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Review

Catalysis of Redox Processes by Hydrous Oxide Surfaces*

Werner Stumm

Institute for Environmental Science and Technology (EAWAG), Swiss Federal Institute of Technology (ETH Zürich), CH – 8600 Dübendorf, Switzerland

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Much progress has been made in the identification, physicochemical charaterization and determination of the quantity of solute species in natural waters. Most chemical processes in natural systems occur at the surface of minerals and inorganic and organic particles. The concept of active surface sites at the solid-water interface, and the characterization of the surface sites (surface speciation) is essential in understanding surface controlled processes. Here the role of hydrous oxide surfaces in catalyzing redox processes in natural waters is illustrated by three case examples:
1) Oxidation of Fe(II) by $O_2 \cdot$ Fe(II) and other transition elements adsorbed to hydrous oxide (in inner-sphere surface complexes), as well as their hydrolysis species, are readily oxygenated; it can be shown that outer-sphere electron transfer is rate determining.
2) Reduction of nitroaromatic substances by adsorbed Fe(II). Fe(II) adsorbed to Fe_3O_4, γ-FeOOH and α-FeOOH and other suitable hydrous oxides is an efficient reductant for nitroaromatic and other organic substances; rate determining step is most likely the formation of a precursor product between the reductant and the nitroaromatic substance.
3) Adsorbed chromate is an efficient oxidant of organic substances, *e.g.*, hydroxy carboxylic acid and their esters. Adsorption enhances the oxidizing power of chromate and increases the lability of the oxogroups at the Cr(VI) center.
Redox processes catalyzed by mineral surfaces play an important role in the evolution of the earth's surface and its natural waters.

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[*] Dedicated to Marko Branica on the occasion of his 65th birthday.

INTRODUCTION

Solution chemists have learned that speciation (the form of occurrence of solutes) is the key to understand the reactivity and bioavailability of solutes.[3,4,46] Our ability to accurately determine trace metal concentrations and their speciation in marine and fresh water systems has undergone a revolution in the last two decades. Branica and his colleagues,[3] above all, have influenced this field. The solid-water interface, mostly established by minerals and particles in soils and in natural waters, plays a commanding role in regulating the concentrations of most dissolved reactive elements in soil and natural water systems in catalyzing redox processes and many organic transformations such as the hydrolysis of esters and in the coupling of various hydrogeochemical cycles. Expressed in a simple way, surface speciation is equally important to predict surface reactivity as solute speciation is in predicting solute reactivity. In a similar way as progress has been made in understanding solute speciation by the investigation of model electrolyte systems, the basic forces operating in interfacial processes can be interpreted atomistically and quantified with the help of models used in electrochemistry, in solution coordination chemistry, and in crystallography.

Figure 1 portrays schematically the surface of an oxide, hydroxide or silicate solid phase interacting with solutes of the solution phase. An electric charge may arise at the surface of the solid from chemical reactions at the surface, above all the acid-base behavior of the surface hydroxyl groups ($\text{S-OH}_2^+ \rightleftharpoons \text{S-OH} \rightleftharpoons \text{SO}^-$ or, $\text{S–OH}_2^{½+} \rightleftharpoons \text{S–OH}^{½-}$) or from binding (adsorbing) solutes to solid surfaces. The distribution of charge accross the interface is idealized as an electric double layer (a fixed charge attached to the particle or solid surface and the other charge is more or less diffusively distributed in the liquid in contact). Several double layer models have been proposed for the oxide-water interface.[10,27,33,38,42] The central issue in these models is how to relate chemical concepts (*e.g.*, inner-sphere *vs.* outer-sphere complex species) to meanfield electrostatic concepts (charge density and electric potential).[52] Recently the concept of inner-sphere *vs.* outer-sphere surface complexes have been validated at the atomic level by several spectroscopic studies.[25]

Figure 1 shows specifically bound (predominantly covalent bonds) species, *e.g.*, protons, phosphate, Fe(II) ions (inner-sphere species) and non-specifically adsorbed (chloride and sodium ions), separated from the surface by one or more water molecules with the diffuse layer extending outward from the outer-sphere ions.

Surface Reactivity Depends on Surface Structure

The understanding of the dynamics of the mineral-water interface (dissolution, crystal growth, catalysis) requires an appreciation of the structure and chemical bonding at the interface and of the reactions which describe

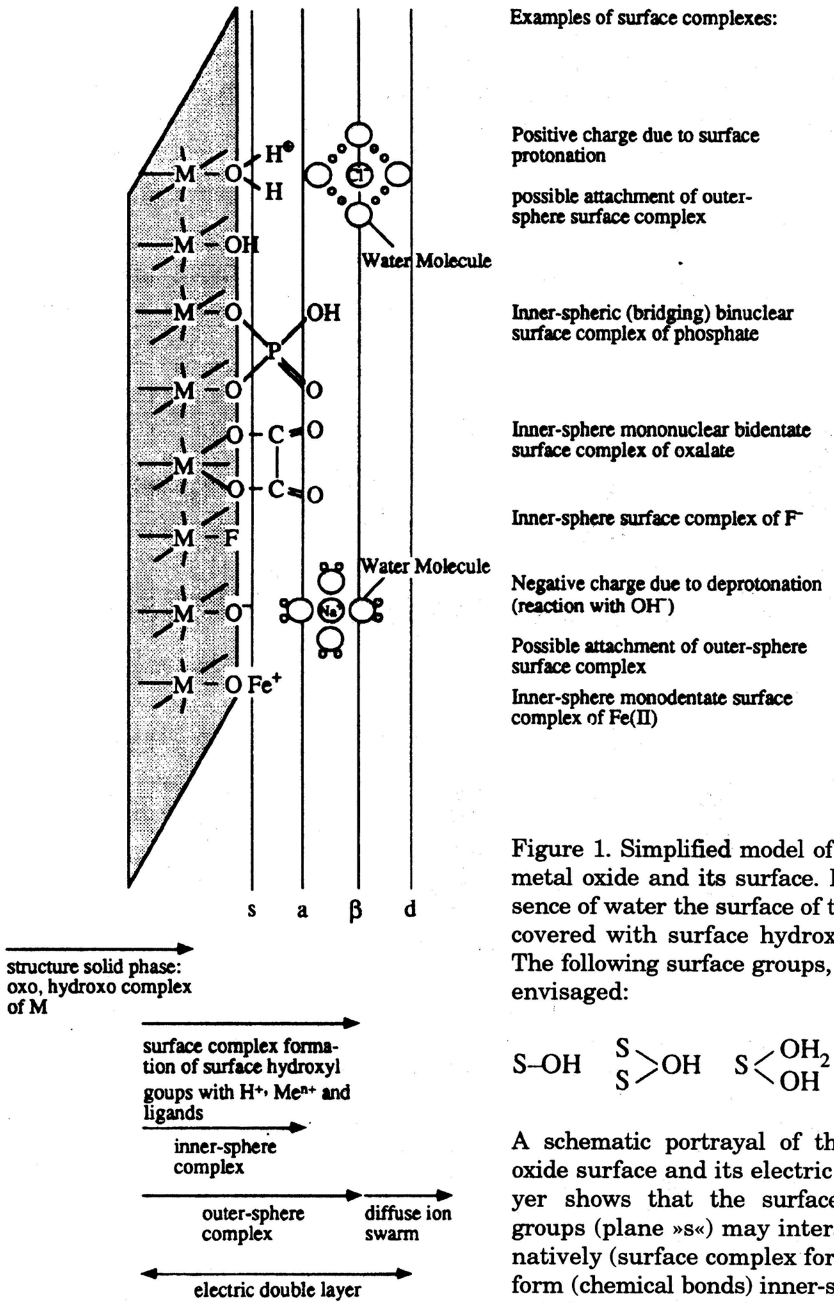


Figure 1. Simplified model of a hydrous metal oxide and its surface. In the presence of water the surface of the oxide is covered with surface hydroxyl groups. The following surface groups, S–, can be envisaged:

