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Nucleation and Growth of Phosphate on Metal Oxide Thin Films

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The kinetics of phosphate uptake by hematite, titania, and alumina were examined by exposing freshly prepared thin films to phosphate solutions at incremental times and subsequently analyzing the surfaces by Auger electron spectroscopy (AES), temperature programmed desorption (TPD), and atomic force microscopy (AFM). Thin film hematite exposed to a sodium phosphate solution demonstrated initially rapid phosphate chemisorption during the first 10 min of solution exposure, followed by island growth. For titania and alumina exposed to a calcium phosphate solution, the initially rapid reaction was completed after 1 and 3 h, respectively. Subsequent rapid three-dimensional growth occurred after 3−4 h for titania and 25−30 h for alumina. The trend in the rate of formation of phosphate film on titania and alumina was comparable to those of in-situ studies using the same solutions. AFM data on the $10-20\text{-}\mu m$ scale did not show distinct changes between clean and phosphate-covered alumina and iron oxide surfaces; however, structures $200-500$ nm in diameter could be observed on these surfaces after exposure to phosphate solution.

Introduction

The interest in the uptake of phosphate by metal oxides such as iron, alumina, and titania arises from current problems found in the study of soils, corrosion, and biomimetic materials. Phosphate reactions with iron and aluminum oxides and hydroxides have been extensively studied by soil chemists, since these soil components are the most abundant of the naturally occurring metal oxides[1,2] and are the inorganic soil constituents primarily responsible for phosphate reactions in soils.[3,4] In addition, phosphate reactions with titania have been studied due to its relevance in understanding biomineralization processes involved in promoting bone growth on titanium implants.[5]

Few surface-sensitive techniques have been employed to examine phosphate uptake from solution by aluminum and titanium oxide surfaces. An investigation using angle-resolved X-ray photoelectron spectroscopy (XPS) concluded that phosphate accumulated at the surface of gibbsite and did not seem to be incorporated into the bulk structure.[6] However, phosphate reactions may be dependent upon particle size. Studies using ^{31}P magic angle spinning

nuclear magnetic resonance (MAS NMR) have shown that P can react with surface hydroxyls on alumina and form monomeric and polymeric phosphate.[7] It was found that, for larger particle sizes, phosphate was limited to surface reactions and did not become incorporated into the bulk structure. However, for smaller particle sizes phosphate did react to form aluminum phosphate crystallites.[8] Investigators in the area of heterogeneous catalysis have examined alumina and titania into which phosphoric acid had been incorporated.[9] It was found that POH groups at the surfaces of both oxides act as Brønsted acids. Investigators posited that, upon activation of the catalysts in vacuum by heating, the incorporated phosphate may have lost a proton, which may have combined with OH groups on the oxide surface to form H_2O. This would have created an ionic bond between the phosphate and the oxide surface.

Kinetic studies with iron oxides have divided phosphate reactions into two categories:[10] an initially rapid first layer chemisorption followed by either (1) reactions characterized by slower uptake kinetics thought to arise from solid-state diffusion, diffusion through surface pores, and migration from within aggregated particles to surface sites or (2) precipitation of insoluble phosphates at the surface.[11] Most of these studies have focused upon the initial chemisorption reaction, particularly of phosphate with goethite (α-FeOOH). Models developed from studies of this iron oxide have served as a paradigm for phosphate reactions with other oxides.

One of the pivotal early investigations into phosphate reactions with iron oxides postulated that ionic solution phosphate species reacted with OH groups at the surface

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by donating a proton to form OH_2. The phosphates would then exchange with this species to form bonds to structural iron.[12] Later investigations using ex-situ transmission infrared spectroscopy showed that the hydroxyl groups involved in phosphate ligand exchange reactions were those singly coordinated to iron.[13] From these investigations, phosphate is thought to bind to two OH groups, forming a binuclear structure.

