

Application of Surface Spectroscopies and Microscopies to Elucidate Sorption Mechanisms on Oxide Surfaces

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Abstract

Retention reactions on particulate of soils and waters are of environmental and agricultural significance because these reactions can greatly affect the risk imposed by contaminants and the availability of plant nutrients. The surface structure of the sorbate determines their potential for remobilization to the aqueous environment and the physical/chemical modifications of the sorbent. Therefore, it is essential to employ experimental techniques that provide direct and accurate information on sorption mechanisms. In this study, the use of multiple surface probing techniques for investigating sorption reactions is demonstrated for Cr(III) retention on a commonly occurring natural sorbent, amorphous SiO₂ (silica). Extended X-ray absorption fine structure (EXAFS) spectroscopy, diffuse reflectance infrared Fourier transform spectroscopy (DRIFT), high-resolution transmission electron microscopy (HRTEM), and surface probing microscopy (SPM) were used to discern the structural environment of Cr(III) on silica. Chromium(III) formed a monodentate surface complex on silica, which with increased Cr(III) levels resulted in a nucleated γ -CrOOH type structure. The initial nucleation expanded on the silica surface, but as precipitation progressed discrete highly-ordered γ -CrOOH surface clusters formed rather than a precipitate that was distributed over the surface. Consequently, when modeling the retention reaction surface complexation and precipitation must be considered; desorption would be dominated by the dissolution of the chromium hydroxide surface clusters.

Introduction

Reactions at the solid/solution interface have dramatic influences on environmental quality and agricultural productivity. Characterization of solids in soils and waters, in addition to reactions which occur at their surfaces, is necessary to assess the reactivity of a system. Obtaining direct evidence on interfacial reactions is important to definitively identify reaction products and the stability of these species. Recent advances in surface characterization techniques has greatly enhance one's ability to study reactions at the solid/solution interface. Unfortunately, no single technique provides a complete depiction of most systems. Accordingly, it is important for researchers to employ multiple techniques to accurately study a system and thus obtain detailed information of reactions mechanisms.

Surface spectroscopies and microscopies have advanced rapidly and offer a host of capabilities. For studying retention mechanisms and the properties of the sorbate and modified sorbent, methods which yield electronic and structural information on the sorbate and surface structural (morphological) information on the sorbent/sorbate composite are necessary. To our knowledge no single technique provides all of this information. Accordingly, it is essential to employ a multitude of complimentary techniques. The electronic state of sorbed species can be determined with electronic (UV/VIS) or x-ray absorption spectroscopies. In some cases, scanning tunneling microscopy (STM) can also be used to derive electronic states of surfaces.

Magnetic, vibrational, and x-ray absorption spectroscopies can be used to determine the local structure of a sorbate. Microscopic techniques, such as electron and scanning probe microscopies, are needed to discern the structure and morphology of the sorbent/sorbate surface.

A powerful means for studying the local chemical and structural environment of an element in solutions, suspensions, or solids, is x-ray absorption fine structure (XAFS) spectroscopy. XAFS provides one with information on the oxidation state of the x-ray absorbing element along with its local structure on a very quantitative basis. While atomic information is probed with XAFS, Fourier transform infrared (FTIR) spectroscopy can be employed to ascertain molecular interactions of a sample. Often XAFS can be used to give precise structural information as to the source of FTIR spectral features. Neither of these spectroscopies, however, provide spatial resolution unless the probed element or molecule is limited to a certain region of the sample--which is the case for most spectroscopies except, for example, Auger spectroscopy. Microscopic techniques thus complement spectroscopic studies since they provide spatial information, often which can be obtained with atomic resolution. They do not, however, provide information exclusive to a single element. Transmission electron microscopy (TEM) can be employed to discern the atomic ordering of a sample along with surface modifications. However, surface modifications must possess a depth dimension sufficient to attenuate the impinging electrons. This restriction can be circumvented with scanning probe microscopes (SPM), such as atomic force (AFM), which provides detailed atomic and morphological information that is restricted to the surface. Additionally, SPM can be conducted in aqueous systems, thus removing the need to subject the sample to an altered analytical environment. In this study, the utility of a composite surface analysis using XAFS, FTIR, TEM, and SPM will be exemplified with Cr(III) sorption on silica.

Inorganic compounds are potential pollutants which can be particularly problematic due to their stability in the environment. Chromium is an environmentally significant metal used in various industrial processes. Of the two Cr oxidation states that are stable in the environment, Cr(VI) is much more hazardous than Cr(III) and is very mobile in soils and waters. Oxidation of Cr(III) by manganese oxides makes this rather benign species a potential hazard. One possible mechanism for retarding Cr(III) oxidation is its retention by other non-redox reactive sorbents present in soils or waters. This would prevent oxidation by inhibiting Cr(III) from complexing with manganese oxides.

Although commonly only a small fraction of the solids in soils or sediments, hydrous oxides (i.e., hydroxides, oxyhydroxides, and oxides) can play an important factor in the environmental behavior of metal ions. The influence of hydrous oxides is enhanced by the formation of high surface area particles and surface coatings on other soil materials. Silica (SiO_2) is a commonly occurring hydrous oxide which readily forms coatings on other solids. It often has a very high surface area and thus exerts a large influence on sorption reactions. Moreover, sorption reactions are extremely influential on the risk of metal ions in the environment since the metals are removed from the mobile aqueous phase. Hence, to determine the hazard of Cr in the environment, knowledge of Cr(III) sorption on non-redox reactive solids, such as silica, is necessary.

Determining surface structures is necessary to elucidate reaction mechanisms, the stability of bound species, and for evaluating the physical/chemical properties of the modified sorbent. Therefore, the objective of this study was to investigate the surface structure of Cr(III) sorbed on SiO_2 and to determine the surface modification and stability of the bound phase. By employing XAFS, DRIFT, SPM, and HRTEM a composite of information was obtained, which allowed for an accurate and detailed analysis of the Cr(III)- SiO_2 sorption mechanism. The local chemical and structural environment of Cr(III) was ascertained with XAFS, molecular information with DRIFT, and HRTEM and SPM provided spatial resolution and information on the surface structural modification of the silica after reaction with Cr(III). The DRIFT spectra

were evaluated by comparing vibration modes of 'neat' silica and γ -CrOOH to the Cr-silica systems. The results gleaned with XAFS were compared to the information obtained with DRIFT analysis. This permitted the use of DRIFT for evaluating the effect of an extensive range of reaction parameters on the Cr(III) surface structure. Atomic-ordering and surface alterations induced by Cr(III) sorption on the silica surface were ascertained with HRTEM and SPM.