$$\text{S–OH} \qquad {}^{\text{S}}_{\text{S}}\!\!>\!\text{OH} \qquad \text{S}\!\begin{smallmatrix}\diagup\,\text{OH}_2\\ \diagdown\,\text{OH}\end{smallmatrix} \qquad \text{S}\!\begin{smallmatrix}\diagup\,\text{OH}\\ -\text{OH}\\ \diagdown\,\text{OH}\end{smallmatrix}$$

A schematic portrayal of the hydrous oxide surface and its electric double layer shows that the surface hydroxyl groups (plane »s«) may interact coordinatively (surface complex formation) to form (chemical bonds) inner-sphere type complexes (plane »a«) or (electrostatically) outer-sphere type complexes (plane »β«); ions may also be in the diffuse swarm of the double layer.

the transfer of the chemical species between the mineral and the aqueous solution. Many heterogeneous processes, such as the dissolution of minerals, the formation of the solid phase (precipitations, nucleation, crystal growth, and biomineralization), redox processes at the solid water interface (including photo-chemical reactions) are critically dependent on surface speciation.

Metal-Organic Chemistry and Catalysis on Surfaces

The recent advances in modern surface chemistry has been reviewed by Friend (1993).[11] She illustrates how inorganic and metal-organic chemists

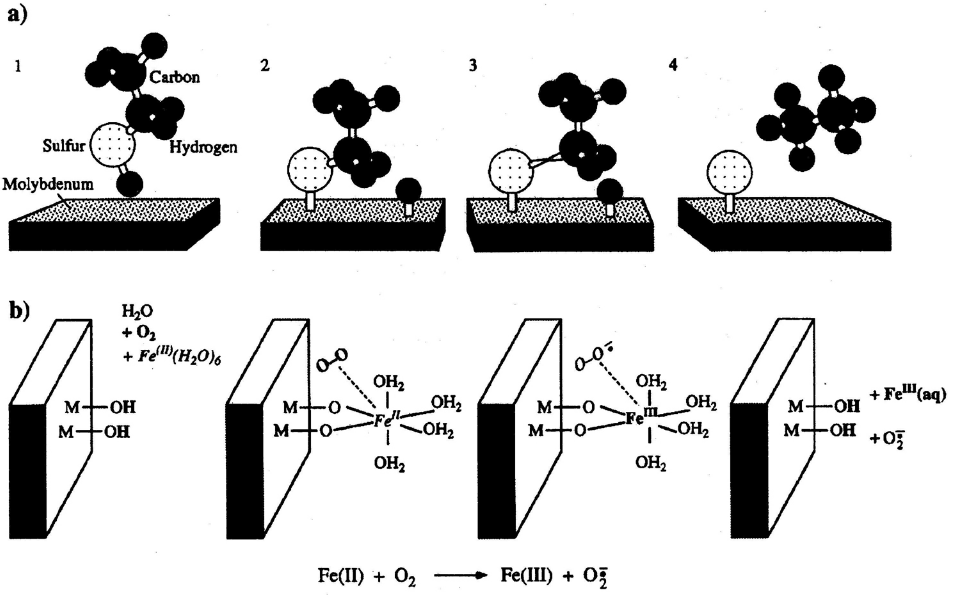


Figure 2. Comparison of surface catalysis a) of a metal-organic process (in the absence of water) and b) a redox process at the solid-water interface.
a) The molybdenum surface catalyzes a reaction that removes sulfur from fuels; when a molecule of ethanediol interacts with molybdenum, it looses a hydrogen and binds to the surface, the bond between carbon and sulfur then weakens and the remaining atoms may recombine to form ethane (adapted from Friend[11]).
b) A hydrous metal oxide surface (TiO_2, Fe_2O_3, Al_2O_3) catalyzes the oxidation of Fe(II) by oxygen; when an Fe(II) binds inner-spherically to the hydrous oxide surface the functional oxygen donor atoms of the surface hydroxyl groups donate electron density to the Fe(II) and make the Fe(II) a better reductant and enable an electron transfer to the outer-spherically bound oxygen. The products of the reaction are superoxide, $O_2^{\bullet -}$, and Fe(III)(aq).
In both cases, the interaction of molecules or ions with the surface leads to a slight alteration of the elctronic structure of the adsorbate; a reaction is promoted whose activation energy is reduced by the surface.

have been able to produce rapid advances by understanding at the molecular level how solids interact with individual molecules to speed reactions and how such catalytic reactions have been used to improve everything from material synthesis to pollution control (Figure 2a). Much of the progress of catalysis has been made with surfaces that are carefully shielded from open air and water. The surfaces of interest to the environmental chemists, on the other hand, are most often in contact with water. But even in presence of water, there is bonding between solid surfaces and solutes; and chemistry and physics come together at these surfaces to influence chemical reactions. In Figure 2 the catalysis of processes important in the desulfurization of fossil fuel on molybdenum surfaces (absence of open air and water) is compared with the catalysis by a hydrous oxide surface on the oxidation of Fe(II) by oxygen. The rate determining step, in the latter case, is the one electron exchange between Fe(II) and Fe(III) on one hand, and O_2 and superoxide, $O_2^{\cdot}$, on the other hand. A simple qualitative explanation for this catalytic effect can be given as follows: The surface OH-groups act as sigma electron donors which increase the electron density of the adsorbed Fe^{2+} making the surface bound Fe(II) a much better reductant than Fe^{2+} in solution (Luther,[21] Wehrli,[47] Stumm and Morgan[42]). In Table I redox equilibria of Fe(II) species with O_2 are given and compared with corresponding rate constants.[42,48] Although the electron exchange (rate determining) is endergonic, the Fe(II) oxygenation to Fe(III) is spontaneous. As shown in Table I, adsorption of Fe(II) to surface hydroxo groups catalyzes the oxygenation in a similar way as hydrolysis (binding with OH^- in solution). In discussing a few case examples, we will illustrate that we can learn how redox processes are often catalyzed by suitable solid surfaces.

