A spectroscopic investigation of phosphate adsorption onto iron oxides

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Phosphate adsorption on a thin Fe$_2$O$_3$ film prepared in ultrahigh vacuum (UHV) was carried out in a liquid flow cell and subsequently returned to UHV for spectroscopic examination. Variations in exposure time to phosphatic solutions of differing pH were used to determine the adsorption/desorption kinetics, speciation of the adsorbed phosphate, and the absolute phosphate coverage. Rapid uptake of phosphate occurred in the first 10 min of exposure resulting in coverages of $3 \times 10^{14}$ molecules per cm$^2$, followed by a 20 min induction period, and then continued phosphate adsorption. Auger electron spectroscopy (AES) indicated that the maximum phosphate coverage realized in this study was $\sim 1 \times 10^{15}$ molecules cm$^{-2}$. X-ray photoelectron spectroscopy (XPS) showed that phosphorus shifted to more oxidized states during longer exposures to phosphatic solutions. © 1996 American Vacuum Society.

I. INTRODUCTION

The geochemical processes by which phosphates interact with soil surfaces and groundwater have presented many perplexing questions for well over a century. An understanding of these questions could have important global ramifications for phosphate contamination and nutrient bioavailability. The development and application of experimental methods from soil/surface chemistry, as well as more traditional wet chemistry, are critical for achieving a comprehensive understanding of the dynamic interactions of phosphate, soil, and aquatic systems. An interactive approach that combines the fundamental techniques available in surface science is the primary emphasis of this article.

One of the most characteristic features of phosphate is its strong retention by soils. An important result of this behavior is that relatively little phosphate is released into the soil solution, regardless of the quantity of phosphate compounds applied. In fact, the capacity of most soils to retain phosphate is orders of magnitude greater than the quantity of phosphate added as fertilizer.

Although soil solution levels are typically low [0.03–3 μg P ml$^{-1}$ (Ref. 3)], phosphate can become a significant contaminant in aquatic systems through its association with soil solids eroding into streams and lakes. If the levels of solution phosphate in these systems reach a concentration of 0.01 μg P ml$^{-1}$, eutrophication may occur. Consequently, a thorough understanding of phosphate reactions is crucial for predicting the chemistry of land applied phosphate materials and optimizing their levels in the environment.

Although there are a multitude of soil constituents, the components of the inorganic fraction which are primarily responsible for phosphate adsorption are the oxides and hydroxides of iron and aluminum. Phosphate reactions with natural and synthetic samples of the iron oxides hematite and goethite have been extensively studied because these minerals are the most abundant metal oxides in soils. However, the mechanisms of phosphate reactions with iron oxides are still poorly understood. Uncertainty has centered around differentiating the conditions which account for phosphate chemisorption and those responsible for precipitation of phosphate as bulk compounds. The lack of understanding of this system has persisted because of numerous interacting variables inherent in soil systems. The research presented demonstrates how such reactions can be investigated under strict conditions using an array of surface analytical techniques including Auger electron spectroscopy (AES), thermal programmed desorption (TPD), and x-ray photoelectron spectroscopy (XPS).

II. EXPERIMENT

Thin films of Fe$_2$O$_3$ were synthesized by a modification of the in situ oxidation technique described by Corneille et al. Iron was deposited on Pt(111) at 300 K in a background of $5 \times 10^{-5}$ Torr O$_2$ under static flow maintained by a turbomolecular pump. The Fe$_2$O$_3$ stoichiometry was confirmed by comparison with reference Auger spectra for Fe in the 40–60 eV kinetic energy range and by comparison with XPS reference spectra of Fe(2p) and O(1s) binding energies. Phase
determination for Fe$_2$O$_3$ was obtained from selected area diffraction (SAD) patterns of thin films (~150 Å thick) grown on carbon-coated copper grids. Further confirmation of phase was provided by lattice fringe spacing at $\times$1.5M magnification, using graphite fringe spacings as reference.