Materials and Methods

Batch Studies

The silica used in this study was a Huber Zeothix[®] 265 amorphous SiO₂ colloid, synthesized as described by Wason (1978). The oxide was washed in pH 3.5 HNO₃ and then dialyzed in doubly distilled deionized water until a stable conductivity resulted for 24 h. The surface area was 221 m² g⁻¹, as determined by the ethylene glycol monoethyl ether (EGME) method (Heilman, 1965). The particle size of the oxide was less than 2.0 μ m.

Batch studies were performed to determine the amount of Cr(III) sorbed on SiO₂ as a function of pH and initial Cr(III) concentration ([Cr]₀). A pH range of 3 to 7 was investigated with initial concentrations of 100, 200, 400, and 5 x 10³ μ M Cr(III). For the batch studies, 0.5 g SiO₂ was dispensed in reaction vessels with 2 L of 0.1 M NaNO₃. A 10 mM Cr(III) stock solution was used to obtain the desired Cr(III) concentrations. The stock solutions were made from ACS reagent grade Cr(NO₃)₃ · 9H₂O, with acidified deionized water (pH \leq 2) and were never allowed to age more than five days to limit potential polymerization.

The oxide was allowed to hydrate for 48 h prior to reaction. After the hydration period the pH was adjusted, the desired amount of Cr(III) was added, and the final volume brought to 2 L, yielding a suspension density of 0.25 g L⁻¹. The pH was held constant with a pH-stat system; upon reaching a steady pH the vessels were placed in a water bath reciprocating shaker. After 48 h the samples were filtered through a 0.22 μ m pore membrane and the solution analyzed for Cr with a JY-70 ICP spectrophotometer. The sorption data and structural information gleaned in this study are representative of the reaction after a 48 h time period, and therefore may not be indicative of sorption at equilibrium (Wehrli et al., 1990).

All reactions were carried out at 25 \pm 0.5 $^{\circ}$ C at 1 atm pressure in a N₂ (g) environment to eliminate the influences of CO₂. The initial solutions were purged with N₂ (g) prior to the addition of the oxide. Thereafter, a N₂ (g) stream was maintained over the surface of the fluid when the vessels were exposed to the surrounding environment.

In this study the data are referenced to the potential surface site occupancy, ϕ ,

$$\phi = (\text{mols Cr sorbed})/(\text{mols surface sites}) \quad [1]$$

One should be aware that this does not imply a site occupancy but only a potential maximum if each sorbed Cr(III) occupied a single site. If polymerization or nucleation occurs then a different amount of the surface sites would be occupied (i.e., an amount less than ϕ would be covered). This parameter, ϕ , is employed because it allows one to easily recognize the quantity of sorbed Cr necessary for monolayer coverage; at less than potential monolayer coverage isolated site binding can account for the total sorption quantity, but at $\phi > 1$ nucleation or multi-layer adsorption is required. An estimated reactive surface site density of 5.5 sites nm⁻² (Fouad et al., 1991) was used to calculate the site density for silica. For XAFS studies, samples reacted at

pH 6 were employed for analysis because this pH is common to soils and waters, and represents complete uptake of aqueous Cr onto the silica surface.

Solids were consolidated prior to their analysis. The equilibrated suspensions were passed through a 45 mm diameter 0.22 μm membrane filter; the filtrate was then rinsed with 100 ml of high purity water to remove the entrained electrolyte. The solid material was then placed in a vial and sealed. The samples remained moist and were never allowed to dry. In addition, a hydrous chromium oxide (HCO) was precipitated by titrating 20 mM Cr(III) to pH 6, with pH maintained at this level for 24 h. This procedure was similar to that used by Charlet and Manceau (1992).

XAFS Studies

XAFS spectroscopy was performed at the National Synchrotron Light Source, Brookhaven National Laboratory, under dedicated running conditions on beam line X-11A. A Si(111) water cooled double crystal monochromator was employed with a sagittally focused beam (Lamble and Heald, 1991). The focused beam provided an intensity greater than three times that provided by the conventional flat monochromator arrangement over the energy range used for this study. A 0.5 mm pre-monochromator slit width was employed, which was readjusted as necessary to compensate for vertical motion of the stored electron beam. Higher-order harmonics were rejected by detuning 30% from the maximum incident intensity (I_0).

Reference materials were run in transmission mode and the transmitted intensity measured with an ionization chamber. All Cr(III)-SiO₂ systems were analyzed by fluorescence detection. Samples were analyzed at ambient and N₂ (1) temperatures (298 and 77 K); no structural differences were discerned between these temperatures and consequently the 77 K spectra are reported due to the reduction in thermal disorder.

All samples were run at least in triplicate. Data analyses were accomplished by optimizing the fit of predicted spectra with Fourier filtered experimental spectra. Phase shifts for O, Si, and Cr were obtained using model compounds: Cr using a Cr-metal and α -Cr₂O₃, O with α -Cr₂O₃, and Si with NiSi. Amplitude parameters were defined based on α -Cr₂O₃. Successive shells were isolated in the Fourier transformed spectra, back-transformed, and the interatomic distances (r 's), coordination numbers (CN's), and Debye-Waller factors ($2\sigma^2$) varied until the best fit was obtained between the predicted and experimental curves. After obtaining the structural information for each successive shell out to 4 \AA , the structural parameters were then combined to model the entire spectra. The resulting r values for the first coordination shell were accurate to ± 0.03 \AA and CN to $\pm 20\%$ based on fits to model compounds--more distant shells will be successively less accurate in both r and CN. Further details on the XAFS analysis are given elsewhere (Fendorf et al., 1993).

Infrared Analysis

Diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy was performed using a Perkin-Elmer FT-IR 1720X spectrometer with a diffuse reflectance accessory. Samples were prepared using the batch methods described earlier; after reaction the solid material was washed with 100 ml of deionized water and the solids dried at 60°C for 24 h. The dried material was then diluted by 90% (by weight) with KBr to reduce the influences of spectral reflectance. Reported spectra are the average of 200 scans.

In addition to the Cr-SiO₂ samples, reference materials were analyzed for comparison. Reference spectra were obtained for HCO (the γ -CrOOH type structure) and SiO₂. EXAFS analysis and electron diffraction patterns confirmed that the precipitated HCO material was γ -CrOOH. The standards were also diluted by 90% (by weight) with KBr prior to DRIFT analysis.

Microscopic Analysis

High-resolution TEM was performed on high surface coverage Cr(III) reacted silica, $\phi = 9.9$. For HRTEM analysis, 0.25 mL of the reacted suspension was dispersed on a holey carbon film supported by a fine mesh copper grid. The oxide coated grids were then rinsed with 50 mL of deionized water, and dried in a glass chamber. Imaging was then performed on a Hitachi 9000NAR electron microscope. Scanning probe microscopy was performed on moist samples after filtration on a Digital Instruments NANOSCOPE II operating under conventional force. A low pass filtering (not Fourier filtering) of the acquired images was conducted to improve image quality.

