Direct scanning tunneling microscope (STM) observation of Cr(III) complexes on hematite (001) surfaces

Dedicated to Paul W. Schindler on his retirement

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ABSTRACT

Scanning tunneling microscopy (STM) is used to observe, at the atomic scale, Cr(III) adsorbed to hematite (001) surfaces from aqueous solution. The Cr(III) adsorbates are relatively immobile, but estimated activation energies for surface self-diffusion are lower than those for water or hydroxyl substitution in aqueous Cr(III). Possible causes are effects of STM imaging (artifacts), high ligand-substitution rates for adsorbed species, or participation of substrate Fe(III) ligand exchange. STM imaging of suitable aqueous surface complexes is shown to be feasible, and constitutes a new way to study the relationships between microscopic and macroscopic chemical behavior of adsorbed species in aqueous systems.

Introduction

Because adsorption of aqueous solutes on mineral surfaces is a fundamental part of chemical processes at the Earth's surface, including many with environmental implications, models for prediction of aqueous adsorption behavior are necessary in a wide range of scientific and engineering applications. Surface complexation theory (e.g., Schindler, 1981; Schindler and Stumm, 1987) is a particularly successful example of such a model; not only can adsorptive partitioning behavior be quantified, but also kinetic phenomena such as mineral dissolution rates can be correlated with concentrations of surface complexes (e.g., Pulfer et al., 1984; Furrer and Stumm, 1986; Blum and Lasaga, 1991). In order to understand such reactions at a more fundamental level, it is necessary to understand the molecular structure of adsorbed species and the reactions mechanisms in which they participate.

Surface diffusion is an important microscopic process that often influences surface reactivity in, for example, heterogeneous catalysis, crystal dissolution and growth, and nucleation (e.g., Burton et al., 1951; Somorjai, 1981), but until recently it has not been directly accounted for in surface-complexation approaches to description of surface re-

activity in aqueous systems (Wieland et al., 1988; Gratz et al., 1991). In heterogeneous catalysis, adsorbates must surface-diffuse until they encounter each other and react. Similarly, aqueous species that promote or inhibit mineral dissolution or precipitation must first adsorb and then diffuse to "active" sites where the reaction can be modulated. Surface diffusion has been studied on well-defined metal surfaces in vacuum (Zangwill, 1988), but the study of surface diffusion at the mineral-water interface has lacked suitable analytical tools.

The purpose of this paper is to report some initial results from scanning tunneling microscopy (STM) studies of chromium(III) sorbed on hematite (α -Fe₂O₃) surfaces from aqueous solution. The intent is first to show that atomic-scale STM imaging of suitable aqueous adsorbates is feasible, and then to show how information on the binding energetics and surface mobility (surface self-diffusion) of individual Cr(III) surface complexes may be obtained. It is hoped that with further development, this and similar methods can be used to extend and improve our ability to use the surface complexation approach in understanding heterogeneous reactions in aqueous systems.

Surface diffusion in aqueous systems

We can distinguish between "outer-sphere" adsorbates that are attracted to surfaces by physical forces but not chemically bonded there (except hydrogen bonds) and do not lose any water of hydration, and "inner-sphere" species that bond to surface sites and lose some water of hydration. The mobility of outer-sphere adsorbates is high because only hydrogen bonds (15–25 kJ mol⁻¹) need be broken; they do not sit in one "site" for more than a few microseconds (e.g., Marichev, 1991). Surface self-diffusion of inner-sphere complexes involves breakage and formation of adsorbate-surface bonds and should be subject to the same kinetic constraints as inner-sphere adsorption and desorption. The rates of adsorption of aqueous metal ions (e.g., Hachiya et al., 1984) and of oxide mineral dissolution (Casey and Westrich, 1991) are proportional to water substitution rates in the primary hydration sphere of corresponding aqueous metal ions. It is reasonable to expect that ligand exchange (e.g., water substitution) must also be a key part of surface diffusion in aqueous systems.

The Cr(III)-hematite (α -Fe₂O₃) system

The Cr(III)-hematite system was chosen for its experimental convenience and environmental relevance. An important attribute of Cr(III) for STM purposes is unusually slow water substitution (e.g., Cotton and Wilkinson, 1988); the rate constant for water substitution in the Cr(H₂O)₆³⁺ ion is about 10⁻⁶ s⁻¹. Inner-sphere adsorbed Cr(III) is therefore expected to be extremely immobile (see above). This is necessary because the STM requires 8.4 seconds to produce a single image; an adsorbate that does not occupy a single site for several seconds cannot be "seen" except perhaps as "ordered" noise (e.g., see Dunphy et al., 1993). Cr(III) is the only species in the aqueous Cr(III)-hematite system that we expect, as a surface monomer, to be so immobile.