Calculations of hydroxyl packing densities for various faces have been performed for hematite.[13] The faces considered theoretically suitable for binuclear bridging complexes of phosphate were the (110), (100), and (223) planes. Calculations which assumed phosphate bonded in a binuclear complex predicted that phosphate uptake for these faces would be 4.2, 4.8, and 3.6 μmol P m^{-2}, respectively. Reported values from adsorption studies[2,14] range from 0.31 to 3.3 μmol P m^{-2}. A reason for the difference between the measured and calculated phosphate concentrations is that hematite can vary widely in crystal morphology, and the planes amenable to phosphate adsorption may not be the most dominant faces.[2]

Initial XPS studies have been performed by investigators interested in phosphate adsorption on iron oxide surfaces. In one study, the surface composition of phosphated synthetic goethite was examined. From estimates of sampling depth and atomic composition, phosphate adsorbed in a binuclear complex was considered plausible.[15] A later study examined phosphate reactions with naturally occurring goethite. Both the initially rapid first-layer chemisorption reaction and the reactions characterized by slower uptake kinetics were studied.[16] It was found that phosphate in the first layer was bound as $H_2PO_4^-$ and comprised ~1.3 atomic % of the surface. Phosphate present at the surface after long reaction times (90 days) existed in crystallites ranging in size from 0.1 to 4 μm on the goethite surface. Thus, after long reaction times phosphate precipitation at the surface was plausible with the composition of the bulk phase phosphate dependent upon solution composition.

From this discussion, it is evident that phosphate interactions with oxides are complex. The relative paucity of available techniques has limited the progress toward an understanding of the chemistry of phosphate uptake on metal oxides. Controversy will continue until more investigations are conducted that directly analyze the nature of the phosphate–oxide surface complexes. The research presented here is an attempt to conduct surface-sensitive measurements of phosphate adsorption reactions under well-controlled conditions.

Experimental Section

Metal oxides were synthesized and characterized in ultrahigh vacuum (UHV). The freshly prepared oxide surface was translated to a liquid reaction cell[17,18] for exposure to phosphate-containing solutions under dry N_2 atmosphere. After completion of solution reactions had occurred, the sample was rinsed with Millipore H_2O to elute species that were unbound to the surface,

brought into an antechamber, pumped to high vacuum, and then translated into the UHV chamber for analysis. In this way, freshly prepared oxide surfaces were exposed to phosphate solutions with minimal atmospheric contamination.

The metal oxide films were grown by evaporation of Ti, Al, and Fe filaments in an oxygen background onto a metal support. Thin film TiO_2 was deposited on Ta foil by evaporation of Ti in an oxygen background of 5×10^{-7} Torr oxygen. Al_2O_3 was deposited on Ta foil by heating aluminum wire in 2×10^{-6} Torr oxygen. Thin films of hematite (α-Fe_2O_3) were synthesized by a modification of the in-situ oxidation technique described by Corneille et al.[18] Iron was deposited on Ta foil and Re(0001) at ~300 K in a background of ~5×10^{-5} Torr O_2. Surface stoichiometry was verified by comparison of AES and XPS spectra to those found in the literature.[19–22] The presence of the α-Fe_2O_3 crystalline phase was verified by transmission electron micrograph (TEM) ring diffraction patterns.

Phosphate adsorption kinetics for titania, alumina, and iron oxide surfaces grown on Ta foil were studied by exposing the oxide surface to laminar flow solution via a liquid reaction cell. The solution, maintained at ~19 °C, used for these exposures contained 3.5 mM $CaCl_2$ and 119 μg of P mL^{-1} as KH_2PO_4. Its pH was adjusted to 6.5 with NaOH using 0.01 M NaCl as the background electrolyte to fix its ionic strength. Solutions were prepared using reagent grade chemicals (Fisher Scientific) and deionized, reverse osmosis (Millipore), CO_2-free water. The solutions were filtered (0.22 mm Millipore) prior to use. The filters were prewashed to remove any residual wetting agents or surfactants.

In addition, the kinetics of phosphate adsorption were investigated by exposing a freshly prepared thin film of α-Fe_2O_3 grown on a Re single crystal to phosphate-containing solutions for various times at ~19 °C. The solutions contained 3 μg of P mL^{-1}, added as H_3PO_4 and had an ionic strength of 0.01 M using NaCl as the background electrolyte and a pH adjusted to 6.7 using NaOH.