Results

Local Structure of Cr(III) on Silica

The extended portion of the XAFS (EXAFS) spectra was utilized to discern the local structural environment of Cr(III) sorbed on silica. A range of initial Cr(III) concentrations (100, 200, 400, and $5 \times 10^3 \mu\text{M}$) at pH 6 were investigated with 0.500 g SiO₂ present. Batch adsorption isotherms revealed that all of the aqueous Cr(III) at pH 6 was depleted. Thus, these initial Cr(III) concentrations correspond to potential site occupancies (ϕ) of 0.20, 0.40, 0.79, and 9.9. The experimental spectra for the Cr-SiO₂ systems are shown in Fig. 1 along with that of HCO, Cr(OH)₃ • nH₂O.

The structural parameters derived from EXAFS analysis are summarized in Table 1. The highest surface loading ($\phi = 9.9$) is not reported due to possible influences from self-absorption processes arising in these more concentrated samples. In all of the Cr specimens approximately six O were observed at 1.99 Å. In γ -CrOOH, a second shell composed of two Cr at 2.99 Å (edge sharing CrO₆ octahedra) and a third shell of 1.5 Cr at 3.98 Å (corner sharing octahedra) were discerned. These results are in good agreement with the structural parameters determined by others for γ -CrOOH (Manceau and Charlet, 1992; Corker et al., 1991). The first two shells (i.e., six O at 1.99 Å, and two Cr at 2.99 Å) in all the Cr(III)-SiO₂ samples were similar to those of the Cr-hydroxide, with slight variations in the CN. However, a different third shell resided in these materials: a single Si atom at 3.39 Å (Fig. 2). Consolidating the structural parameters derived from the isolated shells resulted in good agreement between the predicted and experimental EXAFS functions for the samples (Fig. 3).

The Si-Cr distance of 3.39 Å represents a monodentate complex, in agreement with the CN, and would necessitate a 150° Cr-O-Si bond angle. Beyond the Si shell another Cr shell occurred; however, the EXAFS intensity of this shell is much weaker than the inner-shells and therefore one must place less confidence in the derived structural values. Nevertheless, further structural information can be obtained by considering the crystallographic parameters of the sorbent and sorbate. Assuming that the silica surface is dominated by alternating tetrahedra, then Cr(III)

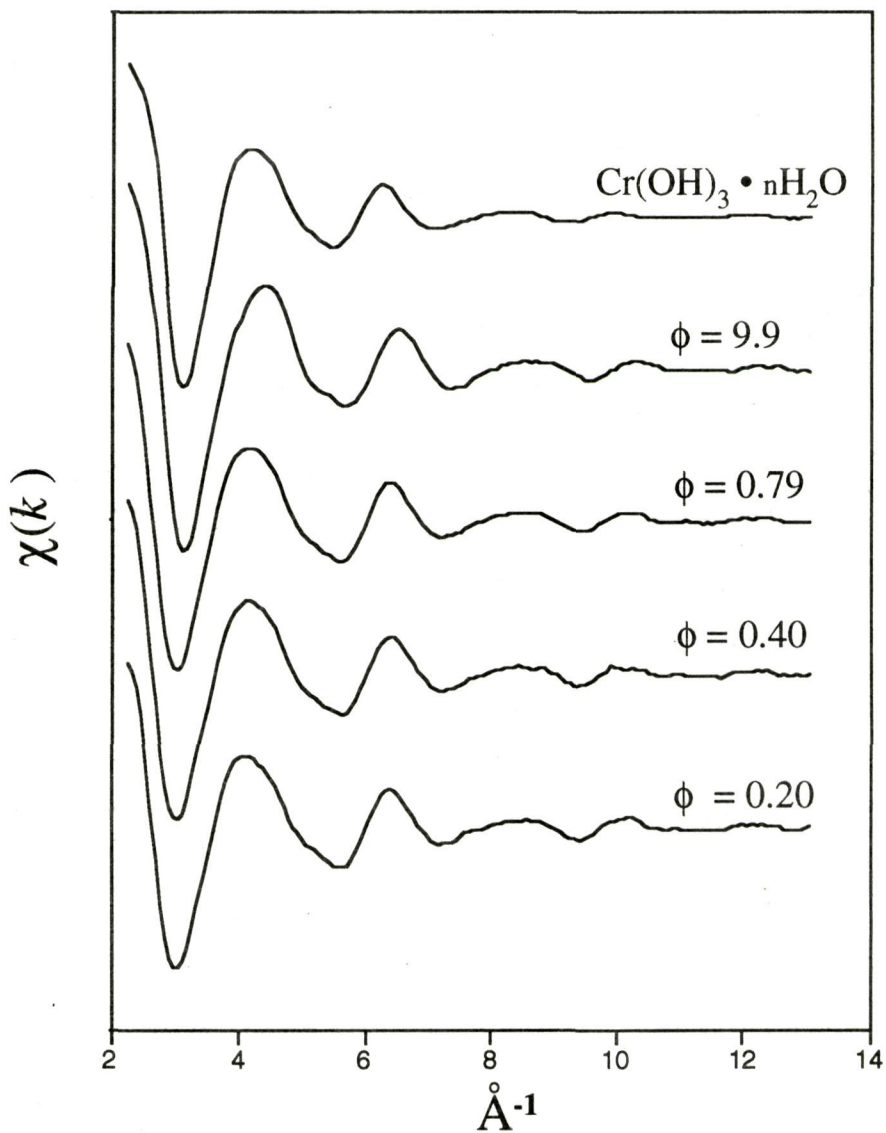


Figure 1. Experimental EXAFS spectra of Cr(III) sorbed on silica.

Table 1. Structural information derived from EXAFS analysis: interatomic distances (r , Å), coordination numbers (CN), and the Debye-Waller factors ($2\sigma^2$, Å²). The O, edge sharing Cr octahedra, and Si coordination shell of a central Cr are reported.^a

	Cr-O			Edge: Cr-Cr			Si-Cr		
	r (Å)	CN	$2\sigma^2$	r (Å)	CN	$2\sigma^2$	r (Å)	CN	$2\sigma^2$
γ -CrOOH	1.99	5.7	0.008	2.99	1.5	0.006			
$\phi=0.79^b$	1.99	6.2	0.005	3.00	2.3	0.010	3.38	1.1	0.009
$\phi=0.40^b$	1.99	6.0	0.005	2.98	2.5	0.010	3.40	1.0	0.008
$\phi=0.20^b$	1.98	6.2	0.005	3.01	2.9	0.011	3.39	0.71	0.009

^aBased on standards and internal deviation, the reported values are accurate to within $r \pm 0.03$ Å., CN $\pm 20\%$.
^bPotential surface site coverage for Cr(III) sorbed on silica (mols Cr / mols surface sites).

in a monodentate complex with a bond angle of 150° would result in a favorable distance, approximately 3.9 Å, for hydroxyl bridging between adjacent Cr(III). Based on this premise, the resulting surface structure is a monodentate surface Cr(III) complex and a HCO precipitate with the γ -CrOOH type structure that is shown in Fig. 4.

