

Spectroscopic studies of the reaction of water with metal oxide surfaces

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The reaction of water with mineral surfaces is one of the most fundamental natural reactions in near-surface environments, yet little is known in detail about its mechanism. We have undertaken a series of synchrotron-based photoemission and L-edge studies of the reaction of water with several clean metal oxide surfaces under ultra-high vacuum conditions. Surfaces studied include MgO(100), CaO(100), α -Al₂O₃ (0001) and (1-102), α -Fe₂O₃ (0001) and (1-102), Fe₃O₄ (001) and (111), and α -FeOOH. Most of the samples were synthetic single crystals prepared by bulk growth (MgO, CaO, α -Al₂O₃) or multiple beam epitaxial (MBE) growth on appropriate lattice-matched substrates (α -Fe₂O₃ on α -Al₂O₃ and Fe₃O₄ on MgO). We also studied the reaction of water on natural single crystal samples of α -Fe₂O₃, Fe₃O₄, and α -FeOOH. Each of these samples was cleaved or sputtered and annealed in vacuum, and surface contamination was checked by XPS. LEED patterns are consistent with unreconstructed surfaces in each case. Because these materials are insulators, surface charging during photoemission experiments was mitigated using a low energy electron flood gun operated at voltages of 4-6 eV. Water exposures at various water vapour pressures (ranging from 10⁻⁹ Torr to >1 Torr) surface for fixed exposure times (typically 3 minutes) were accomplished using a water dosing needle placed near the sample. Additional exposures to bulk water were accomplished by removing samples from the UHV chamber into a N₂-filled glove bag and immersing the sample in DDI water for 10 minutes then returning the sample to the UHV chamber for analysis. In all cases of water vapour exposure, we observed initial reaction of water vapour with surface defect sites, resulting in the formation of surface hydroxyl groups at coverages of

less than 0.1 monolayer (ML). After this initial dissociative chemisorption reaction, no further changes in the O1s, O2s, and valence band spectra were observed until a threshold pressure was reached, which varied with the surface studied.

In the case of MgO(100) and CaO(100), these threshold pressures were 10⁻⁴ Torr and 10⁻⁹ Torr, respectively [1]. Comparison of the MgO O1s photoemission spectra with similar spectra of MgO(100) surfaces immersed in bulk water and of polycrystalline Mg(OH)₂ indicates that water chemisorbs dissociatively in two distinct stages on 'low defect' MgO(100) surfaces, forming surface hydroxyl groups. The first stage occurs at water vapour exposures $\leq 3 \times 10^{-5}$ Torr for 3 min. ($\leq 5.4 \times 10^3$ L) or for 30 min. ($\leq 5.4 \times 10^4$ L) and involves a relatively fast reaction with surface defects (corner and edge-step sites and point defects) comprising 5-10% of the surface sites, in agreement with recent first-principles electronic structure calculations using density functionals. The second stage occurs at higher water vapour pressure [$\geq 10^{-4}$ Torr for 3 min.] and involves dissociative chemisorption of water on terrace sites, which is not predicted by recent first-principles calculations. The apparent sticking coefficient for the first reaction stage (≥ 0.16) is about four orders of magnitude larger than that for the second reaction stage ($\geq 3 \times 10^{-5}$), suggesting that the second reaction stage requires significantly more activation energy than the first stage. Our results also suggest that the hydroxylation reaction is not sensitive to exposure time below a threshold pressure of $\sim 10^{-4}$ Torr. Although both kinetic and thermodynamic interpretations are possible, a thermodynamic analysis of the hydroxylation reaction (using bulk solid free energies) predicts approximately the same threshold pressure

as observed. After the surface is fully hydroxylated, additional water can be physisorbed on the hydroxyl layer. Analysis of O 1s spectra taken from the same surface but at different photon energies indicates that hydroxyls are formed predominantly on the surface and not in the bulk under these exposure conditions.

In the case of α -Al₂O₃ (0001) and α -Fe₂O₃ (0001), the observed threshold pressures for dissociative chemisorption of water are 1 Torr and 10⁻⁴ Torr, respectively. We find that water uptake is independent of surface preparation or orientation for these samples. The dissociative nature of initial chemisorption is revealed by the size of the O 1s, O 2s core-level chemical shifts and identification of the 1 π and 3 σ features in the valence band region. Additionally, above 10⁹ Langmuirs (dosed at 10 Torr pressure) water uptake steeply increases and new features in the spectra are identified as being due to physisorbed water. The hydroxylated hematite surfaces obtained at the highest water doses are passivated and show no further reactions with water in ambient air (5 min exposure).

A comparison of O 1s photoemission results for clean Fe₃O₄ and α -Fe₂O₃ surfaces exposed to higher water doses at higher vapour pressures indicates a quantitative difference between the two iron oxide surfaces. While, hydroxyl coverages for hematite remain in the submonolayer range for doses as high as 10⁹ L, the magnetite (001) and (111) surfaces react very strongly with water, resulting in hydroxylation extending several layers deep.

The Fe L_{2,3} and O K near-edge spectra of selected

iron oxides and hydroxides were also measured in an attempt to establish how the presence of water and/or hydroxyls are manifested in the spectra. Our results serve as a reference for studies of surface reactions of iron oxides with water and aqueous solutions. The studies were performed on natural samples of hematite (α -Fe₂O₃), magnetite (Fe₃O₄), goethite (α -FeOOH), and limonite (FeOOH·nH₂O), as well as on MBE-grown thin films of hematite, magnetite, wüstite (Fe_{1-x}O), and maghemite (γ -Fe₂O₃). These data were taken with total yield as well as with more surface sensitive Auger yields. Our data indicate that while the L-edge spectra of iron hydroxides strongly resemble that of hematite, a new absorption band appears in the O K-edge spectra for the hydroxides. To compare these data with those for iron oxide surfaces reacted with water, we performed water dosing experiments on vacuum-cleaned surfaces of hematite and magnetite. Although these surfaces are hydroxylated as shown by photoemission spectroscopy, no additional structure is detected with surface sensitive near-edge spectra. These results indicate that no goethite-like structure is formed on water-dosed surfaces of iron oxide, which contrasts with the results of several recent studies.

References

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