The powder oxide samples used in the nucleation experiments were α-Al_2O_3 (AKP-30, Sumitomo), TiO_2 (P25, Degussa), and SiO_2 (PST-3, Nissan). The specific surface areas, measured by BET methods were 6.8, 56.9, and 15 m^2 g^{-1}, respectively. Suspensions were prepared by ultrasonic dispersion in 0.01 M NaCl, pH 6.5 for at least 3 days prior to use in nucleation experiments. Suspension pH was adjusted by the addition of either sodium hydroxide or hydrochloric acid solution. Surface charge characteristics were measured via ζ potentials using a Matec ESA-8000 instrument (in a 0.01 M NaCl aqueous solution at 25 °C). It was shown from these measurements that the surface charge is a function of solution pH and is zero for Al_2O_3 and TiO_2 at pH = 6.5.[23]

In-situ nucleation and growth experiments were performed using the constant composition (CC) technique developed by Nancollas.[24] A calcium ion-selective electrode (Orion) was calibrated by the addition of aliquots of calcium chloride to sodium chloride medium electrolyte in a reaction vessel. Supersaturated CaOx solutions were then prepared by the slow addition of potassium oxalate solution. When equilibrium was attained, a known volume of the oxide seed slurry (total surface area = 0.2670 m^2) was added to the mixture. Any decrease in calcium ion activity due to nucleation and/or growth was sensed by the calcium electrode, which triggered an automatic titrator potentiostat (Metrohm) to add titrant solutions of calcium chloride and potassium oxalate from mechanically coupled burets. The titrant solutions also contained sodium chloride in order to maintain a constant ionic strength (0.01 M NaCl). The time between seed addition and the addition of titrants as well as the volume of titrant consumption as a function of time was recorded.

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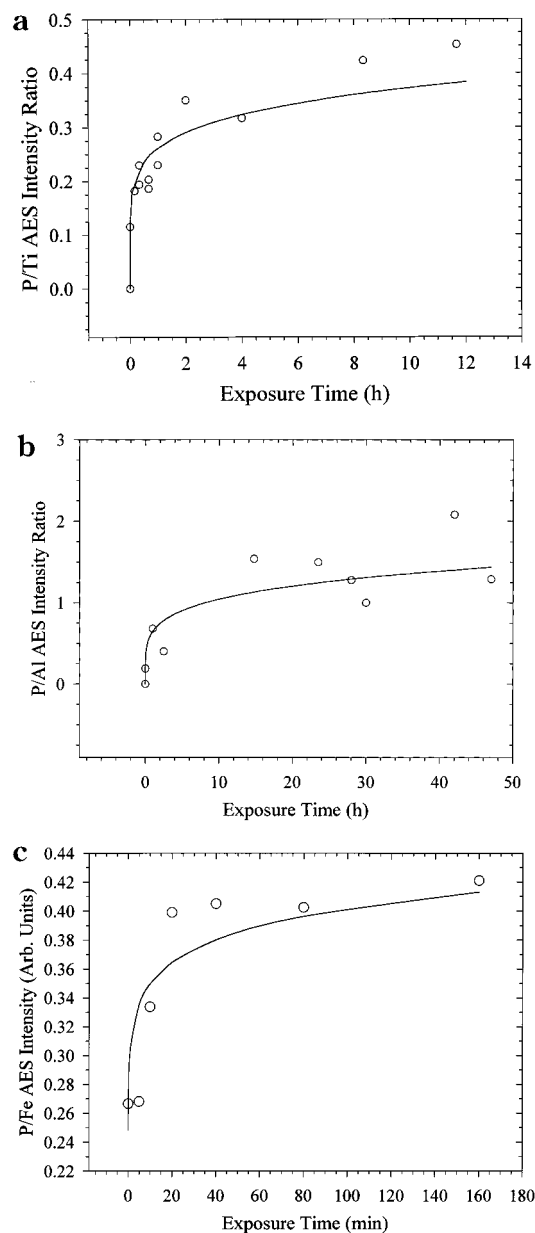
Figure 1. Phosphorus to metal AES peak ratios as a function of exposure to a phosphate-containing solution for the phosphate 110-eV peak compared to (a) the titanium 387-eV peak, (b) the aluminum 60-eV peak, and (c) the iron 651-eV peak. The titania and alumina surfaces were exposed to a solution containing 119 μg of P mL^{-1}, and the iron oxide surface was exposed to a solution containing 3 μg of P mL^{-1}. The curves do not represent a fit through the data points but are shown to guide the eye.