DRIFT Analysis

The DRIFT spectrum for γ -CrOOH is shown in Fig. 6. One notes a strong, sharp absorbance at 1385 cm⁻¹ and a broader one at 1417 cm⁻¹. These peaks are characteristic of the bending modes for metal oxyhydroxides (Me-OH-Me) with the boehmite type structure (γ -MeOOH) (Ryskin, 1974) and correlate well with the previously defined deformation modes of γ -CrOOH (Snyder and Ibers, 1962). The 1385 cm⁻¹ peak is thus assigned to the in-plane (γ -OH) bending mode and the 1417 cm⁻¹ to the out-of-plane (δ -OH) mode. The presence of these modes in the Cr-SiO₂ systems may be evidence for the formation of a γ -CrOOH precipitate. The DRIFT spectrum of unreacted SiO₂ is also given in Fig. 7. The 'neat' silica has a strong characteristic water vibrational band at 1630 cm⁻¹. However, the absorbance in the range of 1350-1600 cm⁻¹ is minimal, and thus does not interfere with the prominent bending modes of γ -CrOOH. Consequently, it appears that the 1385 and 1417 cm⁻¹ bands in the Cr-SiO₂ spectra should be good evidence for the formation of a γ -CrOOH surface precipitate, while their absence would suggest that surface nucleation of this phase did not occur.

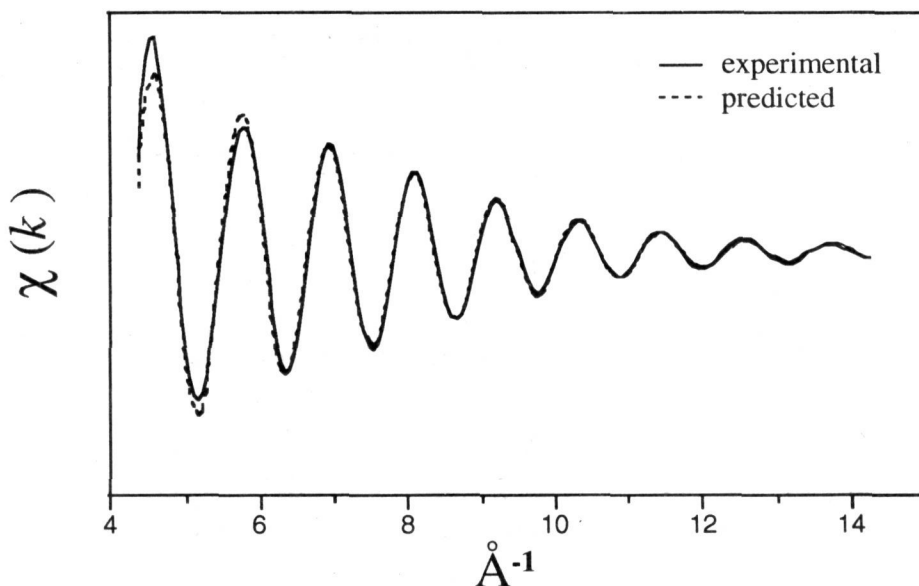


Figure 2. The Fourier back-transformed EXAFS function for the isolated second peak of the Fourier transformed spectra. The predicted fit was obtained by incorporating Si and Cr shells.

A third spectrum is shown in Fig. 7: Cr(III) sorbed on silica ($\phi = 9.9$). In this spectrum 1385 and 1417 cm^{-1} peaks are visible but additional absorbances at 1450 and 1550 cm^{-1} are also apparent. The 1385 and 1417 cm^{-1} absorbances are identical to those observed for the deformation modes in $\gamma\text{-CrOOH}$ and therefore represent the formation of a surface precipitate. The 1450 and 1550 cm^{-1} peaks are not found in the Cr-hydroxide spectra; their appearance and magnitude are correlated except under conditions where the 1450 cm^{-1} peak is obstructed by the 1417 cm^{-1} absorbance. These peaks may be representative of a Cr-O-Si interaction. The $\delta\text{-O}$ and $\gamma\text{-O}$ bending modes in a monodentate Cr-O-Si bond should be shifted to higher energies than for Cr-OH-Cr (Ryskin, 1974). Consequently, the 1550 cm^{-1} peak is assigned to the $\delta\text{-O}$ and the 1450 cm^{-1} to the $\gamma\text{-O}$ vibration in a Cr-O-Si linkage. Table 2 presents the assignment of the peaks for the DRIFT spectra of these materials. With the assignment of the DRIFT peaks in the 1350 to 1600 cm^{-1} region one can identify structural factors arising from the sorption of Cr(III) on silica. In addition, the limits of DRIFT for detecting the surface phases in these systems can be determined.

The DRIFT spectra of 40, 100, 200, 400, and $5 \times 10^3 \mu\text{M}$ $[\text{Cr}]_0$, resulting in ϕ values of 0.079, 0.20, 0.40, and 9.9, are presented in Fig. 7. The latter four conditions were identical to those used in the XAFS study permitting a comparison of results from these two techniques. With $\phi = 0.040$ no alteration from the unreacted SiO_2 spectrum was observed. As ϕ increased

