at high pH, cause a shift in the p.z.c. and, at low pH, bind nitrates through covalent bonds.* These sites are present on surfaces which have not been washed at pH > 10.5, and cause them to differ from regular oxide surfaces. Surfaces which have been transformed by washing at pH > 10.5 have lost these sites; they may regain them slowly if they are equilibrated at pH < 2.

Washing at pH between 6 and 10.5

This transformation causes the *release of covalently bound nitrates,* and it affects the *stability of the dispersion.* The time scales for both processes appear different: the release of covalently bound nitrates occurs within hours of the washing process, whereas the aggregation process may take days to bind all particles. Conversely, upon lowering the pH to 3, the readsorption of covalent nitrates is complete within 24 h, whereas the redispersion takes 40 days. Still, both processes occur in the same pH range, and one is not observed without the other. Thus, by the time the surfaces have reseparated, most nitrates have readsorbed. Hence, it is worth investigating whether or not there is a cause-and-effect relation between them, i.e., whether it takes the adsorption of nitrates to keep the surfaces apart.

The classical DLVO analysis of colloidal stability rests on a comparison of electrostatic attractions and Van der Waals attractions. Van der Waals attractions diverge at contact, where they cause particles to stick to each other permanently. Electrostatic repulsions are longer range; if the height of the electrostatic barrier is sufficient the particles are unable to come within reach of Van der Waals attractions. Then the dispersion has colloidal stability.

For nanometric particles, Vervey and Overbeek had already remarked that this condition is never achieved (2). Because the collision frequency is quite high, the repulsive barrier would have to be at least 15 kT to keep the particles apart. Electrostatic potentials of this magnitude are never reached with nanometric particles. In particular, for the ceria particles, the height of the contact potential is 8 kT. Con-

sequently the particles have frequent collisions which bring them in direct contact.
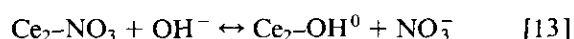
Yet the nanometric dispersions of ceria at pH $\leqslant$ 2 are stable. They can be flocculated by addition of salt, and this flocculation may be reversed by diluting the salt. This reversibility indicates that something keeps the particles from falling all the way into the Van der Waals trap. Moreover, this protection is removed at higher pH, when the covalent nitrates have been removed, and it is restored after they have been readsorbed. This suggests that adhesion of particles to each other is prevented by nitrates which are bound to the surfaces through covalent bonds, and that it becomes possible when they are removed. The only alternative would be that adsorption of protons prevents the condensation of surfaces at low pH; however, this is not expected to occur unless the concentration of protons is close to that required to dissolve the oxide, at pH $\approx$ 0.

Nature of Unwashed Surfaces

According to the results of the experiments presented here, the different states of the surfaces can be described as follows. At pH below 6 the surfaces are covered with strongly bound nitrates and unable to stick to each other. Between 7 and 10 they have lost all the strongly bound nitrates but they still present active sites which may, at lower pH, readsorb nitrates; these sites also cause a shift in the p.z.c. Finally, at pH > 10.5 these sites are eliminated during a restructuring of the surfaces, and the p.z.c. returns to the value of the fired oxide. It is not possible to identify these structural differences without making some assumptions about the nature of surface sites on the ceria particles.

According to electron microscopy and X-ray diffraction, the particles are crystalline. If the surfaces are crystal planes, then the surface sites may be identified. There are 3 possible coordinations for surface hydroxyls: monodentate, bidentate, or tridentate. According to MUSIC predictions, bidentate sites have pK values on either side of the accessible pH range; consequently they do not gain or lose charges in this range, and do not influence the p.z.c.. Still, they may take part in nitrate binding equilibria. The mono and tridentate sites have pK values at 10.4 and 5.5, respectively; the p.z.c. of the surfaces is an average of these values weighted by the respective numbers of sites of either type. For crystalline surfaces, the numbers of mono- and tridentate sites are equal, in which case the p.z.c. must be at 7.9. For surfaces which have not been transformed by washing at pH > 10.5, the p.z.c. is higher, and this indicates that there is a relative excess of monodentate sites, or a lack of tridentate sites.

This restructuring must also explain the changes in binding of nitrates. Therefore we need to examine nitrate binding equilibria for each type of surface site. These equilibria are

$$Ce_2-NO_3 + OH^- \leftrightarrow Ce_2-OH^0 + NO_3^- \qquad [13]$$

$$Ce_3-NO_3^{+0.5} + OH^- \leftrightarrow Ce_3-OH^{+0.5} + NO_3^- \qquad [14]$$

$$Ce_1-NO_3^{-0.5} + OH^- \leftrightarrow Ce_1-OH^{-0.5} + NO_3^-. \qquad [15]$$

The first two equilibria correspond to a hydrolysis of the nitrate ligand by hydroxyls, and they are pH dependent; thus they could indeed cause the observed release of nitrates in the range of pH 2 to 6. The last one may be ruled out as a source of nitrates in this range. Indeed, it would be followed by a protonation of the monodentate hydroxyls (the pK is 10.48):

$$Ce_1-OH^{-0.5} + H^+ \leftrightarrow Ce_1-OH_2^{+0.5}. \qquad [16]$$
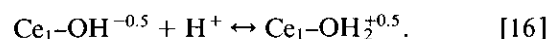
The balance of reactions [15] and [16] corresponds to a hydrolysis of nitrate ligands by water:

$$Ce_1-NO_3^{-0.5} + H_2O \leftrightarrow Ce_1-OH_2^{+0.5} + NO_3^-. \qquad [17]$$

This reaction must occur at very low pH, upon addition of water to cerium nitrate. In our conditions, with a large excess of water, it must be completely displaced to the right-hand side; consequently, there are no monodentate sites which are still complexed with nitrates.