Eskolaite (α -Cr₂O₃) and hematite (α -Fe₂O₃) are isostructural semiconductors with 1.7 and 2.2 eV bandgaps, respectively (Merchant et al., 1979), and similar sizes (the *a* dimensions of the Cr and Fe structures are 4.961 Å and 5.033 Å, respectively). This suggests that inner-sphere adsorption of Cr(III) to iron oxides should be "epitaxial", with Cr atoms occupying the same types of sites that Fe atoms occupy (e.g., Charlet and Manceau, 1992). Cr(III) should be distinguishable from Fe(III) in STM images because of electronic-structure differences; Cr(III) doping of hematite surfaces narrows the bandgap (Merchant et al., 1979), suggesting that Cr(III) contributes surface electronic states within the bulk bandgap of hematite. Such states should be visible in STM images as points of high tunneling current. The fact that Cr(III) forms isostructural oxides with Fe(III) and several other metals is important because it suggests that what we learn about the behavior of Cr(III) may give hints as to the behavior of other metals as well (see below).

Iron oxides are common in natural systems and have been used in many aqueous adsorption experiments (e.g., Dzombak and Morel, 1990). As a pollutant, Cr(VI) is particularly hazardous because it is a strong oxidant, is mobile in aqueous systems, traverses cell walls easily, and is a carcinogen. Reduction of Cr(VI) to Cr(III) and scavenging of Cr(III) by Fe(III) oxide particles (Kieber and Helz, 1992), is a natural removal mechanism in which sorption of Cr(III) to Fe(III) oxides is a key step.

Experimental

Natural specular hematite crystals were fractured along the (001) plane. Fresh surfaces were placed in Cr(III) solutions (see below) for 2 hours, removed, and wicked dry. This treatment did not approach equilibrium, but was only intended to sorb sufficient Cr(III) to be relatively easily seen. Cr(III) solutions (10⁻⁶ M, pH = 4.8–5.0) were made from Cr(NO₃)₃. A small amount of the Cr(III) probably dimerizes in solution (Rotzinger et al., 1986). A Nanoscope III STM was used with a 61 Hz line-scan cycle requiring 8.4 seconds for completion of each image; setpoint currents and bias voltages are given in the figure captions. It is generally difficult to image oxide surfaces under ambient conditions, particularly after exposure to electrolyte solutions. STM tips tend to oxidize, and conduction by "loose" ions can swamp tunneling currents. Tips change their resolving ability frequently (Rohrer et al., 1992). Two approaches were used to minimize these problems; Tungsten tips were covered with an inert oil that protects the tip from oxidation and does not appear in STM images (Eggleston and Hochella, 1990). Platinum/Iridium tips (far less prone to oxidation) were used for imaging in air. In both cases, the sample was "wet" in that its surface was coated with layers of water adsorbed from air.

Results

Figure 1 shows two STM images of a hematite (001) surface after exposure to Cr(III) solution. Under the imaging conditions used, electrons tunnel from the sample valence band into the tip, and the images show the surface distribution of occupied electron states near the top of the valence band. Previous STM imaging of hematite (Eggleston and Hochella,

Figure 1. Two successive STM images of a hematite (001) surface after exposure to a Cr(III) solution, taken at -320.2 mV and 1.1 nA average tunneling current in constant height mode (image contrast is due to variation in tunneling current). Current relief is 220 pA. These images are part of a longer image sequence spanning 1.5 minutes, and show the reproducibility of surface features. A) A linear defect is found in the upper-left corner; other features that are reproduced in B) are marked. B) Site 2 is one atomic row nearer to site 1 than in A, suggesting that site 1 has moved to the right or that site 2 has moved to the left.

1992) showed that under these conditions the periodicity of the oxygen sublattice is seen. Although individual atoms are not well-resolved in Fig. 1, the spacing of the near-vertical rows (~ 2.3 Å) is consistent with the oxygen sublattice. In the upper left is a linear defect that serves as a landmark, with a small bright site [1] below the defect. In lower left is a larger bright site [2].

I contend that the bright sites correspond to adsorbed Cr(III). They were not observed on fresh hematite surfaces. They often occupy a single site for several scans, but then disappear; such sites sometimes appeared on “clean” areas of the surface. Therefore, it is unlikely that they represent bulk defect outcrops. Their immobility is consistent with the expected immobility of adsorbed Cr(III). They are points of high tunneling current, consistent with expectation (see above). Finally, X-ray absorption spectroscopy of Cr(III) sorbed on goethite (Charlet and Manceau, 1992) shows that Cr(III) indeed forms inner-sphere complexes and clusters on iron oxide.