The experiments were performed in a combined ultrahigh vacuum chamber and electrochemical apparatus described previously. This chamber had a base operating pressure of $\sim$7×10$^{-10}$ Torr and was equipped with AES and TPD. Another chamber was used for XPS measurements, and has been described before. Modifications were made to the original electrochemical cell for the adsorption and desorption experiments. A solution delivery column (Fig. 1) was constructed of Teflon to allow investigations of a wide range of acidic and basic solutions. A peristaltic pump was added to maintain a constant solution flow rate of 5 ml min$^{-1}$, providing fresh solution to the sample throughout the experiments. A further modification was the installation of a nitrogen jet which was used to remove excess solution remaining on the surface of the sample before withdrawal from the adsorption cell.

III. RESULTS AND DISCUSSION

Transmission electron microscopy (TEM) images showed the vapor deposited Fe$_2$O$_3$ to be polycrystalline, with particle sizes ranging from 5 to 10 nm. This size distribution falls within the 5–100 nm size range of iron oxide particles occurring naturally in soils. Ring patterns from selected area diffraction indicate that the iron oxide is primarily hematite ($\alpha$-Fe$_2$O$_3$), consisting of small particles and amorphous components.

To test if vapor deposited hematite thin films reacted with phosphate in a manner similar to naturally occurring soils, adsorption experiments were patterned after those of a representative soil science adsorption study. The source of solution phosphate was KH$_2$PO$_4$ and the ionic strength was adjusted to 0.02 M using KCl. CO$_2$ contamination was minimized by purging the electrochemical cell with N$_2$ and by sparging all solutions with N$_2$ before use. Thin films ~20 ML thick were brought into contact with the meniscus of

![Fig. 1. A diagram of the liquid flow cell and the end of the manipulator holding the single crystal sample. Continuous flow of the reactant solution over the sample was made possible by contacting the sample with a meniscus of electrolyte.](image)

![Fig. 2. A representative Auger spectrum of (a) a clean Fe$_2$O$_3$ surface prepared in UHV by dosing Fe at room temperature in an oxygen background on a Ru(0001) surface; (b) phosphated Fe$_2$O$_3$ showing chemisorbed phosphate with the double peak at 95 and 110 eV. The surface corresponding to the spectrum in (b) was immersed in an aqueous phosphatic solution of 3 µg P ml$^{-1}$, pH5, and 0.01 M NaCl.](image)

![Fig. 3. Phosphorus to iron Auger intensity ratios for Fe$_2$O$_3$ thin films exposed to solutions of increasing phosphorus concentrations (a). Phosphorus to iron Auger intensity ratios for a phosphated Fe$_2$O$_3$ thin film exhibiting phosphate desorption in water as a function of exposure time (b).](image)
each solution for 5 min at room temperature under continuous solution flow. AES was used to detect adsorbed P at the iron oxide surface (Fig. 2). After each adsorption experiment, the iron oxide surface was removed by exposing the sample to 0.1 M HNO₃.

The results of the adsorption experiments are shown in Fig. 3(a). The presence of P as PO₄ at the surface was confirmed in AES by principal minima occurring near 94 and 110 eV kinetic energy. AES P/Fe intensity ratios were calculated from measurements of the P (LMM) transition at 110 eV and the Fe (LMM) transition at 651 eV. The relative AES intensities plotted against solution P concentration yield a so-called “L-curve” isotherm, which is believed to result from two primary mechanisms. The initial steep slope may reflect the high affinity of iron oxide for phosphate at low concentrations. As phosphate surface coverage increases, steric factors may limit the adsorption of more phosphate, as evidenced by the more gradual slope in the adsorption isotherm. This type of curve is commonly used to describe phosphate adsorption on synthetic and naturally occurring iron oxides.

In natural systems, phosphate desorption is partially irreversible. Typically, the amount of phosphate desorbed from iron oxides decays exponentially with time. To test for this behavior under more controlled conditions, desorption experiments were conducted by placing phosphated thin films in contact with doubly deionized water. Phosphate desorption occurred under continuous flow, for total times of 0, 30, 90, and 120 min. The change in surface phosphate concentration was monitored with AES after transferring the sample back into the UHV chamber. The results of these experiments indicate that phosphate desorption from thin film iron oxide behaves similarly to that observed for natural systems.