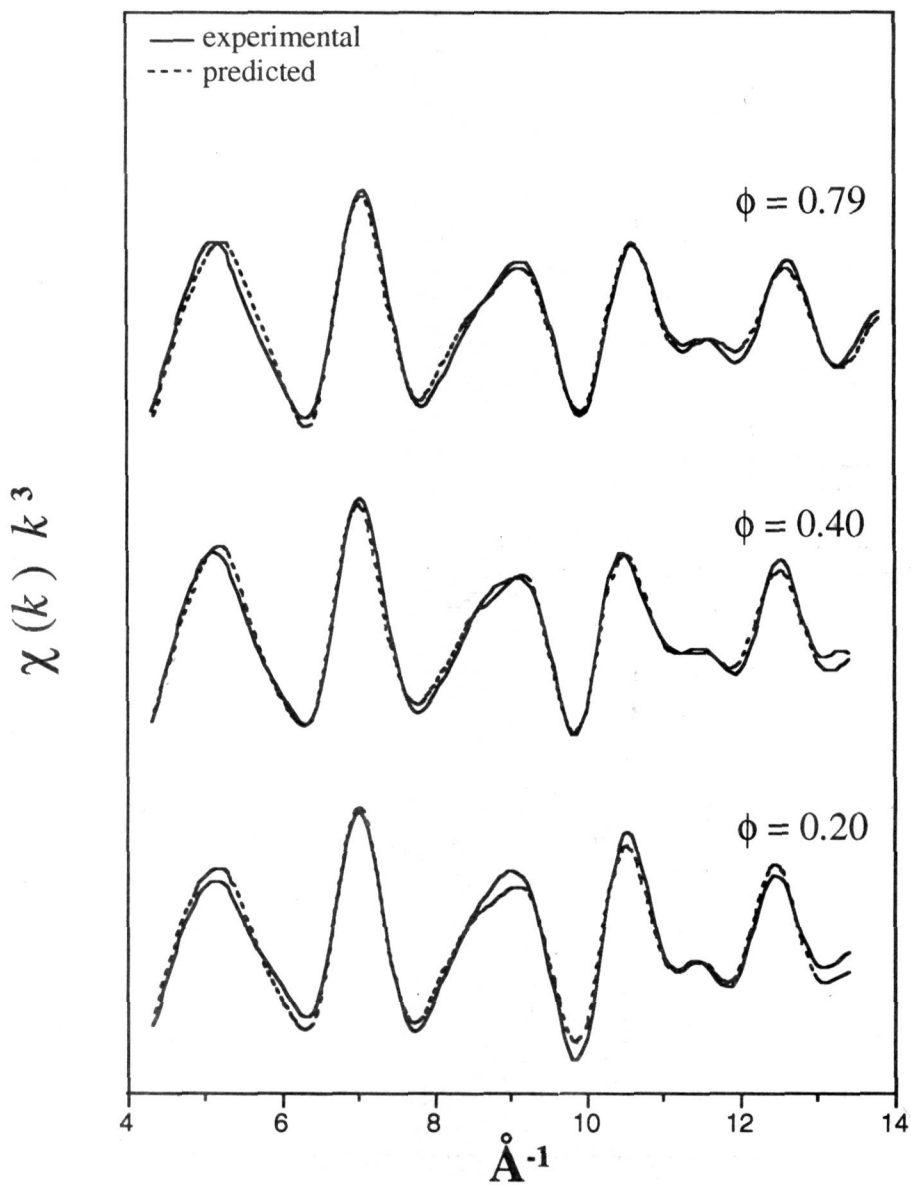


Figure 3. The EXAFS function for the Fourier back transformed spectra. The theoretical line was derived with parameters obtained from analysis of the isolated shells.

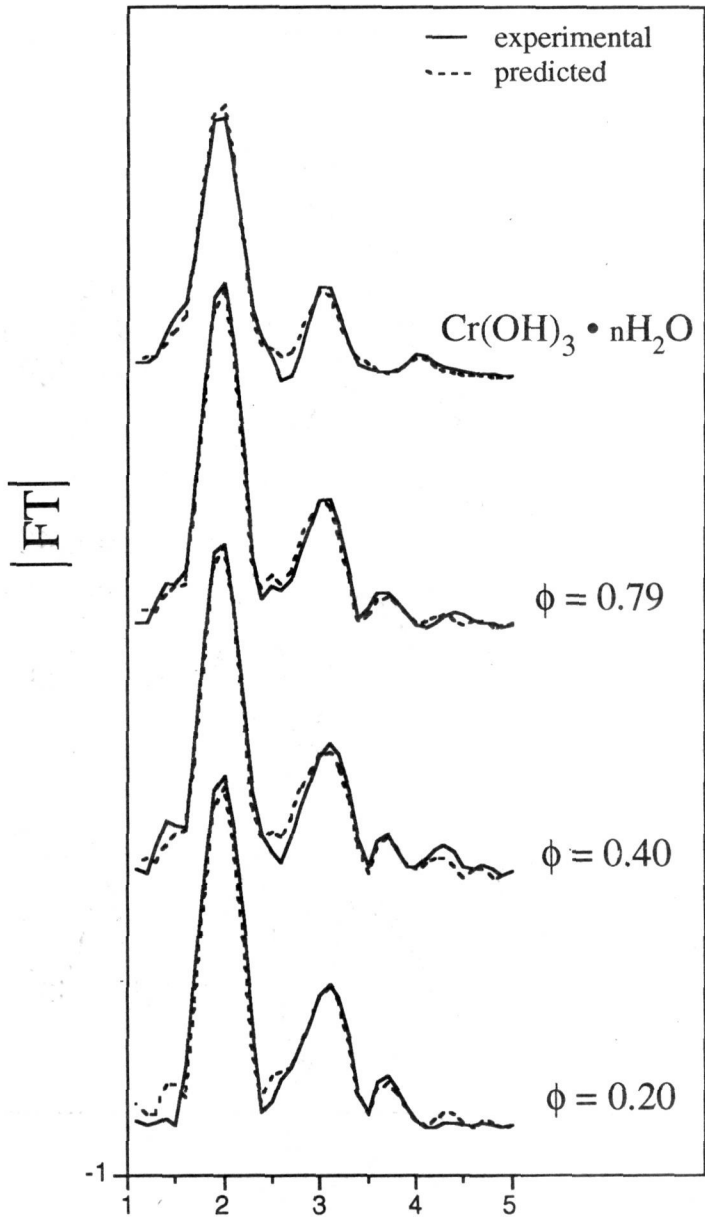


Figure 4. Fourier transformed spectra resulting in the radial structure function (RSF) of the inner 4 Å shells: HCO and Cr sorbed on silica are shown. The first peak results from six O at 1.99 Å; the second from Cr at 2.99 Å. In the presence of Si, the second peak incorporates Si at 3.39 Å.