TABLE I

Equilibrium constants and reaction rate constants for rate determining steps in oxygenation of Fe(II)

	Reaction	Rate Constant ($M^{-1}s^{-1}$)a)	Equilibrium Constants b)	
$Fe^{2+} + O_2 \longrightarrow$	$Fe^{3+} + O_2^{\overline{\cdot}}$	; $\log k_0 = -5.1$;	$\log K_0 = -15.7$	b)
$Fe(OH)^{+} + O_2 \longrightarrow$	$Fe(OH)^{2+} + O_2^{\overline{\cdot}}$	; $\log k_1 = 1.4$;	$\log K_1 = -8.45$	b)
$Fe(OH)_2 + O_2 \longrightarrow$	$Fe(OH)_2^{+} + O_2^{\overline{\cdot}}$	; $\log k_2 = 6.9$;	$\log K_2 = -3.04$	b)
$(\equiv Fe^{III}O)_2Fe^{II} + O_2 \longrightarrow$	$(\equiv Fe^{III}O)_2\ Fe^{III+} + O_2^{\overline{\cdot}}$	; $\log k_3 = 0.7$;	$\log K^{s} = -9.0$	c)
$\equiv Si{-}Fe^{II} + O_2 \longrightarrow$	$\equiv Si{-}Fe^{III} + O_2^{\overline{\cdot}}$	; $\log k_s \approx 0$;	$\log K_{Si} = -8.3{-}11.4$	d)

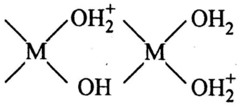
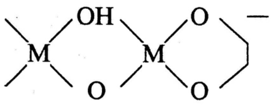
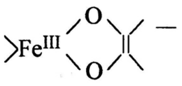
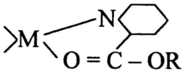
a) Data for oxidation of Fe^{2+}, $FeOH^+$ and $Fe(OH)_2$ from Singer and Stumm,[30] of $(\equiv Fe^{III}O)_2\ Fe^{II}$ (Fe(II) adsorbed on goethite) from Tamura *et al.*[44] (Rate determining reactions are second order.)
b) Computed from free energy of formation data (Bard *et al.*[1])
c) Tamura *et al.*[44]
d) White and Yee[54]

Catalysis of Redox Processes by Surfaces

The surface (heterogeneous catalyst) provides an alternative mechanism for the reaction that is energetically more favorable.[15] For catalysis of processes by surfaces at least one of the reactants, has to become adsorbed at the surface (Table II). The binding of an oxidant or reductant species to a surface often changes mode and rate of the electron transfer processes. Adsorption of a reductant or oxidant, especially in an inner-sphere surface complex (*e.g.*, Figure 2b) changes the geometry of the reactants coordinating shell and electronic structure and thus influences redox intensity (free energy of redox reaction) and reactivity (rate of electron transfer) (Table III).

TABLE II

Processes catalyzed by mineral surfaces

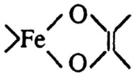
Reaction	Example Surface Complex	References
Acid promoted dissoluion of oxides and silicates		Furrer and Stumm[12] Stumm and Wollast[40] Stumm[38]
Ligand promoted dissolution	 *e.g.*, oxalate	Furrer and Stumm[12] Stumm[38]
Reductive dissolution	 *e.g.*, ascorbate	Stumm and Sulzberger,[41] Stone and Morgan[36]
Ester hydrolysis	 *e.g.*, picolinate	Torrents and Stone[45]
Optical racemination and isotope exchange		Spiro[32]
Redox processes	Surface complex of reductant or oxidant (see Table III)	
Photo redox processes[a)]	Adsorbate at semiconductor surface	Sulzberger[43]

[a)] A photoredox reaction is a redox reaction that occurs after electronic excitation of one or several reaction partners. A semiconductor may be one of the reaction partners.

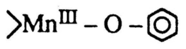
TABLE III

Examples of adsorption of reductants and oxidants on hydrous oxide surfaces (Charges omitted)

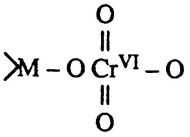
$>M-O\,Cr^{II}(H_2O)_n$ $>M-O\,Fe^{II}(H_2O)_n$ 1)[a]



e.g., ascorbate

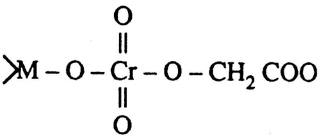


e.g., phenols 2)[a]



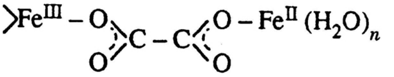
$$>M-O\,\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{Cr^{VI}}}-O$$

3)[a]



$$>M-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{Cr}}-O-CH_2\,COO$$

4)[a,b]



5)[c]

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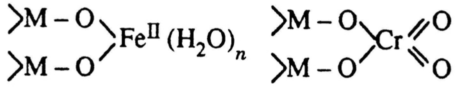
[a] The hydrous oxide minerals may also form binuclear surface complexes, e.g.,

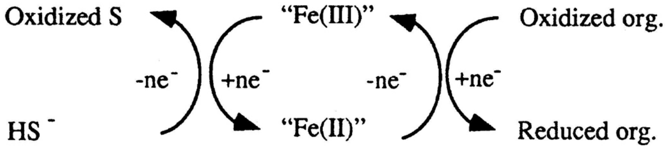


[b] Encounter complex of adsorbed CrO_4^{2-} with hydroxycarboxylic acid.

[c] The adsorbed oxalate serves as bridge to reductant such as Fe(II).

The oxidant and reductant have to encounter each other in a suitable structural arrangement to make an electron exchange possible. The surface may assist in various ways to facilitate such an encounter. Furthermore, adsorption may accelerate ligand exchange kinetics. Thus, cations will exchange their ligands faster once they are adsorbed to an oxide surface, e.g., exchange of H_2O or other ligands in the coordination sphere of an adsorbed metal ion, or oxogroups are more labile in adsorbed oxoanions, e.g., chromate.

Electron transfer often occurs between the adsorbent oxide and the adsorbed (surface complex) reductant, resulting in the reductive dissolution of the oxide (e.g., Fe(II,III) oxide and Mn(III,IV) oxide).[35,38,41] Stone[35] has shown that the rate of oxidation of various substituted phenols by Mn(III,IV) oxides can be correlated to the free energy of the one-electron oxidation reaction of these substituted phenols. The hydrous ferric oxide surface often mediates redox reactions of organic substances. An example is given by the scheme below.



(1)

Electron transfer mediator

Different electron mediating systems such as porphyrin complexes, MnO_2/Mn(II) and quinone-like systems are, in addition to the Fe(II)/Fe(III) system, operative in natural systems. Furthermore, the organic carbon oxidation can be coupled by bacteria to the dissimilatory reduction of iron(III)oxides.[20,27] The solubilization of iron(III)(hydr)oxides is of great importance in the iron cycle, as well as in the general electron cycling which occurs in natural waters, in sediments, soils and in atmospheric waters.[41] Electron transfer reactions mediated by Fe(III)(hydr)oxide/Fe(II), or other heterogeneous redox couples often substitute for, or supplement microbially mediated redox cycling, especially at high redox gradients occurring at oxic-anoxic boundaries (Macalady *et al.*[22], Schwarzenbach *et al.*[29]). The heterogeneous and homogeneous Fe(III)/Fe(II) couple also plays a dominating role in the electron cycling in atmospheric water.[2,16,17]

Heterogeneous Photochemistry

Surfaces play an important role as catalysts in photochemical redox processes.[16,17,43] Two mechanisms can be distinguished:

1) Organic or inorganic solutes adsorbed (or surface complexed) to particle transfer, upon absorption of light energy, and electron to the lattice metal ion (ligand to metal charge transfer). Thus, multivalent metal oxides such as those of iron and manganese are reductively dissolved.[43]

2) Semiconductors, upon absorption of light energy, produce charge separation, *i.e.*, electrons in the conduction band and holes in the valence band; thus, reducing and oxidizing sites at the particle surface are formed. Often it is difficult to establish whether the semiconductor surface or the adsorbed substance is the chromophore. Surface complex formation of ligands to semiconducting TiO_2 has been shown[26] to enhance electron transfer from the conduction band to oxidants in solution.