Changes in the vertical distance between sites 1 and 2 could simply be a drift artifact. However, note that site 2 spans the third and fourth rows to the right of site 1 in Fig. 1A, but spans the second and third rows to the right of site 1 in Fig. 1B. Either site 1 has moved to the right one row, or site 2 has moved to the left one row. Site 1 has certainly moved, because it is closer to the linear defect; it may have also moved to the right. Later, sites 1 and 2 both disappeared.

Site 2 “covers” at least three surface oxygen sites; site 1 is much smaller, affecting apparently only one surface oxygen site. Interpretation of the electronic states involved in STM imaging will require a computational study, but we may speculate that site 1 appears smaller than site 2 simply because it has fewer bonds to the surface, perhaps 1 instead of 3.

Figure 2. A sequence of STM images taken in constant-height mode at -565 mV and average current of 821 pA; current contrast is 600 pA. The sequence spans 34 seconds. The text discusses sites 1–3 marked in (A). These sites are reproduced in (B) and (C), although motion of sites 1 and 3 occurs in this time (black arrows point to the positions of the sites; white arrows show the direction of movement since the last image). Site 3 disappears in (D), and a surface dimer is visible along the upper-left edge of (D).

Figure 2 shows a sequence of STM images of a Cr(III)-exposed hematite surface. These images were made at higher bias voltage than previous occupied-state STM images of hematite (Eggleston and Hochella, 1992), and show (where visible, e.g., Fig. 2C) periodicity characteristic of the iron rather than the oxygen sublattice. This may reflect iron states lying deeper in the valence band than sampled in the earlier study, or it may reflect a dependence of the image characteristics on tip-sample distance. In any case, the “background” surface structure is poorly resolved. However, several types of change are observed. Several of the bright sites in Fig. 2A disappear by Fig. 2C, approximately 17 seconds

Figure 3. An STM image (constant height mode, 1100 mV, 1.1 nA, current contrast is 350 pA) showing a surface cluster and two nearby monomers. The monomers disappeared in later scans.

later. We concentrate our attention on the three bright sites labeled in Fig. 2A. Site 3 moves roughly 3 Å down and to the left between Figs. 2A and 2B, and then disappears in Fig. 2D. Site 1 moves about 5 Å downward between Figs. 2B and 2C, and then moves about 3 Å closer to site 2 between Figs. 2C and 2D. A dimer is visible along the upper left edge of Fig. 2D. We cannot be absolutely sure that the short hops are not desorption of one adsorbate and adsorption of another, but this seems unlikely if adsorption to unoccupied sites is equally likely anywhere.

The short hops seen in Fig. 2 are not typical, but are presented to show that short hops do occur. More often, however, bright sites such as site 2 in Fig. 1 were immobile for several scans, up to 9 minutes in one case, but then disappeared through desorption (e.g., site 3 in Fig. 2).

Surface clusters were also observed, as predicted by Charlet and Manceau (1992). An example of a surface cluster, with perhaps four or five members, is presented in Fig. 3. Fig. 3 is part of a longer sequence, and shows two monomers near the cluster. The lower monomer was immobile for one minute before disappearing; the monomer near the cluster was visible for only two scans (about 17 seconds). The cluster was immobile throughout the sequence.

Discussion

The study of surface diffusion by STM observation of individual species is in its infancy, even in chemically simpler ultra-high vacuum systems; only a few examples exist (Ganz et al., 1992; Hwang and Golovchenko, 1992). The present study is an initial step toward STM study of aqueous surface diffusion; the observations to-date are not sufficiently numerous to provide reliable statistical averages, but general comments can be made about thermally-activated surface self-diffusion of Cr(III). In addition, we can make use of the fact that Cr(III) and Fe(III) form isostructural oxides to comment on the probable surface behavior of Fe(III) in dissolution and growth.

The image sequences presented here, as well as other sequences, show that individual adsorbates stay in one location for times ranging from probably somewhat less than the single-image acquisition time (8.4 seconds) up to several minutes, the longest observed immobile period being 540 seconds. The residence time in a single site τ is related to the activation energy barrier E_a and attempt frequency ν according to

$$\tau = \nu^{-1} \exp(E_a/RT)$$

where R is the gas constant and T is temperature in K . We have no measure of ν for Cr(III) surface self-diffusion, but we can make estimates. Table I shows E_a for surface mobility of Cr(III) based on example site-residence times that bracket the STM data, calculated assuming attempt frequencies of 10^{13} s^{-1} and 10^6 s^{-1} . The high value is kT/h (h is Planck's constant) and overestimates E_a ; ligand-exchange controlled surface mobility is likely to require cooperative motions of neighboring atoms, so its ν should be much lower than kT/h . The low value is the frequency found for surface self-diffusion of Pb on Ge(111) surfaces in vacuum (Ganz et al., 1992) where Pb mobility depends on cooperative motions of neighboring Ge atoms and thus compares to the present situation. Table I shows that even for the limiting case, the activation energy for Cr(III) self-diffusion on hematite (001) is lower than for aqueous water exchange.