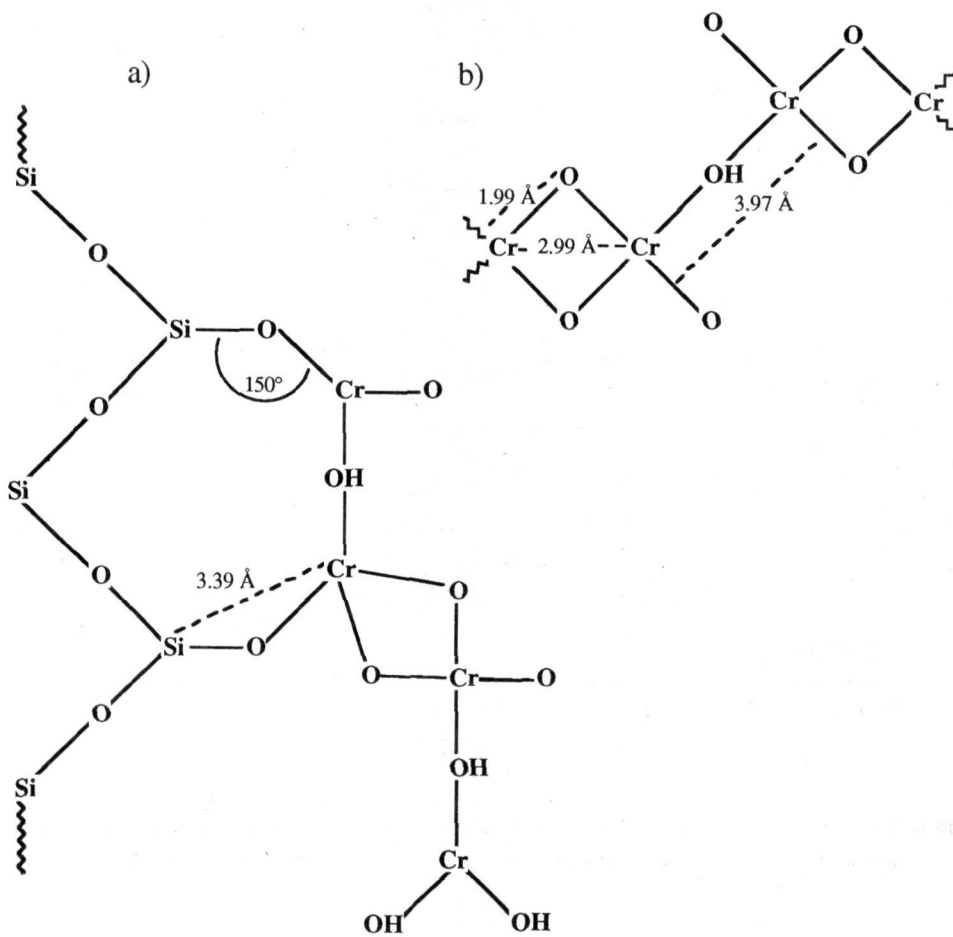


Figure 5. A depiction of the surface structure derived by EXAFS analysis (a) showing the interatomic distances for Cr sorbed on silica. The γ -CrOOH type structure is shown forming in (a) and in (b) the interatomic distances of this phase are given.

to 0.079 relatively broad bands become apparent at 1450 and 1550 cm^{-1} . These broad bands increase in magnitude with further increased ϕ and are the most prominent at the highest coverage ($\phi = 9.9$) depicted in Fig. 7. A sharp peak at 1385 cm^{-1} and a broader band at 1417 cm^{-1} are apparent at $\phi = 0.20$ ($100 \mu\text{M}$ $[\text{Cr}]_0$). The four peaks at 1385, 1417, 1450, and 1550 cm^{-1} all increase with continued increases in surface coverage, but the 1385 and 1417 cm^{-1} peaks clearly begin to dominate this spectral region at higher surface coverage. At $\phi = 9.9$, the 1450 cm^{-1} becomes only a poorly resolved shoulder on the 1417 cm^{-1} absorbance.

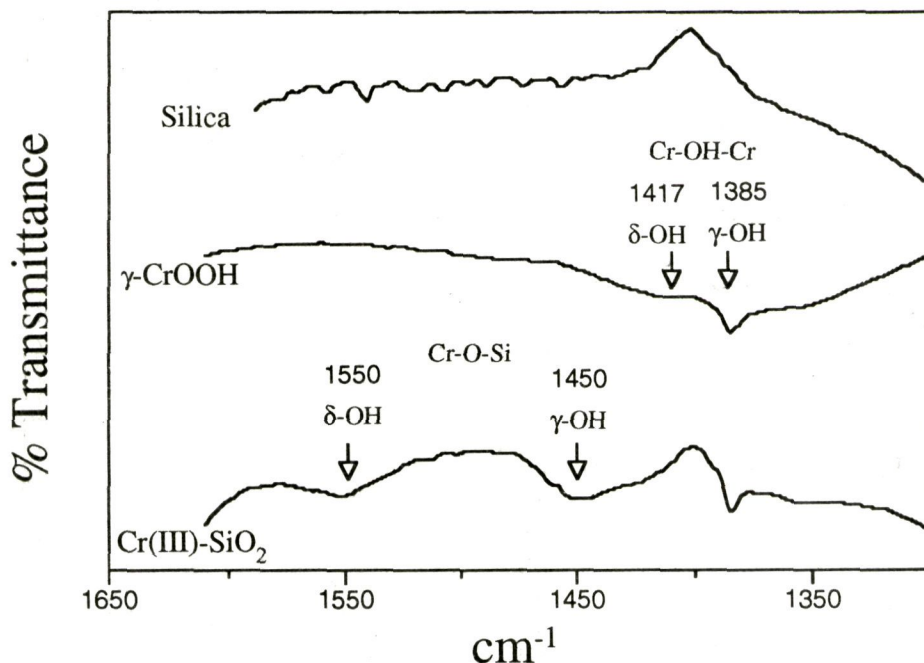


Figure 6. The DRIFT spectra for silica, $\text{Cr}(\text{OH})_3 \cdot n\text{H}_2\text{O}$, and for Cr(III) sorbed on silica with $\phi = 9.9$. The peaks at 1385 and 1417 cm^{-1} arise from the Cr-OH-Cr deformations, and the 1450 and 1550 cm^{-1} peaks are due to Cr-O-Si deformation.

At $\phi = 0.040$ ($20 \mu\text{M} [\text{Cr}]_0$), no structural modifications are apparent with DRIFT spectra. However with a two-fold increase in coverage, 0.079 , the monodentate surface complex (Cr-O-Si) was observed. Hence the detection for sorbed Cr on silica in this study was between 0.04 and 0.08 surface coverage. The 0.079 coverage spectra do not indicate the presence of nucleated Cr-hydroxide. Nucleation of $\gamma\text{-CrOOH}$ is discerned at 0.20 coverage as noted by the 1385 and 1417 cm^{-1} absorbances. Hence, DRIFT spectra indicate that a monodentate surface complexation of Cr on silica occurs at $\phi < 0.20$ ($100 \mu\text{M} [\text{Cr}]_0$), and $\gamma\text{-CrOOH}$ nucleation appears at $\phi \geq 0.20$.

Table 2. The assignment of the deformation modes for γ -CrOOH and surface complexed Cr(III) on silica.

frequency (cm^{-1})	bond type	mode
1385	Cr-OH-Cr	γ -OH
1417	Cr-OH-Cr	δ -OH
1450	Cr-O-Si	γ -O
1550	Cr-O-Si	δ -O