In redox processes, different reaction steps, such as generation of reactive sites or surface complexes, formation of a precursor complex, or actual transfer of the electron, may be rate limiting. Three exemplary cases will be used for illustration; in the first two cases the specific adsorption of the reductant, in the third case the adsorption of the oxidant is a prerequisit for the prompt occurrance of the redox reaction:

1) Oxygenation of adsorbed Fe(II). Here adsorption (surface complex formation) of the Fe(II) ion enhances the reducing power of Fe(II). The fact that the free energy of the critical redox reaction step can be related to the rate of the reaction indicates that the (outer-sphere) electron transfer is rate determining.

2) Adsorbed Fe(II) as a reductant of nitroaromatic substances. The surface bound Fe(II) is a powerful reductant. Comparison of the role of redox reaction with various substituted nitrophenols indicates that the formation of the precursor between the adsorbed Fe(II) and the nitroaromatic substance rather than the actual electron transfer is most likely rate determining.

3) Chromate as an adsorbed oxidant. Studies on the reduction of chromate by organic substances illustrate that adsorbed, inner-spherically bound, chromate is a more powerful oxidant than dissolved chromate and that surface catalysis enhances the reactivity by increasing the exchange lability of the oxogroups on the Cr(VI) center.

Finally, we will briefly reflect on the corroding Fe° system, that provides different catalytic surfaces and a variety of reductants and is capable of reducing recalcitrant organic molecules such as chlorinated hydrocarbons.

Surface Catalyzed Oxidation of Transition Metal Ions

The reaction steps involved in the oxidation of Fe(II) by oxygen as catalyzed by a hydrous oxide surface was illustrated schematically in Figure 2b. Fe^{2+} specifically adsorbed to a suitable hydrous oxide surface is much more reactive towards oxygenation than $Fe(aq)^{2+}$; *i.e.*, the inner-spherically bound Fe^{2+} is a better reductant. Adsorption with hydroxo surface groups of hydrous oxides has a similar effect as hydrolysis (association with OH^-).[21,48–50] As explained by Luther[21] the OH^- ligands donate electron density to the Fe(II) ion through both, the σ and π systems which results in metal basicity and increases reducing power.

For the oxygenation of Fe(II) *in solution* (at pH > 5), the empirical rate law shows a second-order dependence on OH^- concentration (Stumm and Lee, 1961[39]), that is,

$$-\frac{d[\mathrm{Fe(II)}]}{dt} = k\ [\mathrm{Fe(II)}]\ [\mathrm{OH^-}]^2\ [\mathrm{O_2}]\,. \qquad (2a)$$

This dependence is consistent with the predominant reaction of O_2 with the hydrolyzed, solute species, $Fe(OH)_2$, within the pH range of natural waters, or

$$-\frac{d[Fe(II)]}{dt} = k' \, [Fe(OH)_2] \, [O_2]. \qquad (2b)$$

Similarly, the rate of oxygenation of Fe(II) bound to the surface hydroxyl groups of a hydrous oxide can be expressed in terms of the surface species. Thus,

$$-\frac{d[Fe(II)]}{dt} = k'' \, \langle Fe(OM{\equiv})_2 \rangle \, [O_2]. \qquad (3)$$

The surface hydroxyl groups facilitate, similar to $OH^-(aq)$, the electron transfer to O_2. Depending on pH, the species of adsorbed Fe(II) may also be present as surface hydrolyzed species, *i.e.*, $OHFe(OM{\equiv})_2$.[57]

Eq. (2) for the oxygenation of Fe(II) in solution, valid at pH > 5, can be extended (Millero[23]) to the entire pH range (Figure 3a):

$$-\frac{d[Fe(II)]}{dt} = (k_0 \, [Fe^{2+}] + k_1 \, [Fe(OH)^{2}] + k_2 \, [Fe(OH)_2]) \, [O_2] \qquad (4)$$

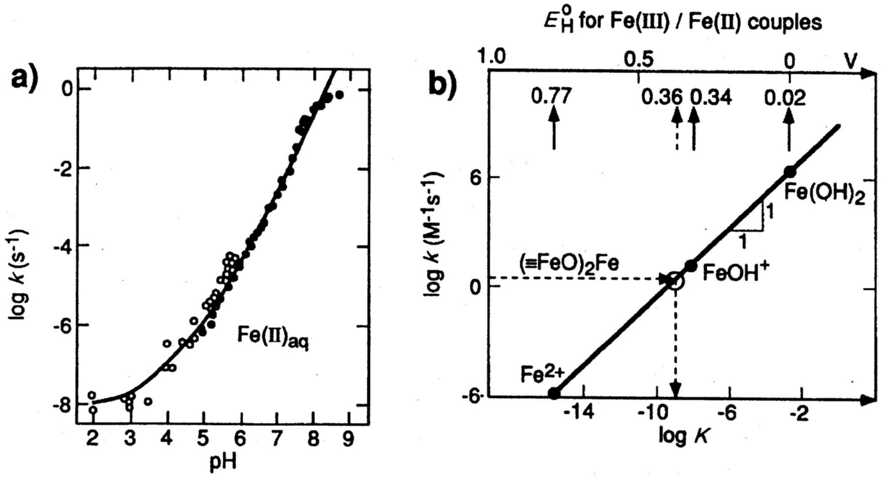


Figure 3.
a) Oxidation of Fe(II) by O_2. Open circles, data are from Singer and Stumm;[30] dots are data from Millero *et al.*[24] (*cf.* Eq 4).
b) Log of the reaction rate constants (as given in Table 1) are plotted vs log of equilibrium constants of the reaction $Fe^{II}(OH)_i^{(2-i)} + O_2 \rightleftharpoons Fe^{III}(OH)_i^{(3-i)} + O_2^{\cdot}$ or the redox potential, E_H^0, for the Fe^{III}/Fe^{II} couple). From the observed rate of the oxygenation of Fe(II) inner-spherically adsorbed on a goethite surface an equilibrium constant or redox potential can be estimated. Data for Fe^{2+} and $Fe(OH)^+$ from Singer and Stumm,[30] for $Fe(OH)_2$ from Millero *et al.*[24] for $(\equiv FeO)_2Fe$ goethite surface from Tamura *et al.*[44] Figure b) is modified from Wehrli.[47]

i.e., the pH dependence changes from $R \propto [H^+]^{-2}$ to $R \propto [H^+]^{-1}$ below pH 5 and the rate is pH independent below pH = 3. Parallel occurring rate determining steps for the various iron species and their experimentally determined reaction rates k [$M^{-1}s^{-1}$] and their equilibrium constants are compared in Table I.

