

Distribution of Reduced Iron at Ferric Oxide Surfaces

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Using a simple ionic model with polarizable oxygen ions and dissociating water molecules, we have calculated the energetics governing the distribution of Fe(II)/Fe(III) ions at the reduced (2×1) surface of α -Fe₂O₃ (hematite) (012) under dry and hydrated conditions. The results show that systems with Fe(II) ions located in the near-surface region have lower potential energy for both dry and hydrated surfaces. The distribution is governed by coupling of the ferrous iron centers to positive charge associated with missing oxygen atoms on the dry reduced (2×1) (021) surface. As the surface is hydroxylated, the missing oxygen rows are filled and protons from dissociated water molecules become the positive-charge centers, which couple more strongly to the ferrous iron centers. At the same time, the 1st-layer iron centers change from four-fold or five-fold-coordination to six-fold-coordination lowering the potential energy of ferric iron in the first layer and favoring migration of ferrous iron from the immediate surface sites. This effect can also be understood as reflecting better solvation of Fe(III) by the adsorbed water molecules. The balance between these two driving forces, which changes as a function of hydration, provides a compelling explanation for the anomalous coverage dependence of water desorption in ultra-high vacuum experiments[1].

References

[1] Henderson, M.A. Joyce, S.A., and Rustad, J.R. (1998) Surface Science, 417, 66-81.