LETTER TO THE EDITOR

Surface Precipitation Reactions on Oxide Surfaces

Retention of heavy metal ions on solid surfaces is an important process for many catalytic and electrochemical reactions and for maintaining environmental quality. Determining reaction mechanisms is essential for understanding such processes. However, various mechanisms have been proposed for the sorption of cationic heavy metals on oxide surfaces. In this study, we provide direct evidence using high-resolution transmission electron microscopy (HRTEM) for the formation of a surface precipitate prior to bulk solution precipitation. Furthermore, the type of surface present influenced the onset of surface precipitation. At pH 5 and 400 \( \mu M \) Al(III), a surface precipitate was observed on MnO\(_2\) (the birnessite phase) but was not apparent on TiO\(_2\) (the rutile phase). Thus, surface precipitation reactions must be considered in modeling the sorption mechanisms of hydrolyzable metal ions on oxide surfaces. © 1992

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The mechanisms of metal ion retention on colloidal particles are of great interest to colloidal and environmental scientists. The reactivity, high surface area, and coating ability of oxide materials make them very influential in the sorption of metal ions. Numerous thermodynamic approaches have been used in describing metal sorption processes on oxide surfaces (1–8). However, these macroscopic approaches do not give direct evidence for the mechanisms of sorption reactions. Spectroscopic studies have indicated various mechanisms for the sorption of metal ions. Here, we provide direct experimental evidence, using an advanced structure analysis technique, high-resolution transmission electron microscopy (HRTEM), that surface precipitation can occur prior to bulk solution precipitation and is influenced by the type of surface. Consequently, such phenomena need to be considered in catalytic and environmental processes. Mechanistic models proposed to describe cationic metal ion sorption reactions should incorporate surface precipitation reactions rather than modeling the total sorption process as just an isolated-site binding mechanism.

In this study, samples were prepared for HRTEM examination by dispersing powdered oxide, MnO\(_2\) (the birnessite phase) and TiO\(_2\) (the rutile phase), on a holey carbon film supported by a copper mesh grid. The surface areas of the oxides were determined by an EGME method (9) and were 223 m\(^2\) g\(^{-1}\) for MnO\(_2\) and 44 m\(^2\) g\(^{-1}\) for TiO\(_2\). To have similar surface areas of each oxide, 1 mg TiO\(_2\) and 0.2 mg MnO\(_2\) were dispersed on the grids—at 10 ml solution volumes this resulted in 0.1 g liter\(^{-1}\) TiO\(_2\) and 0.02 g liter\(^{-1}\) MnO\(_2\). Reactions were carried out by suspending the oxide-containing grid in a 10 ml solution of 0.1 M NaNO\(_3\) and 400 \( \mu M \) Al(III) at pH 5, 20°C, and 1 atm pressure. After a 24-h reaction period the grids were removed from solution, rinsed in deionized water, and air dried at 20°C. Results were consistent between replicates and within each sample; thus, the results do not appear to be artifacts of individual preparations. Micrographs illustrated in this paper are representative of each treatment. Further details on the HRTEM imaging technique are given elsewhere (10).

High-resolution TEM images show that the unreacted MnO\(_2\) was partially crystalline (Fig. 1a). The characteristic balls of needles of synthetic birnessite are depicted (11). Interpersed with amorphous material, there are layers of parallel atomic planes exhibiting severe bends and twists which in some cases form distinctive needle-shaped protrusions. In the unreacted MnO\(_2\), the needles are prominent and clearly delineated. After reaction with Al(III), the basic structure of the MnO\(_2\) appears to be unchanged (Fig. 1b). However, under closer inspection a structural alteration of the colloid can be discerned. The characteristic needles are still present, but are no longer as sharply defined as in the unreacted material. An amorphous layer can be seen along the edges of the MnO\(_2\) particles, filling in between the needles as well as coating the edges. In addition, an overall loss of detail in the image is apparent. This persisted over a range of focus settings bracketing the optimum value, indicating that the electron beam has passed through an incoherently scattering (noncrystalline) layer in addition to the material that was previously being imaged. Therefore, we conclude that an amorphous layer developed after reaction with Al(III) and completely enveloped the MnO\(_2\) surface. The amorphous material is expected to be a precipitate of Al(OH)\(_x\), where \( x \) denotes molecularity of hydroxyl species associated with each Al; \( x \) may vary depending upon the bonding arrangement of Al with the OH groups and with the surface.