Figure 3b plots the log of the rate constants, k (M^{-1} s^{-1}) *vs.* the log of the equilibrium constants of the rate determining steps:[47]

$$Fe^{II}(OH)_i^{(2-i)} + O_2 \rightleftharpoons Fe^{III}(OH)_i^{(3-i)} + O_2^- \qquad (5)$$

The slope of unity of $\log k$ *vs.* $\log K$ is predicted by Marcus theory for endergonic outer-sphere electron transfer steps. The oxygenation of inner-spherically adsorbed Fe^{2+} (to α-FeOOH) is nearly six orders of magnitude faster than that of non-adsorbed Fe^{2+}. The equilibrium constant for the rate determining reaction step $(\equiv Fe^{III}O)_2Fe^{II} + O_2 \rightleftharpoons (\equiv Fe^{III}O)_2\ Fe^{III} + O_2^-$; $\log K^s = -9.0$ can be obtained by extrapolation of the plot in Figure 3b. The idea can be extended to Fe(II) bound within or near the surface lattice of Fe(II) silicates[54] (see Table I). Structural Fe(II) at the surface of hornblende or augite is oxidized faster by O_2 than Fe(II) in solution at pH < 5.[53] The reducing power of structurally bound Fe(II) is evident also from the observation that hydrogen can be generated in a reaction between iron rich minerals in basalt and groundwater.[34]

Another example of heterogeneous redox kinetics is given in Figure 4 for the oxygenation of VO^{2+} and in Figure 5 for the oxygenation of Mn^{2+}. Figure 6 compares the approximate half-lifes of V(IV), Fe(II) and Mn(II) towards oxidation by oxygen. In each case the relative effect of hydrolysis and adsorption is significant and often similar. Obviously, the aqueous surface of

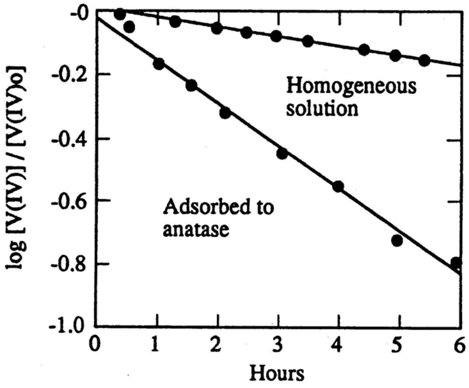


Figure 4. First-order plots demonstrating the catalysis of VO^{2+} oxygenation by an oxide surfaces at pH 4 and p_{O_2} = 1 atm. (From Wehrli and Stumm[48])

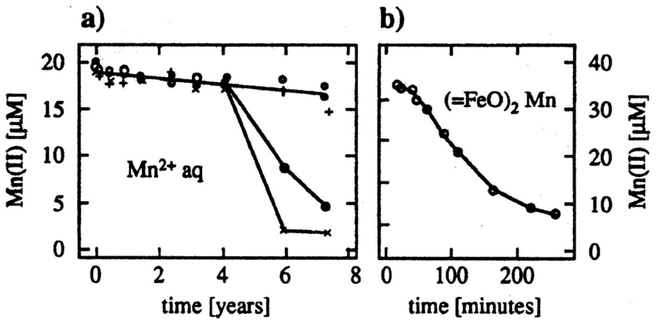


Figure 5. Oxygenation of Mn(II)
a) homogeneous solution at pH 8.4. The curves which show a decrease in $[Mn^{2+}]$ after 4 years are for experiments where small quantities buserite (6×10^{-7} M MnO_x) were added as a catalyst. Data from Diem and Stumm.[8]
b) 10 mM goethite suspension at pH 8.5, data from Davies and Morgan.[5]
The surface complex reacts within hours, whereas the homogeneous Mn(II) solutions are stable for years.

particles are very reactive chemical environments with respect to oxygenation. (In case of Mn(II) oxygenation electron transfer may be inner-spheric; and electron transfer may not be rate determining.) An interesting case is the oxidation of Co^{2+} to Co^{3+} and of Cr(III) to CrO_4^{2-} on MnO_2 surfaces.[25]

Surface-Bound Fe(II) as a Reductant of Nitroaromatic Substances

As shown in Figures 2b and 3b, Fe(II) coordinatively bound to a surface functional group of a hydrous mineral surface is thermodynamically and ki-

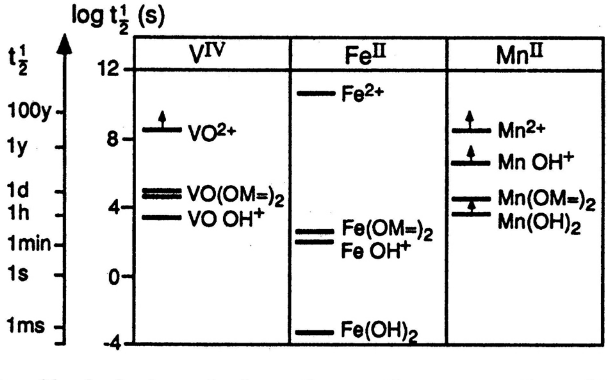


Figure 6. Effects of hydrolysis and adsorption on the oxygenation of transition-metal ions (p_{O_2} = 0.2 atm). *Arrows* indicate lower limit. (From Wehrli and Stumm[49], where references for individual data are given.)

netically an efficient reductant of O_2. Surface bound Fe(II) is also a »good« reductant for other electron acceptors such as chromate, nitrate, nitroaromatic substances and halogenated compounds.[13,14,18,19,31,56]

The reduction of nitroaromatic substances occurs as follows:

$$ArNO_2 \xrightarrow[2\,H^+]{2\,e^-} ArNO \xrightarrow[2\,H^+]{2\,e^-} ArNOH \xrightarrow[2\,H^+]{2\,e^-} ArNH_2 \qquad (6)$$

(Ar stands for an aromatic structure, *e.g.*, a benzene ring)

Heijman *et al.*[14] and Klausen *et al.*[18] have shown that nitroaromatic substances are readily reduced to the corresponding aromatic amines by adsorbed Fe(II) in presence of minerals such as Fe_3O_4, α-FeOOH or γ-FeOOH (Figure 7). As illustrated, solutions of solute Fe(II) are unreactive. The reduction sequence shown in (6) involves two electrons to yield stable intermediates or products. In the majority of abiotic redox reactions, the two electrons are transferred in sequential steps. With the transfer of the first electron, a radical species is formed

$$ArNO_2 + e^- \rightleftharpoons ArNO_2^{\cdot -}\ ; \quad \log K \text{ (nitrobenzene)} = -8.2 \qquad (7)$$

which is more reactive than the parent compound. The redox reaction step (7) is reversible; its endergonic nature is an indication that the reduction of nitrobenzene is difficult.