Results and Discussion

Titania. All of the titania surfaces used in these experiments were approximately 15−20 monolayers thick and were free of contaminants such as carbon. The intensities of the kinetic energy peaks at 110 eV for phosphorus and 387 eV for titanium were used to calculate the P/Ti AES intensity ratios shown in Figure 1a. These ratios were plotted as a function of exposure time to phosphate solution and show a clear break at approximately 1 h. The average thickness of the phosphate species was estimated from the attenuation of the inelastic mean free path (IMFP)[25] of the Ti(LMM) Auger electrons. (It should be noted that this method assumes a homogeneous coverage of phosphate on top of the substrate

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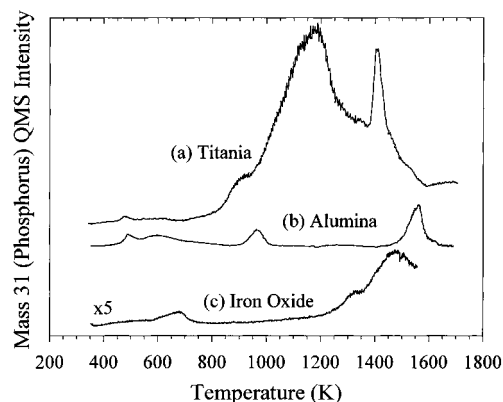
Figure 2. TPD spectra corresponding to the desorption of phosphate as mass 31 (P) for (a) 15-h exposure of a titania surface to a solution containing 119 μg of P mL^{-1}, (b) 30-h exposure of an alumina surface to a solution containing 119 μg of P mL^{-1}, and (c) 24-h exposure of an iron oxide surface to a solution containing 3 μg of P mL^{-1}.
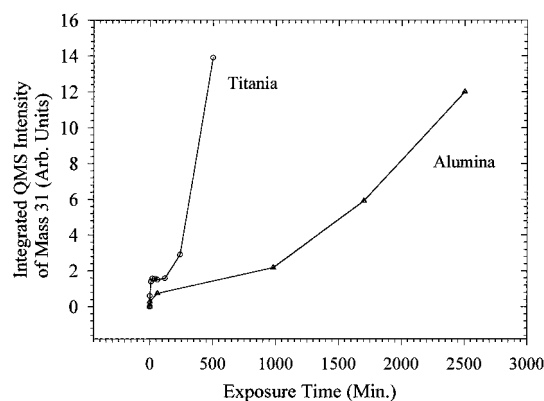

Figure 3. Integrated TPD spectra for mass 31 (P) from titania and alumina surfaces as a function of exposure to a calcium phosphate solution containing 119 μg of P mL^{-1}.

and hence is an inexact estimation.) After an exposure of 1 h, the phosphate film thickness was approximately 6 Å on titania. This break, when interpreted in conjunction with temperature programmed desorption (TPD) spectra, signified the time required for chemisorption and the beginning of phosphate precipitation.

TPD was used to determine the kinetics of phosphate adsorption on titania as well as provide a means of distinguishing phosphate desorption behavior from the different oxide surfaces. TPD spectra of P on titania showed features at 1200 and 1400 K (Figure 2). An adsorption isotherm was constructed from integration of TPD peak desorption features for mass 31 (P) associated with increasing exposure time to calcium phosphate solution (Figure 3). The rapid onset of phosphorus adsorption that begins at approximately 200 min (in Figure 3) is denoted by the appearance of the large desorption feature at 1200 K (in Figure 2).

