

COURSE NOTES

CHAPTER 4. Adsorption and Reactions of selected organic molecules on clay mineral surfaces

(1) (P. 81) Introduction -

(1) "It is generally agreed that the clay fraction [of soil] is the most important in influencing the reactivity of organic molecules."

(2) "An understanding of the reactivity of even simple organics on clay mineral surfaces, whether pristine or chemically modified, can aid in the prediction and perhaps prevention of groundwater contamination."

(2) (p. 82) 4-1 Factors affecting clay surface reactivity

(1) Figure 4-1 (p. 82) - surface functional groups in smectite clay

(2) Definitions: Lewis Acid = An electron pair acceptor $[Al^{+3}] + :B \rightarrow [Al:B]$ eq (1)

Lewis Base = An electron pair donor

Bronsted Acid = A proton donor. (In aqueous solutions, all acids transfer proton to water molecule, to give hydronium ion, H_3O^+ . $[Al-OH-Si] \rightarrow [O^-] + H^+$ eq (2)

$[O^-] + M^+ = [OM]$ eq (3)

Bronsted Base = A proton acceptor. (In aqueous solutions, a base accepts a proton from a water molecule, forming the hydroxide ion, OH^- .)

(3) In presence of liquid water:

edge positions: OH^- groups and Lewis acid sites (e.g., Al^{+3});

Aquated sites may be source of Bronsted acidity $[Al-OH_2] \rightarrow O^- + H^+$ eq(4)

(4) Terminal OH groups engage in coupling reactions with organic containing functional groups: $[Si-OH]_{edge} + ROH \rightarrow [Si-OR]_{edge} + H_2O$ eq (6)

(5) Most important property of smectite clays - ability to swell in presence of water and thereby provide access to large internal surface area [interlamellar adsorption] and reactivity [hydrolysis of exchange ions] of gallery exchange cations. Hydrolysis = Splitting by water

$[M(H_2O)_nX^+]_{gallery} \rightarrow [M(H_2O)_{n-1}(OH)^{(x-1)+}] + H^+$ eq (7)

(6) Fig. 4-1 illustrates ability of smectite clays to **shuttle electrons** between structural redox centers ($Fe^{+2, +3}$) and organic molecules adsorbed on the external or internal gallery surfaces.

$[M^{n+}]_{layer} + RH \rightarrow [M^{(n-1)+}]_{layer} + R\cdot + H^+$ eq (8)

$[M^{n+}]_{layer} + An \rightarrow [M^{(n-1)+}]_{layer} + Ar^{+}$ eq (9)

(3) Skip 4-2 (pp. 84-85)

(4) (p. 85) 4-3 Adsorption of phenolic compounds

(1) Characteristics: Bronsted acids, tendency to ionize, oxidation to humic and fulvic acids, polymerization reactions.

(2) Oxidation and oxidative polymerization processes facilitated by clays and other mineral surfaces containing redox-active metal ions (e.g., $Cu(II)$, $Fe(III)$, $Mn(IV)$).

(5) (p. 85) Sec. 4-3.1 Organo Clays

(1) Tendency for smectite clay to adsorb organic guest molecules can be facilitated by ion-exchange reactions involving organo-cations.

(2) (p. 86) "**Designer Clays**" - replace exchangeable Na^+ with alkylammonium cations

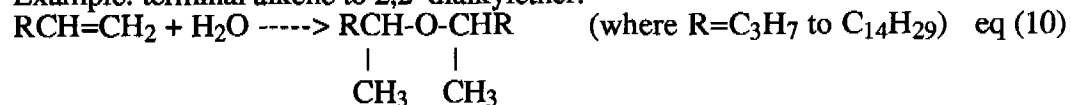
Implications for engineering: "organo-clays may have utility as selective adsorbents as liners in waste ponds and burial sites." (p. 86).

(6) Skip 4-3.2 (pp. 86-88)

(7) Sec. 4-4 Selected Organic Reactions, Sec. 4-4.1 - Bronsted & Lewis Acid Catalysis

(1) "Organic reactions on clay minerals can be selective & efficient."

(2) Example: terminal alkene to 2,2'-dialkylether:



This reactions occurs on Al(III), Cr(III), Fe(III), and Cu(II)-exchanged smectites with specificity.

(3) Skip the remainder of section (to p. 93) (chemistry not needed)

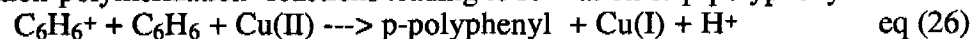
(8) Sec. 4-4/2 - Electron Transfer Reactions

(1) For an e⁻ from Ar ring to metal ion center, metal ions must be partially dehydrated to allow for close approach of the two species and for binding of Ar ring to metal center via pi electron donation.

(2) Example: Cu(II) with benzene



The radical cation reacts further with neutral benzene to initiate further "oxidation-polymerization" reactions leading to formation of p-polyphenyl:



Implications: (1) The Cu(I) formed in these reactions can be **reoxidized** by air, thus making the oxidative polymerization reaction catalytic!!

(2) (p. 94) Dibenzo-p-dioxin (dioxin) reacts with Cu(II) smectite to form radical cations. Radical cations react to form oxidative polymerization products (mainly dimers).

Suggestions to oxidative polymerization reaction to convert dioxins to less mobile and, perhaps, less toxic products!!

(3) (p. 94) PCP formed 2,3,5,6-TeCP upon reaction with Cu(II) smectite.

End Chapter 4

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