Structure of the Hydrated α-Al_2O_3 (0001) Surface

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Introduction

The interaction of liquid water with the surfaces of natural solids is one of the most fundamental chemical reactions occurring in nature. Its importance extends from geochemical processes, such as mineral dissolution and sorption/desorption reactions,[1] which play major roles in chemical weathering, contamination of ground waters, environmental restoration, and the biogeochemical cycling of elements, to the growth of crystals and partitioning and sequestration of trace elements in aquatic systems. The reactivity of metal oxide surfaces depends on the type(s) of functional groups exposed at the surface, which is strongly influenced by the degree of surface hydroxylation. Therefore, it is important to determine the structures and compositions of hydrated metal oxide surfaces directly. We are able to address this problem by employing the technique of crystal truncation rod (CTR) diffraction[2,3] to determine the atomic arrangement of single-crystal, metal oxide surfaces under ambient or *in situ* conditions (i.e., in the presence of bulk solution at ambient temperature)

We chose to study the α-Al_2O_3 (0001) surface because of its importance as a model system for understanding the reactivity of naturally abundant phases of Al-containing (hydr)oxides, such as gibbsite or aluminosilicate clays. Furthermore, knowledge of the structure of hydrated metal oxide surfaces is required for testing models of the structure, reactivity, and charging behavior of metal-(hydr)oxide surfaces.[4-6]

Experimental Methods

A highly polished single-crystal (0001) wafer of α-Al_2O_3 was used in this study. After a clean-and-wash procedure, the sample was characterized by x-ray photoelectron spectroscopy (XPS), which showed that the surface is composed of Al, O, and adventitious C. In previous photoemission studies of the hydroxylation of the clean alumina (0001) surface, a water vapor pressure of about 1 Torr was sufficient to fully hydroxylate the surface. Therefore, following our wash procedure, the surface is expected to be fully hydroxylated.

Measurements were performed at the Advanced Photon Source (APS) on beamline 13-ID. X-rays from the first harmonic of an APS undulator A were monochromatized to 10 keV using a Si (220) monochromator and focused to a 100×100 µm spot size. Diffraction data were collected on the sample under ambient conditions (relative humidity > 40%). A total of 882 structure factors were determined by integrating rocking scans through the crystal truncation rods.[7] After averaging symmetry equivalents, the final data set consisted of 525 unique data points from 10 crystal truncation rods.

Results

Our major finding[8] (Fig. 1), is that, unlike the vacuum-prepared clean surface where Al-terminated[9,10] or mixed Al/O-terminated surfaces[11] are reported, the hydrated surface is O-terminated with a 53% contracted double aluminum layer directly below. The best-fit relaxed surface appears to be an intermediate between the bulk oxygen terminated α-Al_2O_3 (0001) surface and the gibbsite (γ-$Al(OH)_3$) basal plane. A disordered oxygen layer at ≈ 2.3 Å above the terminal oxygen layer is interpreted as sorbed water.

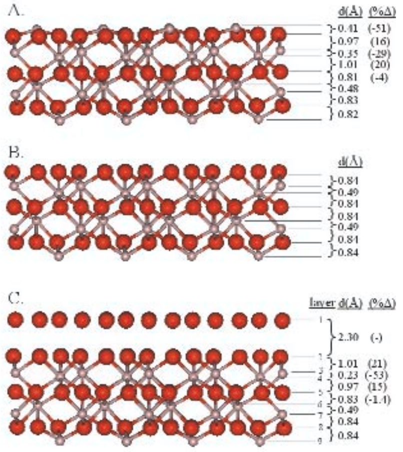

FIG. 1. Side view of a section of the a-Al2O3 unit cell. Red, silver and gray spheres indicate O, Al and H atoms, respectively. (A)-(C) show the atomic layering sequence and layer spacings (d) along the [0001] direction for various terminations: (A) the single Al terminated surface model from Guenard et al. (10), (B) the ideal (un-relaxed) oxygen terminated surface, and (C) the best fit relaxed surface model for the oxygen terminated surface from this work including the oxygen (water) overlayer. (D) Side view of a layer sequence from the gibbsite structure. In (A) and (C), %D is the percent change in the layer spacing from the ideal termination (B).

The reactivity of the UHV-clean surface will differ markedly from an alumina surface in the presence of water. The surface Al sites in the Al-terminated model are strong Lewis acid sites, whereas the OH groups in the OH-terminated surface are Lewis bases. Following hydroxylation of the α-Al_2O_3 (0001) surface, all surface sites become weak Lewis bases with lowered reactivity to water but enhanced overall reactivity toward metals.

Conclusions

These results provide a firm experimental basis for understanding the reactivity and properties of the hydrated α-Al_2O_3 (0001) surface. Furthermore, they provide a starting point for further first-principles theoretical studies of the interaction of water with the α-Al_2O_3 (0001) surface and for future exploration of other surface orientations of α-Al_2O_3, and other metal oxide-water interfaces, which should lead to a broader understanding of aqueous-solid interactions in the natural environment.

Acknowledgments

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References

[1] G.E. Brown, Jr., et al., Chem. Rev. **99**, 77-174 (1999).

[2] I.K. Robinson and D.J. Tweet, Rep. Prog. Phys. **55**, 599 (1992).

[3] G. Renaud, Surf. Sci. Reports **32**(1/2), 1 (1998).

[4] T. Hiemstra, P. Venema, and W.H. Van Riemsdijk, J. Colloid Interface Sci. **184**, 680 (1996).

[5] T. Hiemstra, H. Yong, and W.H. Van Riemsdijk, Langmuir **15**, 5942 (1999).

[6] D.A. Sverjensky and N. Sahai, Geochim. Cosmochim. Acta **60**, 3773 (1996).

[7] I.K. Robinson, *Surface Crystallography*, Vol. 3, G. Brown and D.E. Moncton, eds. (Elsevier Science Publishers, 1991) pp. 221-266.

[8] P.J. Eng, T.P. Trainor, G.E. Brown, Jr., G.A. Waychunas, M. Newville, S.R. Sutton, and M. Rivers, Science **288**, 1029-1033 (2000).

[9] J. Ahn and J.W. Rabalais, Surf. Sci. **388**, 121 (1997).

[10] P. Guenard, G. Renaud, A. Barbier, and M. Gautier-Soyer, Surf. Rev. Lett. **5**, 321 (1998).

[11] J. Toofan and P.R. Watson, Surf. Sci. **401**, 162 (1998).