Therefore the sites which release nitrates in the range pH 2 to pH 6 may be either bidentate and tridentate sites. The choice can be made according to the experimental results, indicating that (a) these sites cause a shift in the p.z.c.; (b) they are restructured by washing at pH > 10.5. The first condition corresponds to a lack of tridentate sites or to an excess of monodentate ones; since monodentate sites are ruled out as a source of nitrates, the lack of tridentate sites must be caused by an excess of bidentate sites, i.e., bidentate sites at locations which, according to crystal structure, should have been tridentate.

This model matches the experimental results. Indeed, when nitrates are replaced with hydroxyls according to Eq. [13] the surface charge would remain the same, as observed. When the surfaces are washed with a large excess of hydroxyls, these excess bidentate sites are restructured as tridentate; this creates an excess consumption of hydroxyls, as observed in titration cycles which have been extended to pH 12.

In summary we can propose the following picture for the surfaces of the original dispersion. These surfaces are made of monodentate and tridentate sites, which take part in equilibria for binding of protons and hydroxyls, and bidentate sites which are inactive in the accessible range of pH. Some of the sites in tridentate locations are actually bidentate and complexed with nitrates. As the pH is raised up to pH 6, these covalent nitrates are released. Then the particles may aggregate, and this loss of surface consumes some of the active monodentate and tridentate sites. The remaining active sites determine the p.z.c., which is then at pH 10. When

the dispersion is washed with hydroxyls at pH > 10.5 the surfaces restructure by transforming the bidentate sites into tridentate ones. The resulting surfaces have a p.z.c. at 8.6; they have the structure and composition of regular oxide surfaces, and they have lost the ability to bind nitrates with partly covalent bonds.

CONCLUSIONS

Nanometric dispersions of lyophobic colloids are rare. For oxides, they are stable only in specific ranges of pH. This is in contrast with the behavior of micrometric dispersions, which can be cycled across the whole range of pH. Understanding these different behaviors is of great practical importance, as materials of very high surface area are needed for industrial applications. This can be done in three steps: (a) what makes the micrometric dispersions stable against aggregation; (b) why are the nanometric dispersions usually not stable; (c) what are the relations between stability and surface chemistry?

(a) Micrometric dispersions have a comparatively small surface area; moreover, they are made of polycrystalline particles with rough surfaces. Consequently short range forces such as Van der Waals attractions or chemical reactions are blocked for steric reasons over most of the surface area. Therefore the drop in free energy upon aggregation is weak. By comparison, long range forces such as electrostatic repulsions are strong. They can keep charged surfaces apart from each other, or reseparate them if they have been stuck to each other during a cycle in pH or ionic strength.

(b) Nanometric dispersions have an extremely large surface area. When they are made of single crystallites, it is possible for the particles to come in direct contact, which will lower the free energy of the dispersion through short range attractions or reactions between surfaces. By comparison, electrostatic repulsions between charged surfaces are weak, because the magnitude of the total charge per particle is low and also because the concentrations of counterions are usually higher. Therefore stability can only be achieved by using surface chemistry to modify short-range interactions.

(c) In this work the relations between surface chemistry and colloidal stability have been clarified in one particular example: nanometric dispersions of a tetravalent metal oxide, ceria. These dispersions are typical of the problems encountered with nanometric oxide dispersions: they are stable only in a limited range of pH; washing them outside this range destroys this stability and allows the dispersion to reduce its surface area. We have found that, in the range where the dispersions are stable, the surfaces are complexed with nitrate counterions; washed surfaces which have lost these complexing agents cause the dispersions to become unstable.

This control of stability by complexing agents raises three questions: (d) How do they function; (e) how are they generated; and (f) is this a general mechanism?

(d) The complexing agents, i.e., in this case the covalently bound nitrates, function by preventing direct contact between particles and making reactions between surfaces impossible. This is similar to the mode of action of some "hydration forces," which cause effective repulsions between surfaces through protrusion of hydrated groups (11).

(e) How are such protected surfaces generated? We have found that the ligands are bound to special surface sites which reflect the way the particles were synthesized. This memory of the synthesis may be wiped out by washing the surfaces; then the surfaces become identical to regular oxide surfaces in fired oxides.

(f) This last point provides a connection with the function of complexing ions during the synthesis of colloidal particles. Indeed it is well known that certain ligands may orient the growth of colloidal particles during precipitation processes, resulting in specific morphologies for particles grown with different ligands (12). It has been proposed that the mechanism for this speciation is a poisoning of certain crystal faces by the complexing ions; such mechanisms are operative in specific ranges of pH where complexation is efficient. In this sense it is not too surprising that similar mechanisms should operate for the reactions between the surfaces of particles, and that these mechanisms should be revealed by the colloidal stability of nanometric dispersions.

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