The rutile polymorph of TiO\(_2\) is depicted in Fig. 2a prior to reaction with Al(III). The micrograph shows that this material is polycrystalline, with distinctly faceted grains of fairly uniform size. Atomic planes are visible within many of the grains and allow orientation differences between grains to be observed directly. After reacting with
FIG. 1. High-resolution TEM image of (a) unreacted MnO₂ (the birnessite phase) and (b) MnO₂ after reaction with 400 μM Al(III) at pH 5. After MnO₂ has reacted with Al(III), an amorphous layer has enveloped the MnO₂ surface, which is shown by the amorphous material deposited at the edges of the needle structures and a resulting overall loss of detail in the image.

Al(III) (Fig. 2b), the TiO₂ appears to be unaltered. Even very close inspection of the images does not reveal the formation of a surface precipitate; the crystalline structure remains unchanged, and no amorphous material is present.

The MnO₂ and TiO₂ surfaces differ in their ability to induce surface precipitation in systems of 400 μM Al(III) at pH 5. At pH 5, the MnO₂ (zero point of charge, ZPC = 2.8) (13) surface was strongly negatively charged, while TiO₂ (ZPC = 6.7) was positively charged. The absence of a precipitate on the surface of the TiO₂ discounts the possibility that a colloid acts only as a nucleation site for the formation of a precipitate. The enhancement of precipitation in between the needles of the MnO₂ may be due to electrostatic effects, which are increased due to the close
proximity of the charged surfaces, rather than simply an abundance of nucleation sites. Hence, the lack of precipitation in the TiO$_2$–Al(III) system substantiates (i) that surface precipitation can occur prior to bulk solution precipitation (as exemplified by the MnO$_2$ system in this study), and (ii) that the properties of the surface do affect the formation of a surface precipitate.

Hypothesized mechanisms for cationic metal sorption on oxide surfaces include adsorption of the free ion or hydrolysis products (3–7), adsorption of polymerized species (13, 14), surface cluster formation (15), and the formation of a surface precipitate (1, 8, 16–19). The multinuclear metal species observed at lower surface coverages by spectroscopic techniques (14, 15) may be a precursor
to the formation of a surface precipitate. The mass action balance proposed by Bleam and McBride (15) to explain the progression from isolated-site binding to the formation of multinoval sorbed clusters with increases in solution metal concentration may explain the formation of a surface precipitate at the even greater solution metal ion concentrations used here. Direct evidence has also been obtained using X-ray photoelectron spectroscopy (XPS) for the formation of a Co(II) surface precipitate on oxide surfaces (17-19). Crowther et al. (19) observed XPS spectra characteristic of Co(OH)2 on the surface of a synthetic birnessite when critical pH and Co(II) concentrations were exceeded. However, the results of the XPS studies have been questioned (14). As demonstrated here, HRTEM provides a tool for obtaining direct evidence for the formation of a surface precipitate. Clearly, the MnO2 surface structure underwent an alteration, while the TiO2 surface appeared unaltered.

The formation of a surface metal precipitate prior to bulk solution precipitation has important implications for environmental quality and catalytic processes. Surface precipitation represents a means of metal removal from solution which will be less subject to desorption reactions releasing metals back to solution—only dissolution of the precipitate will release the metal to solution. Moreover, the surface precipitate will mask the properties of the original sorbent, and only the surface properties of the metal hydroxide will be exhibited by the resulting conglomerated colloid.

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