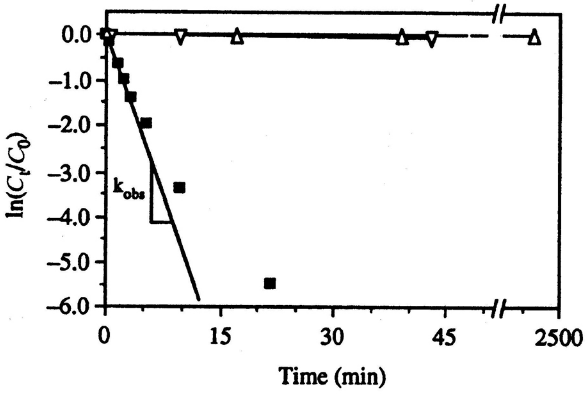


Figure 7. Reduction of a nitroaromatic compound by surface-bound Fe(II) Reduction of 50 μM 4-chloronitrobenzene (4–Cl–NB) in the presence of 17 $m^2\ L^{-1}$ magnetite and an initial concentration of 2.3 mM Fe(II) at pH 7.0 and 25 °C (■). Plot of ln (C/C_0 *versus* time). Note that experimental points deviate from pseudo-first-order behavior for long observation times. 4–Cl–NB was not reduced in suspensions of magnetite without dissolved Fe(II) (∇) or solutions of Fe(II) without magnetite (Δ). The final product of the redox process is 4-chloroaniline. (From Klausen *et al.*[18])

In Figure 8 the reduction of different nitroaromatic compounds, on one hand, by H_2S in presence of natural organic material (NOM) and, on the other hand, by Fe(II) in presence of Fe_3O_4, is compared by plotting the log of the reduction rates *vs.* log of the equilibrium constants of the respective one-electron equilibrium constants. A good linear correlation was obtained between reactivity (given by k_{NOM}) and the equilibrium constant. In Figure 8a the slope is unity. The direct relationship between k and K, *i.e.*, a direct proportionality between the activation energy and the free energy of the electron transfer reaction, is – similar to the example given in Figure 3b – a strong indication that the actual electron transfer from the NOM moieties to the nitroaromatic compound is rate limiting.

In Figure 8b, however, for the reduction by adsorbed Fe(II), the slope between log k and log K is only *ca.* 0.4; furthermore, for ortho-substituted nitrobenzenes (2 $-CH_3C_6H_4NO_2$ *etc.*) significantly higher relative rates were obtained than for meta- and para-substituted nitrobenzenes. The slope of 0.4 in the log k *vs.* log K relationship clearly indicates that in case of surface bound Fe(II) as a reductant, not the electron transfer itself but probably the formation of the precursor complex (between adsorbed Fe(II) and $ArNO_3$) is the rate limiting step in the transfer from the electron of the Fe(II) to a given $ArNO_2$. This hypothesis is corroborated by the behavior of the ortho-substituted nitrobenzenes and by the fact that strong competition was ob-

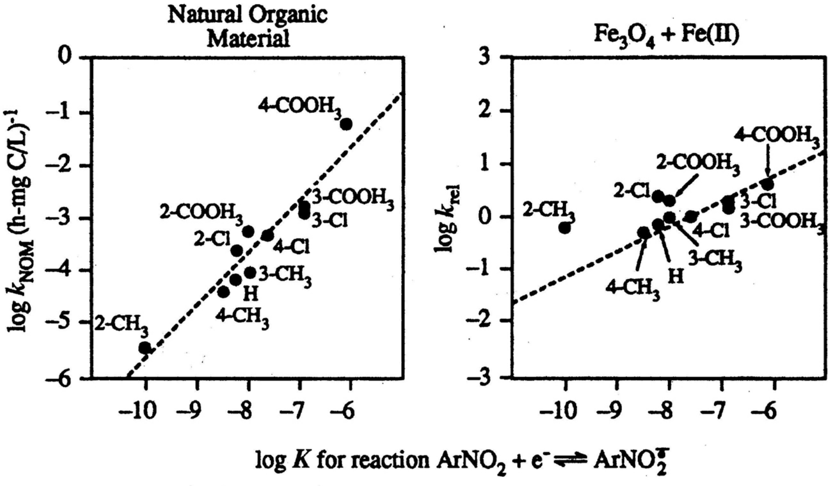


Figure 8. Comparison of reduction of nitroaromatic substances
a) by natural organic material (in presence of H_2S)
b) surface-bound Fe(II).
The rate log of the rate constant k is plotted vs the equilibrium constant of the one-electron reduction of $ArNO_2$ ($ArNO_2 + e^- \rightleftharpoons ArNO_2^{\cdot}$). (Figure a from Dunnivant *et al.*[9]; Figure b from Klausen *et al.*[18])

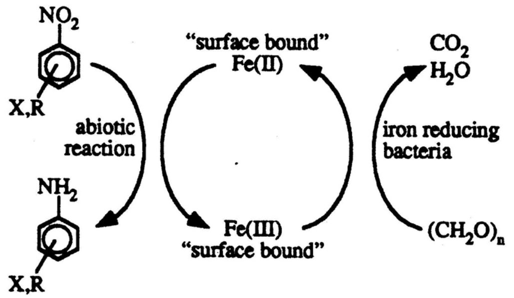


Figure 9. General reaction scheme proposed by Heijman *et al.*[14] for the reduction of nitroaromatic compounds in aquifer columns under ferrogenic conditions.

served[18] in binary mixtures. Figure 9 gives a general reaction scheme proposed by Heijman *et al.*[14] for the reduction of nitroaromatic substances in aquifers under ferrogenic conditions. It illustrates the experimental findings that nitroaromatic compounds are reduced to the corresponding amino compounds by a process in which the abiotic reduction of nitroaromatic substances by adsorbed Fe(II) is coupled to the biological process of iron(III) reduction by organic matter mediated by iron-reducing bacteria.[14]

Reduction of NO_3^- by Adsorbed Fe(II) in Presence of Traces of Cu

The reducing power of adsorbed transition ions is also exemplified by recent observations by Davison[6] on the reduction of nitrate by Fe(II) in the presence of trace metals (*e.g.*, copper) and a solid phase as an adsorbent (sterile conditions). These findings are relevant for the fate of NO_3^- in groundwaters under conditions where nitrate reducing bacteria are inactive. A possible interpretation of the reaction sequence could be sketched as follows:

$$\mathrm{Fe(II)} + \mathrm{Cu(II)} \rightleftharpoons \mathrm{Fe(III)} + \mathrm{Cu(I)}$$

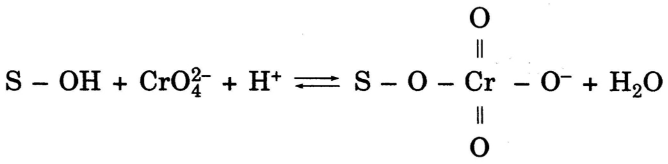
$$\mathrm{Cu(I)} + NO_3^- \xrightarrow{\text{slow}} \mathrm{Cu(II)} + \text{reduced nitrate} \tag{8}$$

$$\text{reduced nitrate} \xrightarrow{\text{fast}} NH_4^+$$

Adsorbed Cu(I) is a better reductant than solute Cu(I).