Table 1. Estimated E_a for Cr(III) surface diffusion (site hopping) based on site residence times (τ) from the STM data and estimated attempt frequencies (ν).

τ (sec)	E_a (kJ mol ⁻¹)	
	$\nu = 10^6 \text{ s}^{-1}$	
	74.2	34.2
10	79.9	39.9
100	85.6	45.6
1000	91.3	51.4

For comparison, E_a for H₂O (or OH) exchange in aqueous Cr(III) species are:

Cr(H ₂ O) ₆ ³⁺	112 kJ mol ⁻¹
Cr(H ₂ O) ₅ OH ²⁺	93 kJ mol ⁻¹

There are several possible reasons for this discrepancy. First, it may be that STM imaging affects the behavior of adsorbates. Ganz et al. (1992) and Dunphy et al. (1993) examined this question and found no influence of the STM, but we nevertheless cannot rule it out here. Second, the ligand exchange energetics of adsorbed species probably differ substantially from those of aqueous ions. Finally, ligand exchange by Cr(III) is not the only possible rate-controlling factor; Fe(III) ligand exchange by substrate atoms may also play a role. For example, adsorption of Cr(III) onto aluminum oxide is much faster than can be explained by ligand substitution of aqueous $\text{Cr}(\text{OH})^{2+}$ (Wehrli et al., 1990), and it is possible that Al(III) ligand exchange plays a role in that case.

In future, temperature-dependent STM studies of Cr(III) surface mobility may be used to directly determine thermal activation parameters. Other metal ions with slow ligand substitution, such as Ru^{2+} , Ru^{3+} and Pt^{2+} , may also be accessible to such techniques. Although these ions do not appear to have much relevance for natural aquatic systems, studying their behavior could prove useful in understanding the behavior of other ions. Sverjensky (1992, 1993) has shown that appropriately formulated linear free-energy relationships allow relatively accurate determination of dissolution rates and adsorption equilibria within isostructural systems. If aqueous ions and solid oxides of "slow" and "fast" metals participate in isostructural reaction mechanisms, knowledge of the behavior of "slow" metals can be used to predict the behavior of more common naturally occurring metals.

As a preliminary example, the fact that Cr(III) and Fe(III) form isostructural oxides suggests that what we learn about the behavior of Cr(III) may also give hints to the behavior of Fe(III) on hematite surfaces. In the BCF model (Burton et al., 1951), the velocity of a train of parallel steps on a surface during dissolution or growth is

$$v_{\text{BCF}} = v_0 \tanh(l/2x_s)$$

where v_0 is the velocity of an isolated step, l is the distance between steps, and x_s is the mean distance moved by adsorbates before desorption. If, as STM results suggest, x_s is very short, such that $x_s \ll l$, then $\tanh(l/2x_s) \rightarrow 1$, $v_{\text{BCF}} = v_0$, and surface diffusion will not affect the growth rate or the step spacing. Although x_s for adsorbed Cr(III) and Fe(III) is probably pH-dependent, step spacing would be pH-independent. Data are not yet available for hematite, but this is consistent with the results of Gratz et al. (1991) in which the slope of a surface consisting of equally-spaced steps on dissolving quartz are independent of pH and ionic strength. This conclusion has also been reached for calcite dissolution (Gratz et al., 1993), albeit for different mechanistic reasons.

Conclusion

STM imaging of Cr(III) adsorbed to hematite surfaces is possible, and can be used to obtain information on site-binding energetics and surface mobility. The surface mobility of Cr(III) on hematite is very low, but not as low as Cr(III) ligand substitution kinetics in aqueous solutions would suggest, indicating either accelerative influences of STM imaging, surface effects on Cr(III) ligand substitution kinetics, or involvement of ligand substitution reactions of the substrate Fe(III).

The STM observations suggest that Cr(III) rarely moves across a surface by a large number of successive single-site hops. Desorption and re-adsorption appear to be more

common. This is consistent with the idea that surface diffusion kinetics are controlled by the same ligand-substitution processes by which adsorption and desorption kinetics are controlled. Observations at the atomic scale, such as those made here, coupled with microtopographic observations and with aqueous dissolution/growth rate experiments, hold great promise in leading to valuable and detailed insight into mineral surface reaction mechanisms and the role of surface complexation in controlling them.

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