Alumina. AES data were used to verify the growth of the Al$_2$O$_3$ surface and to calibrate surface coverage. Fully oxidized aluminum can be identified by a single peak at 60 eV, which has a 10-eV peak shift lower in energy than the aluminum metal transition. From the attenuation of the IMFP of the substrate Ta(NOO) Auger electrons from the substrate, the coverage of the alumina films used was estimated to be ~15 monolayers. The P/Al AES intensity ratios taken for a series of exposure times to calcium phosphate solution show a break at 3−4 h (Figure 1b). TPD spectra of mass 31 (P) at different exposure times to calcium phosphate solution reveal phosphorus desorption
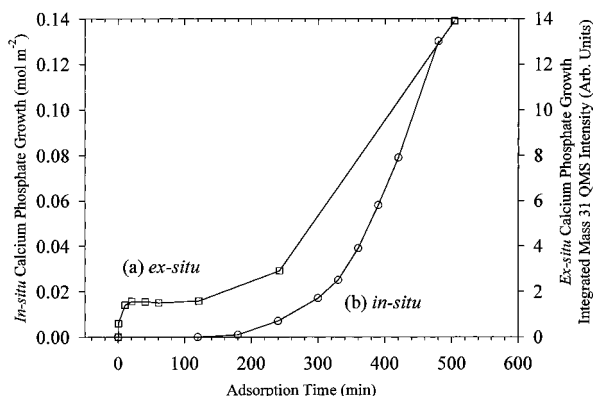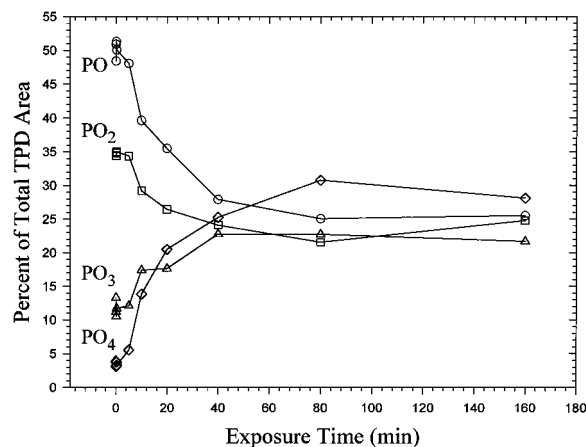
Figure 4. Comparison of the adsorption isotherms for phosphate on titania generated from (a) ex-situ and (b) in-situ adsorption experiments.

from alumina at 450−700 K and a high-temperature feature, which occurs between 1400 and 1560 K (Figure 2). Unlike the case of the titania spectra, the large feature at 1200 K is absent. In addition, at least one new feature can be observed at approximately 450−700 K. Integration of several phosphorus desorption spectra provides the data for an adsorption isotherm shown in Figure 3. Onset of rapid uptake of phosphate is observed between 20 and 25 h.

The ex-situ growth of phosphate on titania and alumina (measured by TPD) is similar to that of in-situ calcium phosphate film formation on titania and aluminum powders (measured by CC methods). Rapid growth of calcium phosphate can be observed on the titania powder by 160 min and on the alumina powder by 1800 min. A comparison of the isotherms generated from the ex-situ and in-situ studies of phosphate growth on titania is shown in Figure 4. It was found that the thin films and powders exposed to identical solutions have comparable trends in the rate of phosphate formation. This is an important conclusion which shows that the chemistry of phosphate adsorption is dominated by surface effects and not by bulk properties such as particle size. Consequently, valid comparisons can be made between results obtained by surface science techniques and more established in-situ solution measurements.

Iron Oxide. Measurements of phosphate formation on iron oxide grown on Ta foil were made with the same solution conditions used for the adsorption experiments on titania and alumina. Auger and TPD confirmed that these conditions were corrosive for the iron oxide surface, with an etch rate of approximately 3 monolayers of iron oxide per hour. The main reaction product was the formation of iron chlorides, which were soluble in water. It is well-known that phosphate-containing salt solutions are capable of forming a passivating film on Cu and Pd metal surfaces, where the degree of protection offered by the passivating film is determined by the composition of the reagent solution.[26−28] To study the formation of stable passivating films on iron oxide, solution conditions were maintained at levels found in natural soil solutions, where an indefinite amount of phosphate adsorbs on iron oxide.