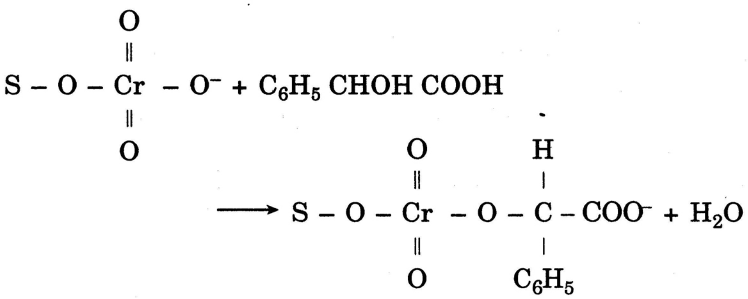
Adsorbed Chromate as an Oxidant

Although CrO_4^{2-} is from a thermodynamic point of view a powerful oxidant, it reacts in the pH-range of natural waters often very sluggishly with reductants, especially with organic substances. Inner-spheric adsorption, *e.g.*, to a hydrous oxide surface, makes the CrO_4^{2-} a better oxidant:



$$S - OH + CrO_4^{2-} + H^+ \rightleftharpoons S - O - \underset{\underset{\displaystyle O}{\|}}{\overset{\overset{\displaystyle O}{\|}}{Cr}} - O^- + H_2O \tag{9}$$

(Depending on the surface of the oxide binuclear surface complexes S_2CrO_4 may also be formed.) Deng and Stone[7] have investigated the reduction adsorbed to TiO_2 (anatase) by mandelic acid. The catalytic effect of the surface is illustrated in Figure 10. The reaction may proceed in the following way: The adsorption is followed by the interaction of the adsorbed chromate with a reductant; this may proceed by an exchange of an oxo group at the Cr(VI) center to form an ester type adduct as a precursor to electron transfer:



$$S - O - \underset{\underset{\displaystyle O}{\|}}{\overset{\overset{\displaystyle O}{\|}}{Cr}} - O^- + C_6H_5\,CHOH\,COOH \longrightarrow S - O - \underset{\underset{\displaystyle O}{\|}}{\overset{\overset{\displaystyle O}{\|}}{Cr}} - O - \underset{\underset{\displaystyle C_6H_5}{|}}{\overset{\overset{\displaystyle H}{|}}{C}} - COO^- + H_2O \tag{10a}$$

(With bidentate reductants a binuclear precursor may also be formed.)

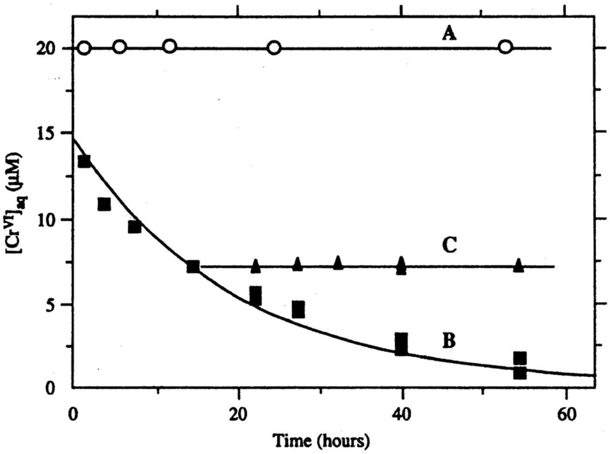
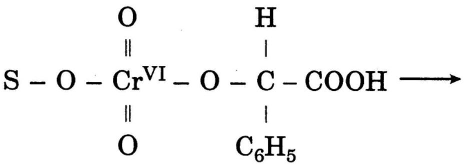


Figure 10. Reduction of chromate (20 μM) by mandelic acid (200 μM) as a function of time (pH = 4.7). A) in absence of surfaces, B) in presence of 1 g/l (40.5 m^2/l) of TiO_2 (anatase) suspension. C) TiO_2 was removed by filtration after 14 hours of reaction. (After Deng and Stone[7])

This is followed by a presumably inner-sphere electron transfer and formation of the products:



$$S - O - \overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{Cr^{VI}}} - O - \overset{\overset{H}{|}}{\underset{\underset{C_6H_5}{|}}{C}} - COOH \longrightarrow$$

$$S - OH + Cr(V) \text{ (or } Cr(IV)) + C_6H_5\,COCOOH \qquad (10b)$$

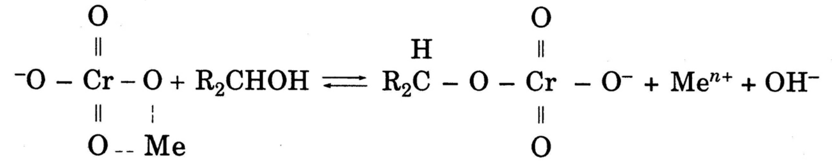
Alternatively, C_6H_5CHO and CO_2 may be formed. In subsequent fast steps Cr(VI) and Cr(V) are reduced to Cr(III).[7]

Deng and Stone[7] have shown that adsorption to other hydrous oxides, like goethite and γ-Al_2O_3, exert also a surface catalytic effect although somewhat less than that observed with TiO_2. They demonstrated that surface catalyzed Cr(VI) reduction generally occurs with α-hydroxy-carboxylic acid and their esters, with α-carboxylic acids, with oxalic acids and substituted phenols. It is reasonable to generalize that surface catalyzed Cr(VI) reduction can occur in soils, sediments and other aquatic environments.

What is the role of the hydrous oxide surface in expressing its catalytic influence? In the chromate surface complex (Eq. (9)) the central ion Ti^{IV}, Fe^{III}, Al^{III} are hard Lewis acids; with CrO_4^{2-} they exchange structural OH. In the inner-sphere surface complex, electron density is shifted toward the central metal ion with two consequences:

1) the chromate becomes a better oxidant; and

2) the oxogroups of the surface bound chromate become more labile. As we have seen this lability is essential for the exchange of the interaction (ligand exchange) at the central ion with the hydroxo group of the organic reductant. The hydrous oxide surface influences the reactivity of the adsorbed chromate in a similar way as protons or metal ions:



$$^{-}O - \overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{Cr}} - \underset{\underset{\cdots Me}{\vdots}}{O} + R_2CHOH \rightleftharpoons \overset{H}{R_2C} - O - \overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{Cr}} - O^- + Me^{n+} + OH^- \qquad (11)$$

The effect of H^+ ion binding on CrO_4^{2-} to form $HCrO_4^-$ and H_2CrO_4 is to increase the lability of the oxogroups at the Cr(VI) metal center. This has been shown by Okumura *et al.*[28] on the rate of chromate ligand substitution using an isotope exchange reaction:

$$CrO_4^{2-} + H_2{}^{18}O = CrO_3{}^{18}O^{2-} + H_2O$$

This isotope exchange reaction has been found to be acid catalyzed (see also Stone *et al.*[37]). It can be implied that surface complex of CrO_4^{2-} with oxides of hard Lewis acids labilizes the oxo groups on the Cr(VI) center and facilitates reactions such as the precursor formation given in Eq. (11).

Deng and Stone[7] have studied the kinetics of the reaction. They conclude that the activation of the chromate surface complex is influencing the reaction rate:

$$S - CrO_4^- \underset{k_{-c}}{\overset{k_c}{\rightleftharpoons}} S - CrO_4^{-*} \tag{12}$$

Activation may arise from the transition from outer to inner-sphere adsorption, the diffusion from inactive to active surface sites, the exchange of oxogroups at the Cr(VI) center, or from other phenomena that alter the stoichiometry, structure and reactivity of the adsorbed Cr(VI). The activated surface complex would then react with the reductant, *i.e.*, ROH to form the precursor complex and subsequently the products:

$$S - CrO_4^{-*} + ROH \xrightarrow{k_d} S - O_3Cr - OR + OH^- \longrightarrow P \tag{13}$$

The steady state approximation can be applied to $d[S - CrO_4^{2-*}] / dt$ and the overall rate of the reduction reaction can be derived:

$$\frac{d[P]}{dt} = \frac{(k_c k_d/k_{-c})\,[ROH]\,[S{-}CrO_4^-]}{1 + k_d/k_{-c}\,[ROH]} = \frac{a[S{-}CrO_4^-]\,[ROH]}{1 + b[ROH]} \tag{14}$$

where $a = k_c k_d/k_{-c}$ and $b = k_d/k_{-c}$.