To address questions related to the kinetics of phosphate adsorption processes, the time of thin film exposure to phosphatic solutions was varied. The solution contained 3 µg P ml⁻¹ with an ionic strength of 0.01 M NaCl. The pH was adjusted to 6.5 using NaOH. Exposure times included 0.13, 5, 10, 20, 40, and 160 min. TPD was used to calculate the amount of adsorbed phosphate because of the high sensitivity of the quadrupole mass spectrometer (QMS) to sub-
monolayer quantities of thermally desorbed species. The masses monitored were PO, PO$_2$, PO$_3$, and PO$_4$, corresponding to mass/charge ratios of 47, 63, 79, and 95, respectively. Heating a phosphate-covered iron oxide surface resulted in TPD spectra consisting of a sharp high temperature state ($\sim$1380 K) and a broad low temperature multilayer state(s) occurring at temperatures from $\sim$500 to 1380 K [Fig. 4(a)]. The TPD spectra in Fig. 4(b) show thermal desorption features of masses associated with the iron oxide film and the adsorbed phosphate after a 40 min exposure to phosphatic solution. The TPD spectrum of Fe$_2$O$_3$ indicates that the phosphate desorbing at high temperatures is likely a result of the decomposition of the iron oxide film. After heating to $\sim$1500 K, Auger analysis indicates that no phosphorous exists on the surface.

TPD spectra of mass 47 (PO) were integrated and converted to surface populations of phosphate molecules [Fig. 4(c)]. To perform this calculation, nanomolar quantities of phosphate were deposited by micropipette on freshly prepared Fe$_2$O$_3$ thin films. Integration of the 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 numbers and densities of phosphate molecules. The curve resulting from this calculation shows an initially rapid increase in phosphate adsorption during the first 10 min of exposure. After this period, no increase in intensity of the 1380 K feature was observed for $\sim$20 min. The coverage at this plateau has been calculated to be $\sim$3$\times$10$^{14}$ molecules cm$^{-2}$. Continued solution exposure resulted in rapid phosphate accumulation, with a major fraction of the desorption species occurring in the $\sim$500–1380 K range.

The data from the kinetic studies suggest that for exposures less than 10 min, the high temperature feature accounts for the entire first layer species. After this rapid phosphate uptake, an induction period occurs corresponding to the plateau in Fig. 4(c). Up to this point two dimensional growth has occurred, corresponding to monolayer coverage. After 30 min of exposure, a rapid multilayer growth begins, corresponding to three dimensional growth.

To test for possible differences in the chemical states of phosphate during the kinetic experiments, freshly prepared hematite was exposed to the same phosphatic solution mentioned previously and analyzed by XPS. However, to aid in the detection of different chemical environments, the range of exposure times was extended to 1.5, 20, 360, 420, 735, and 1570 min. The data in Fig. 5 shows that as hematite is exposed for longer periods to phosphatic solution, the P(2p) binding energy increases by $\sim$0.4 eV. This shift in binding energy indicates that phosphorus at the surface of the iron oxide becomes more oxidized. This suggests that the environment surrounding the surface phosphorus becomes more electronegative with continued exposure to solution.

**IV. CONCLUSIONS**

An ex situ study of the Fe$_2$O$_3$ aqueous interface was carried out using a liquid flow cell interfaced to an UHV chamber. Similarities between the adsorption and desorption isotherms obtained for phosphate on hematite thin films to classic models developed by in situ measurements in soil science validates the use of thin oxide films in these studies.

The thermolysis and desorption of phosphate adsorbed on Fe$_2$O$_3$ occurred, for coverages less than 3$\times$10$^{14}$ molecules cm$^{-2}$, as a single high temperature peak at $\sim$1380 K. Longer exposures resulted in rapid growth corresponding to lower temperature broad features in TPD (500–1380 K). Altogether, these results are consistent with an adsorption model that assumes that phosphate initially grows in a two dimensional layer for the first 10 min. After a short 20 min induction period, multilayer (three dimensional) growth begins. Thus, the nucleation period for three dimensional growth is likely to occur by the end of the induction period, 30 min after the initial exposure.

XPS was used to determine changes in the chemical environment of adsorbed phosphorous during kinetic experiments. Phosphorus was found situated in more electronegative environments as reaction times increased.

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