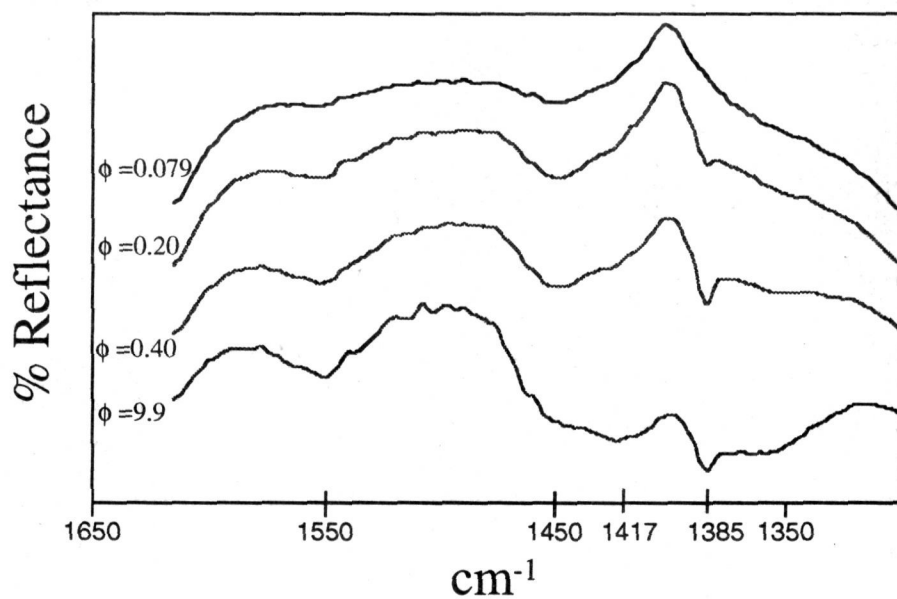


Figure 7. DRIFT spectra for Cr(III) sorbed on silica at $[\text{Cr}]_0$ of: $40 \mu\text{M}$ ($\phi = 0.079$), $100 \mu\text{M}$ ($\phi = 0.20$), $200 \mu\text{M}$ ($\phi = 0.40$), and $400 \mu\text{M}$ ($\phi = 0.79$). The peaks at 1385 and 1417 cm^{-1} represent Cr-hydroxide nucleation, while the absorbances at 1450 and 1550 cm^{-1} indicate a monodentate Cr-SiO₂ complex.

Microscopic Surface Analysis

Although both EXAFS and DRIFT give important information on the local structural environment of Cr(III), it is difficult to determine the spatial proximity and long-range order of the sorbed material with these two methods. Accordingly, HRTEM and SPM were employed to deduce further structural information.

Imaging was performed prior to and after reaction with Cr(III) at $\phi = 9.9$ (Fig. 8). The silica was completely amorphous showing no indications of ordering (marked A). After reaction with Cr(III) distinct crystalline areas approximately 20 nm x 20 nm are clearly visible (marked B). The crystalline areas are a γ -CrOOH surface precipitate. The HRTEM images reveal that even when there was greater than ten times the amount of Cr necessary to occupy all the reactive surface sites discrete crystalline particles formed. This finding indicates that Cr-hydroxide nucleation does not progress over the silica surface but rather formed isolated nucleated areas which, at least with high potential surface coverage, possess long-range order (crystallinity).

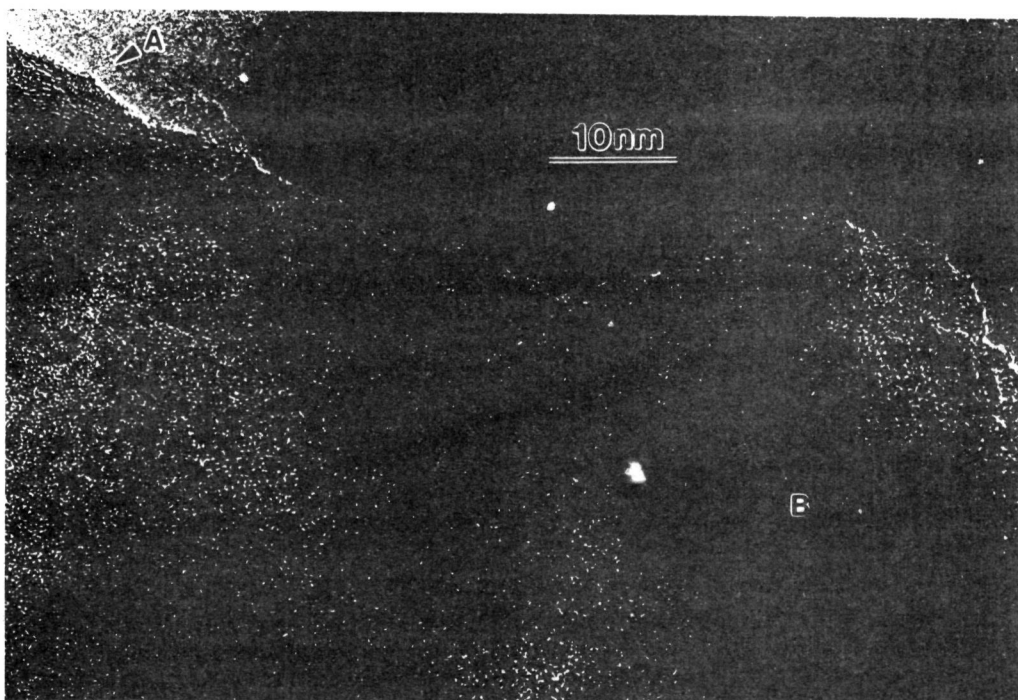


Figure 8. High-resolution TEM image of silica after reaction with 5 mM Cr(III) at pH 6 ($\phi = 10$). A discrete crystalline γ -CrOOH surface precipitate (marked B) has formed on the amorphous silica (marked A).

To further explore the surface distribution and surface morphology of Cr(III) on silica we employed a surface discriminating microscopy: scanning probe microscopy (SPM). A SPM image of the unreacted silica is shown in Fig. 9a. After reacting with Cr(III) a dramatic surface alteration is observed (Fig. 9b). At potential surface coverages ten times monolayer coverage,

discrete island structures are discerned on the silica surface. The SPM images confirm the observations made with HRTEM; the HCO surface precipitate does not distribute over the surface, but rather nucleates forming surface clusters which grow out from the surface. The reacted colloid thus maintains areas of unreacted exposed silica with island structures of HCO protruding from the substrate material. At $\phi = 9.9$, the clusters average about 60 nm in height and 35 nm in diameter--as revealed with SPM. These findings have important implications on the stability of the bound Cr(III) and resulting reactivity of the conglomerated colloid.

Discussion

Both EXAFS and DRIFT analysis indicate that Cr(III) formed an inner-sphere monodentate surface complex on silica. A Si-Cr distance of 3.39 Å was determined; a linear Cr-O-Si arrangement would result in a distance of 3.59 Å, thus a bond angle of 150° is necessary to produce the observed distance. This Cr-Si distance and angle are similar to that observed for Mn in MnSiO₃ (Wyckoff, 1963). Monodentate coordination with a bond angle of 150° implies that the reactive surface O atoms are singly coordinated by Si. This complexation structure agrees with the multisite surface complexation (MUSIC) model (Hiemstra et al., 1989a,b) which indicates that only the singly coordinated O of SiO₂ are reactive in the pH range of 2 to 10. McBride et al. (1984) and McBride (1982) also observed that Cu²⁺ sorbed only to singly coordinated O(H) groups on Al-oxides.