By changing the solution conditions to 3 μg of P mL^{-1}, phosphate films formed on α-Fe$_2$O$_3$/Re(0001) without appreciable loss of the iron oxide film from etching. Phosphate adsorption was monitored at the surface by

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Figure 5. Integrated TPD spectra corresponding to the desorption of phosphate from an iron oxide surface. The desorptions of the PO, PO$_2$, PO$_3$, and PO$_4$ species are presented as a percent of the sum of the mass spectrometer signal for these four masses.

the AES P/Fe intensity ratios, which were calculated from the P(LMM) transition at 110 eV and the Fe(LMM) transition at 651 eV. A plot of this ratio with reaction time showed that phosphate accumulates rapidly at the surface of thin film α-Fe$_2$O$_3$ during the first 10 min of exposure to a phosphatic solution (Figure 1c). The appearance of the TPD desorption feature on the iron oxide surface at 1380 K (Figure 2) was interpreted to denote saturation of surface sites during an induction period following initial rapid growth of phosphate. However, after this initially rapid reaction the Auger P/Fe signal levels off, signifying saturation of the initial chemisorbed layer.

In addition to AES, TPD was used to determine the amount of phosphate accumulating at the surface. Exposure of the iron oxide thin film to phosphate solution for periods as long as 24 h produced phosphate films that corresponded to the P thermal desorption spectra shown in Figure 2, characterized by a high-temperature feature at 1300−1400 K and a smaller broad feature desorbing at 400−500 K. As phosphate adsorption proceeds, more phosphate begins to desorb at lower temperatures. The appearance of the lower temperature desorption features with increasing solution exposure times was representative of the TPD spectra for mass/charge ratios corresponding to PO$_2$, PO$_3$, and PO$_4$. Integration of the TPD peak areas for PO, PO$_2$, PO$_3$, and PO$_4$ (Figure 5) is expressed as a percentage of the sum of all areas of the desorbing PO$_x$ species. The sensitivity of the QMS for the different masses is not known; however, it is clear that the dominant species desorbing at low exposure times is PO and PO$_2$ and that at longer exposure times the dominant desorbing species is PO$_3$ and PO$_4$.

