

Mechanism of redox processes on iron oxides: A spectroscopic study

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Adsorption and reaction of sulfite, cyanide, arsenate, chromate, selenate, manganese(II), ferrous and ferric hexacyanide ions on α - and γ -Fe₂O₃, α -FeOOH, and Fe₃O₄ of similar particle size of about 100 nm and shape were studied *in situ* and *ex situ* by FTIR and X-ray photoelectron spectroscopies. For the first time, it was shown that under geochemical conditions surfaces of all the oxides contain electron-donating Fe²⁺-like defects which have extended (clustered) rather than point character. The energy level of these surface states is located in the band gap, and oxidizing species with an appropriate standard potential (arsenate, chromate, and selenate) are partially reduced upon adsorption. This effect has been previously overlooked in geochemistry.

Regularities in the kinetics and composition of the products suggest that the cathodic process of the heterogeneous oxidation includes some lattice dissolution, along with the O₂ reduction on the electron-donating defects. The relative contribution of the former process depends on 1) the complexing properties of the reagent in the reduced and/or oxidized form, 2) the ionic composition of the buffer, and 3) solubility of the oxide. The rate of the anodic counterpart of the redox reaction for both the catalytic and autocatalytic pathways increases with increasing potential of the Fermi level of the oxide. Another factor that can influence the observed rate of the heterogeneous oxidation is the adsorption rate of the reagent. Depending on the relationship between the rates of the above elementary processes, the oxidation rate of a species in a particular system can be higher as well as lower than the rate of the homogeneous oxidation.

The proposed general model of the redox processes on transition-metal semiconducting oxides was used to explain a number of inconsistencies found in the literature, in particular, those discussed by Rosso et al. (1998) about the mechanism of the heterogeneous oxidation of Mn²⁺.

Reference

Rosso J.J., Hochella M.F., and Rimstidt J.D. (1998). *Geochim. Cosmochim. Acta* **62**, 365-368.

Fluoride sorption onto kaolinite: NMR spectroscopic studies

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Clay minerals are important to understand many aqueous chemical reactions that occur at the Earth's surface. Kaolinite is a commonly found clay mineral in soils, as it is the main weathering product of feldspars. Methods of dissolution and sorption are especially key to understanding the mineral surface reactions at the water-mineral interface.

Kaolinite samples were used in aqueous chemistry and solid state NMR spectroscopy experiments. Fluoride sorption experiments on kaolinite were undertaken at pH 5.0, I = 10⁻³ M, 10⁻² M, and 10⁻¹ M. Fluoride reactions with mineral surfaces are relevant because of the health effects, ligand promoted dissolution, and possibly as a probe of reactive surface sites.

Both single pulse ¹⁹F Magic Angle Spinning (MAS) NMR and ¹⁹F{²⁷Al} Transfer of population in double resonance (TRAPDOR) experiments were performed on kaolinite samples to assign fluoride sorption sites. Several distinct sites were observed in the kaolinite ¹⁹F single pulse experiments, at -122, -131, and -142 ppm. Peaks at -131 and -142 ppm are similar to those observed for bayerite [1] and similarly prepared gibbsite nanoparticles, suggesting assignment to surface Al-sites. The resonance at -131 ppm is attributed to fluoride bridges, and another resonance at -142 ppm is assigned to fluoride bonded at terminal sites. In addition, sorption samples prepared in NaCl and KCl electrolytes show strong peaks near -185 ppm due to precipitation of secondary alumino-fluoride phases, whereas those prepared in CsCl do not.

¹⁹F{²⁷Al} TRAPDOR experiments confirm the assignments of fluoride sorption sites on both the kaolinite and the gibbsite surfaces. Peaks at -131 and -142 both show a TRAPDOR effect, indicating they are bound to Al, but that for the peak of -131 ppm is much stronger, consistent with assignment to Al-F-Al sites. Absence of TRAPDOR effect for the peak at -122 ppm suggests it arises from interlayer sites.

Reference

[1] Nordin, J., Sullian, D.J., Phillips, B.L., and Casey, W.H. (1999) *Geochimica et Cosmochimica Acta* **63**, 3513-3524.