At potential site occupancies (ϕ) below 0.20, only Cr(III) complexed with silica was observed. At coverages equal to and exceeding 0.20, surface nucleation of the γ -CrOOH type structure occurred. A progression from isolated site binding at low coverages to surface hydroxide nucleation of Cu²⁺ on Al-oxides was similarly observed (McBride et al., 1984; McBride, 1982). When nucleation of adjacent surface bound Cr(III) species occurs, HCO nucleation results.

Chromium(III) sorption on α -FeOOH results in a surface precipitate with the α -CrOOH type structure (Charlet and Manceau, 1992); as surface coverage increased nucleation growth expanded over the surface before expanding outward (away from the surface). Further increases in Cr(III) levels resulted in nucleation progressing outward from the α -FeOOH surface and there was a phase transition to the γ -CrOOH type structure. Our results indicate different phenomena for Cr(III) sorption on silica. A monodentate complex of Cr(III) on silica forms; the complexation continues but nucleation of a γ -CrOOH type phase occurs well before monolayer coverage. As nucleation progresses, discrete surface clusters, an island structure, forms rather than distributing over the surface.

It appears that it is more energetically favorable for surface hydroxide nucleation than for complexation of Cr(III) on silica at surface coverages of only 0.20. Furthermore, the precipitate does not grow across the silica surface, but instead forms crystalline clustered structures which protrude away from the surface. Therefore, the sorbent imparts an important influence on surface precipitates. On a surface such as α -FeOOH where the structural environment is similar to that for chromium hydroxides, nucleation progresses over the surface--epitaxial growth. Once a monolayer has been exceeded nucleation progresses outward and some distance from the goethite surface undergoes a phase transformation to adopt a more favorable structure (i.e., a phase transition from α - to γ -CrOOH). A different scenario, however, arises with Cr(III) sorption on silica. Chromium(III) binds to the surface initially in an isolated site mechanism. Increased retention bridges the Cr species, thus beginning nucleation. In response to the energetics of an unfavorable surface O-O distance on silica, nucleation of HCO begins to progress outward from the surface rather than distributing across it. Even at 10 times monolayer

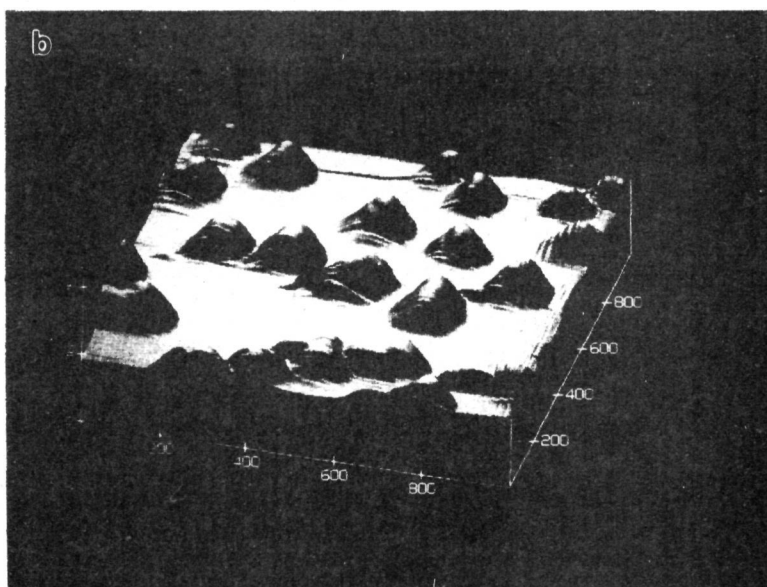
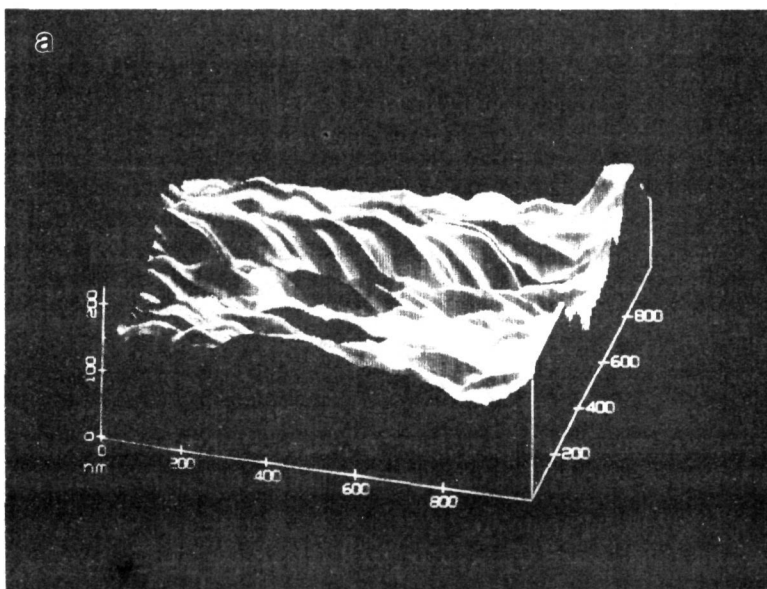


Figure 9. Scanning probe micrograph of (a) silica prior to and (b) after reacting with Cr(III) at potential surface coverages ten times monolayer capacity. The reacted images (b) confirm that the HCO precipitate does not distribute over the surface, but rather forms discrete surface clusters which result in the island structured image. Even at this high surface loading of Cr(III) many areas of the substrate, silica, remain essentially unaltered.

coverage discrete surface clusters are observed with regions of the silica unaltered by the reaction.

Conclusions

Although important information was gleaned with each of the techniques employed, a complete depiction of the Cr(III) sorption mechanism was only discerned by considering the composite of surface information obtained. In order to accurately resolve sorption mechanisms researchers should therefore consider using a multitude of methods that glean atomic information and which support and expand upon each others information. In this study, EXAFS and FTIR spectroscopies were used to obtain molecular information on sorbed Cr(III) while electron and scanning probe microscopies provided surface morphologies and structural alterations.

The results on this study can be summarized as follows: (1) Aqueous Cr(III) is depleted by sorption on silica at pH 6, (2) A monodentate Cr(III)-SiO₂ surface complex forms under these reaction conditions, (3) Chromium hydroxide (HCO) surface nucleation results at ≤ 0.20 surface coverage; the local structure of the sorbate is of the γ -CrOOH type structure, (4) Nucleation of HCO does not progress over the surface but rather forms discrete highly crystalline surface clusters on silica.

Important conclusions relevant to environmental quality and agricultural production are thus gleaned from this information. One must consider monodentate surface complexation and surface precipitation when predicting Cr(III) retention on silica. Additionally, the potential for desorption of Cr(III) will be dominated by the dissolution of the γ -CrOOH islands. And finally, the reacted conglomerated colloid will have physical and chemical properties of both unreacted silica and HCO; future reactions will thus be effected by the properties of these two phases.

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