TPD spectra of mass 47 (PO) were integrated and converted to surface populations of phosphate molecules. To perform this calculation, nanomolar quantities of phosphate were deposited by a micropipet on freshly prepared α-Fe$_2$O$_3$ thin films. Integration of the quadrupole mass spectrometer (QMS) signal corresponding to the thermal desorption of the known quantity of deposited phosphate provided the standard for converting integrated mass spectrometer signals to surface densities of phosphate molecules. The curve resulting from this calculation showed that, after the first 10 min of exposure, phosphate coverage was $\sim$3 × 10^{14} molecules cm^{-2}, representing a surface coverage of $\sim$1/3 of the available iron oxide surface
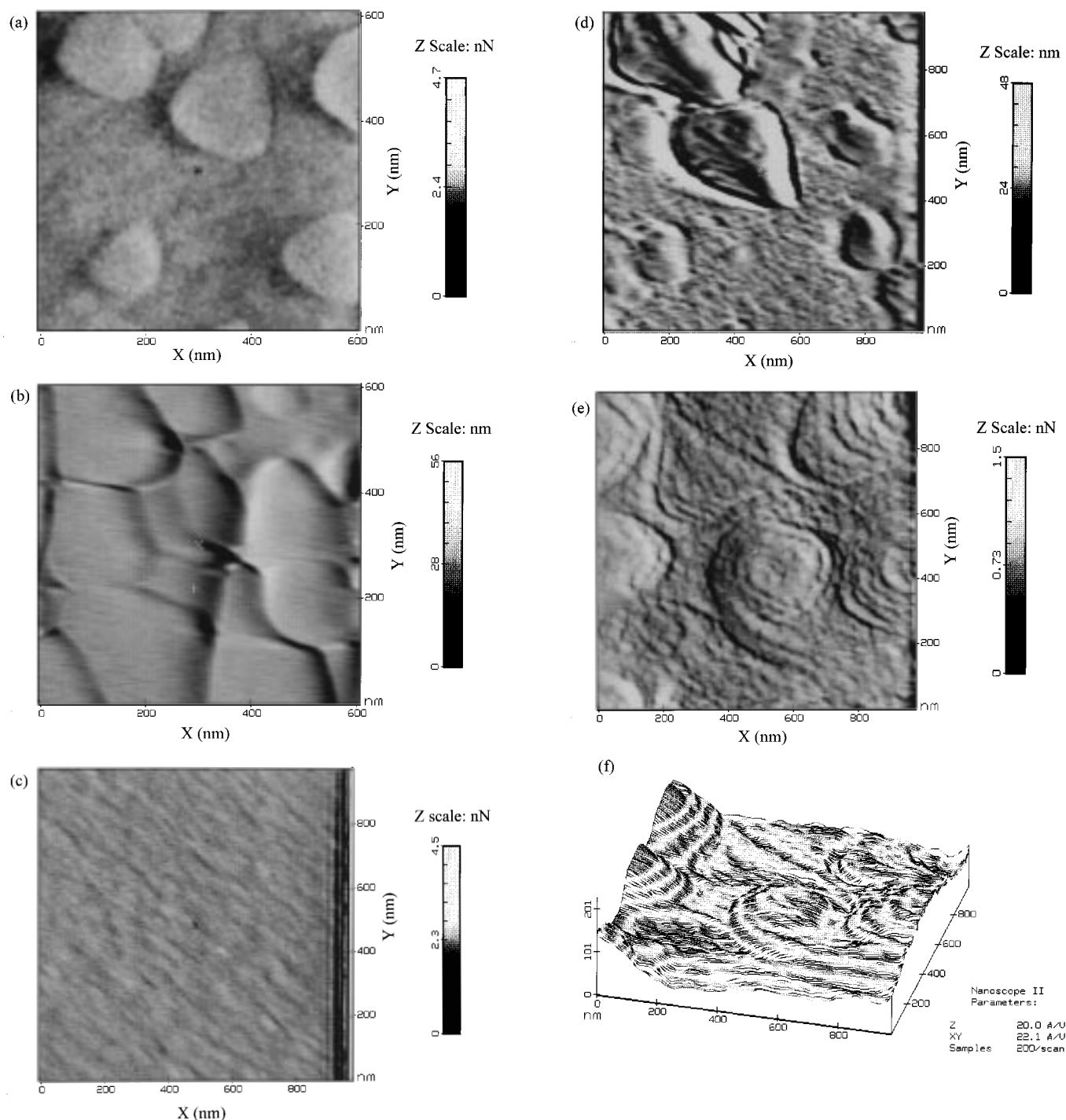
Figure 6. AFM spectra of a clean iron oxide film approximately 100-Å thick grown on a Ta foil substrate (a) and a similar film that has been exposed to a phosphate solution containing 3 μg of P mL^{-1} (b). The AFM image of a clean alumina film approximately 100-Å thick grown on a Mo foil substrate (c) can be compared to that of a similar surface exposed to a solution containing 119 μg of P mL^{-1} for 30 h (d) and for 90 h (e). A line profile plot in part f corresponds to the image in part e.

sites, assuming $\sim 1 \times 10^{15}$ such sites exist.[29] On the supposition that the surface area of the thin film iron oxide is approximately that of the metal substrate (~ 1 cm^2), the accumulation of phosphate is calculated to be one phosphate molecule per 0.33 nm^2, or ~ 5 μmol of P m^{-2}. This coverage is, within experimental error, close to the 3.6–4.8 μmol of P m^{-2} coverage predicted for a binuclear complex on hematite[12] and may indicate that phosphate has completely exchanged with the singly

coordinated hydroxyl groups that form on α-Fe$_2$O$_3$ in aqueous environments. However, it should be noted that phosphate adsorption on this type of surface is corrosive and that these singly coordinated hydroxyls, if present on the surface, can be subsequently altered by local restructuring.

An examination of TPD and AES spectra reveals a general trend in the growth mode of phosphate on these three oxide surfaces. In all three cases, the phosphate to substrate Auger ratios seem to saturate after relatively short time periods: ~ 1 h for titania, 20 min for iron oxide surfaces, and about 3 h for alumina surfaces. Clearly,

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the uptake of phosphate is continuing past these initial periods for all three surfaces according to TPD measurements. The coverage for the adsorption of phosphate on iron oxide has been calculated to be approximately one monolayer at the point of saturation. From this, and the fact that the surface concentration of Fe as probed by AES remains the same for coverages greater than one monolayer, we conclude that rapid and complete first-layer chemisorption occurs within 20 min followed by island formation. This model explains the observed saturation in the Auger ratios, since the amount of iron probed by AES will remain roughly constant, proportional to the surface area between phosphate islands. The amount of phosphate seen by AES will also remain constant once the islands become thicker than the escape depth of the ejected Auger electrons. This is consistent with the observed growth of phosphate in TPD spectra and saturation of the P/Fe ratio in AES spectra.