Experimental results[7] show that the overall reaction rate is proportional to $[S{-}CrO_4^-]$. In the case of mandelic acid as a reductant k_d was found sufficiently high that $k_d/k_{-c} > 1$ and overall reaction is rate limited by the activation of $S{-}CrO_4^-$. In case of methylmandelate as a reductant, k_d is small causing a shift in the rate limiting step to reaction (13), especially at low reductant concentrations.

Corroding Iron Provides Catalytic Surfaces and Diversified Reductants

The remarkable effect of surface catalysis is illustrated by the corroding iron system. Corroding zero-valent iron and some of its corrosion products are reductants of O_2, NO_3^-, CrO_4^{2-} and of refractory organic substances such as chlorinated hydrocarbons (Figure 11):

$$Fe^\circ + RCl + H^+ \longrightarrow RH + Fe^{2+} + Cl^-$$

The reaction has been promoted as an effective remediation technology in aquifers (Wilson[55]). The mechanism is under investigation in various

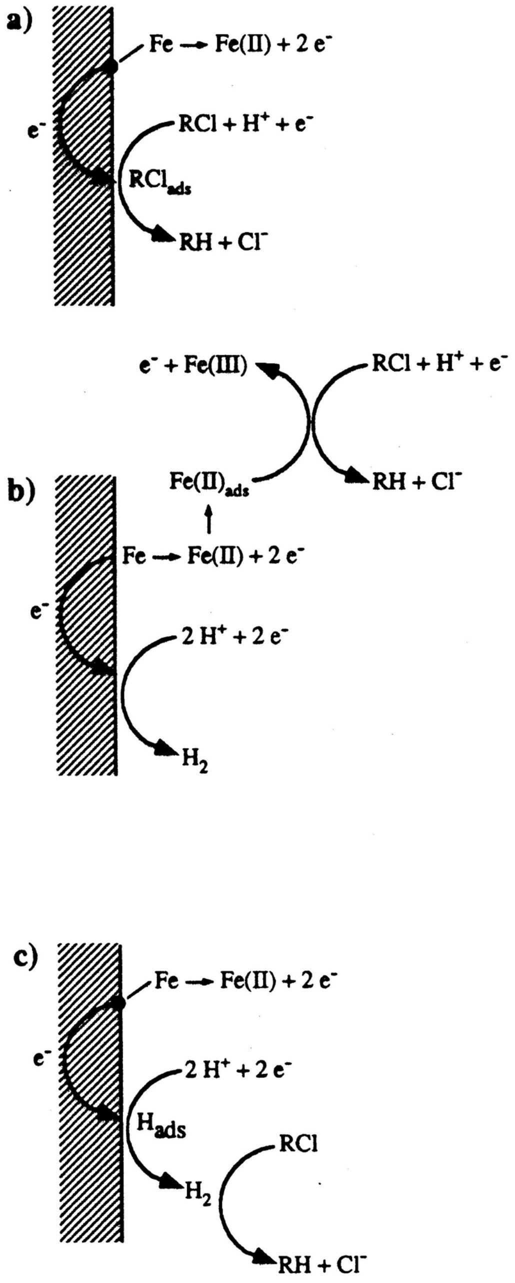


Figure 11. Corroding iron as a reactive system for the reduction of organic substances (*e.g.*, chlorohydrocarbons, RCl). Enhanced by surface catalysis various electron donors D a) zero-valent iron, Fe°, and its (surface) complexes, $Fe°OH^-$, $Fe°Cl^-$; b) Fe(II) adsorbed or bound to corrosion products; and c) H_2 (or atomic hydrogen) react with the chlorohydrocarbons. (After Wilson[55])

laboratories. The corroding iron system provides a multitude of potentially effective surfaces (Fe° and Fe(II)–Fe(III) corrosion products) and a variety of reductants over a broad range of reduction potential (electrons, atomic hydrogen, H_2, Fe°, Fe(II)) bound to various (hydr)oxides.

Outlook

The various reservoirs of the earth (atmosphere, water, sediments, soils, biota) contain material that is characterized by high area to volume ratios. The interaction of rocks with water and the atmosphere in the presence of organic matter continuously produces reactive material of high surface area. Many natural and technical processes are rate controlled by processes occuring at surfaces or catalyzed by surfaces. Many environmental macroscopic processes, and even global processes are controlled at the nanoscale of the solid-water interface.

Branica and his colleagues[3], meeting the analytical challenges, have illustrated that speciation, *i.e.*, the assessment of the chemical nature of an element is necessary to interpret reactivity, bioavailability and toxicity of this element. Speciation of surfaces, *i.e.*, the characterization of the functional groups at mineral surfaces and their surface complexes is equally important to understand the heterogeneous processes and those catalyzed by surfaces. In the exemplification given here on the role of surfaces in mediating redox processes, we have illustrated that the mineral surface, by specifically adsorbing oxidants or reductants, influences redox intensity and reduces the activation energy of the electron transfer reaction. Because inorganic and organic electron acceptors and donors can interact at the mineral surface, the solid-water interface often enhances, electron transfer between inorganic and organic moieties and facilitates the coupled interaction by microbially mediated and surface catalyzed electron transfer. Redox processes at mineral surfaces help govern the long-term evolution of the earth's surface as well as the daily chemical conditions of our environment.[25]

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SAŽETAK

Kataliza redoks-procesa hidratiziranim površinama oksida

Werner Stumm

Postignut je znatan napredak u identifikaciji, fizikalno-kemijskoj karakterizaciji i određivanju količine otopljenih vrsta u prirodnim vodama. Glavnina kemijskih procesa u prirodnim sustavima odvija se na površinama minerala, anorganskih i organskih čestica. Koncept aktivnih površinskih mjesta na vodenoj međupovršini, te karakterizacija površinskih mjesta (površinska specijacija) bitni su za razumijevanje površinski kontroliranih procesa. Ovdje je važnost hidratiziranih oksidnih površina kod katalize redoks-procesa u prirodnim vodama ilustrirana sa tri primjera:

1. Oksidacija Fe(II) sa $O_2 \cdot$ Fe(II) i ioni drugih prijelaznih elemenata adsorbirani na hidratizirane okside (unutarnji površinski kompleksi), kao i njihove hidrolizirane

vrste lako se oksidiraju kisikom; može se pokazati da prijenos elektrona u vanjskoj sferi kompleksa određuje brzinu.

2. Redukcija nitroaromatskih tvari adsorbiranih na Fe(II). Fe(II) adsorbiran na Fe_3O_4, γ-FeOOH i α-FeOOH, kao i neki drugi hidratizirani oksidi učinkoviti su reducensi za nitroaromatske i ostale organske tvari; stupanj koji određuje brzinu najvjerojatnije je nastajanje prekursorskog produkta između reducensa i nitroaromatske tvari.

3. Adsorbirani kromat učinkovit je oksidans organskih tvari, npr. hidroksikarboksilnih kiselina i njihovih estera. Adsorpcija jača oksidacijsku moć kromata i povećava labilnost okso-skupina na Cr(VI).

Redoks-procesi katalizirani mineralnim površinama imaju važnu ulogu u evoluciji površine zemlje i njezinih prirodnih voda.