The titania and alumina surfaces showed analogous behavior in that the saturation point in AES occurred despite continued phosphate growth shown in TPD. The Auger saturation point occurred at the film thickness 6 $\pm$ 1 Å, close to monolayer coverage by phosphate groups. Correlating this with the integrated TPD spectra in Figure 3, the maximum average coverage of phosphate observed on the titania and alumina surfaces was ~40 Å. This is well above the escape depth of the substrate Ti and Al Auger electrons. Since, both Ti and Al Auger signals were observed for average coverages as thick as 40 Å, islands of phosphate species must have formed after the initial complete chemisorbed first layer. This method of analysis provided an accurate and reproducible method for determining the time frame necessary for initial chemisorption and subsequent three-dimensional island growth.

Oxide Morphology. The morphology of these films was explored using atomic force microscopy (AFM). The surfaces used in these experiments were unpolished metal foils. It was found that, for a resolution on the scale of 10−20 μm, no clear morphological changes could be observed for alumina and iron oxide surfaces after exposure to phosphate solution. However, for more localized scales on the order of several hundred nanometers, terraces and islands can be observed ranging in diameter from 200 to 500 nm. These large features we assign to adsorbed phosphate compounds. In Figure 6a, the clean iron oxide surface is characterized by regular island structures about 100 nm in diameter, and in Figure 6b, an example of phosphate islands can be observed as larger plate-like structures. These latter structures resulted from a 3-h exposure to phosphate solution containing 3 μg of P mL^{-1}. In Figure 6c, a clean alumina surface is shown, where no structures on the 1000-nm scale can be observed. After a 30-h exposure to a phosphate solution containing 119 μg of P mL^{-1}, large localized structures 400−500 nm across can be seen (Figure 6d). After an exposure for 90 h, a larger area of the alumina surface was covered. An AFM image after

a 90-h exposure is shown in Figure 6e, and a corresponding line profile plot is shown in Figure 6f. We attribute these changes in morphology to the 3-D growth of a phosphate-containing species.

Conclusions

Our results show that, for thin film hematite exposed to a sodium phosphate solution, initially rapid uptake occurs during the first 10 min of solution exposure in which phosphate completes first-layer adsorption. After this induction period, phosphate species precipitate as islands. The rates of uptake of calcium and potassium phosphate on alumina and titania surfaces can be directly compared from their respective adsorption isotherms. The onset of rapid uptake characterized by 3-D island growth is between 200 and 250 min for the titania surface and between 1500 and 2000 min for the alumina surface. This is comparable to the case of in-situ studies where the onset of rapid growth is 160 min for titania powders and 1800 min for alumina powders. This correlation between in-situ and ex-situ measurements further validates our technique for making kinetic measurements of phosphate adsorption on thin metal oxide films that have been exposed to solution and returned to vacuum.

For all the oxides studied, the rapid growth at longer solution exposure times shown in the TPD adsorption isotherms does not follow the break in the Auger peak ratios. This discrepancy reflects a change in the growth mode of surface phosphate. The Auger rollover corresponds to the rapid completion of the first layer of adsorbed phosphate, which can be defined as the coverage where subsequently adsorbed phosphate does not occupy metal oxide surface sites. Subsequently, phosphate precipitates three-dimensionally on the first layer. AFM images show that large terraces and islands form on the metal oxide surfaces on the order of hundreds of nanometers in diameter.

Perspective

A new methodology has been presented for forming clean metal oxides and exposing them to phosphate-containing solutions for studying chemisorption followed by precipitation on the surface. TPD spectra show clear differences in the desorption temperature features of phosphate species on titania, alumina, and iron oxide surfaces and provide a means for measuring their growth kinetics.