Iron-Laden Mineral Colloids as Naturally Abundant Catalysts for Peroxide-Based In Situ Chemical Oxidation

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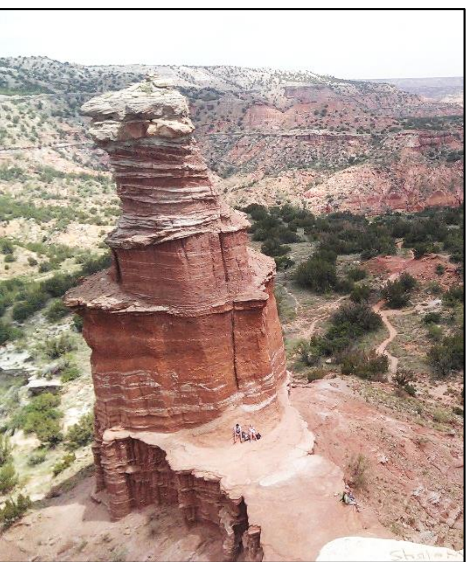

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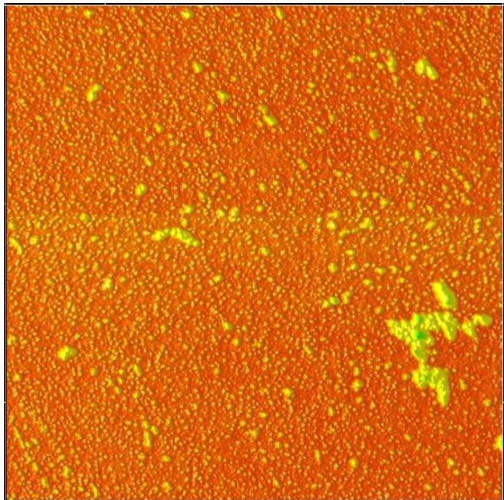
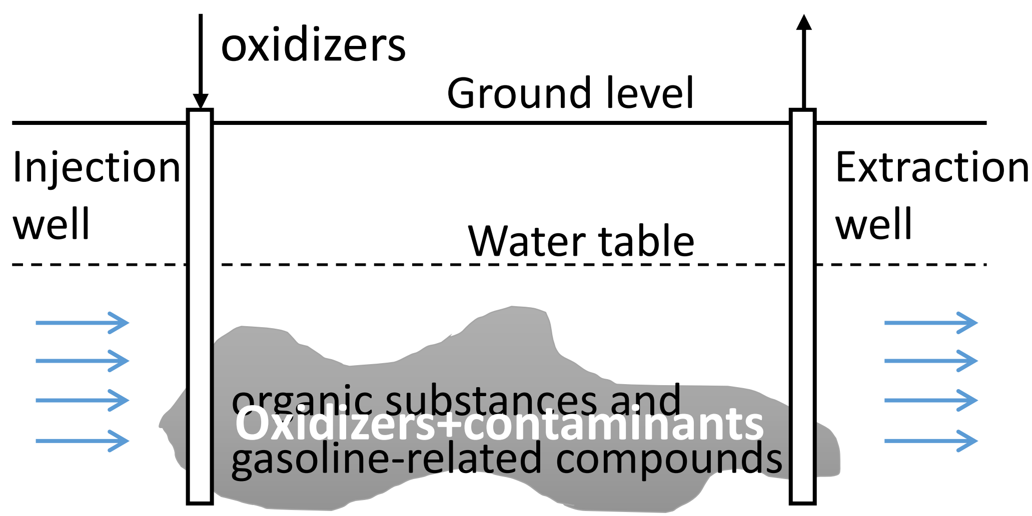


Outline

- ❖ Introduction
- ❖ Objectives of the Study
- ❖ Methods
- ❖ Results and Discussion
- ❖ Conclusion

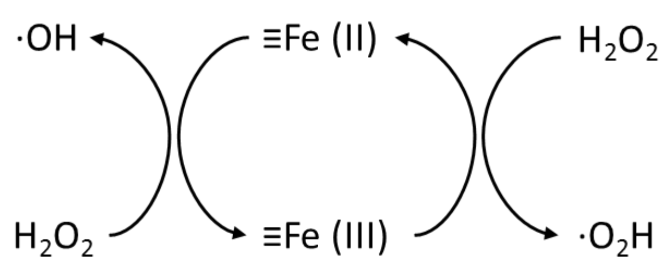
In Situ Chemical Oxidation (ISCO)

- Remediating sites by injecting strong oxidizers directly into the contaminated medium
- Target contaminants include organic substances and gasoline-related compounds
- “In situ” = “in place”, signifying the remediation happens at site of contamination.



ISCO with Catalysts

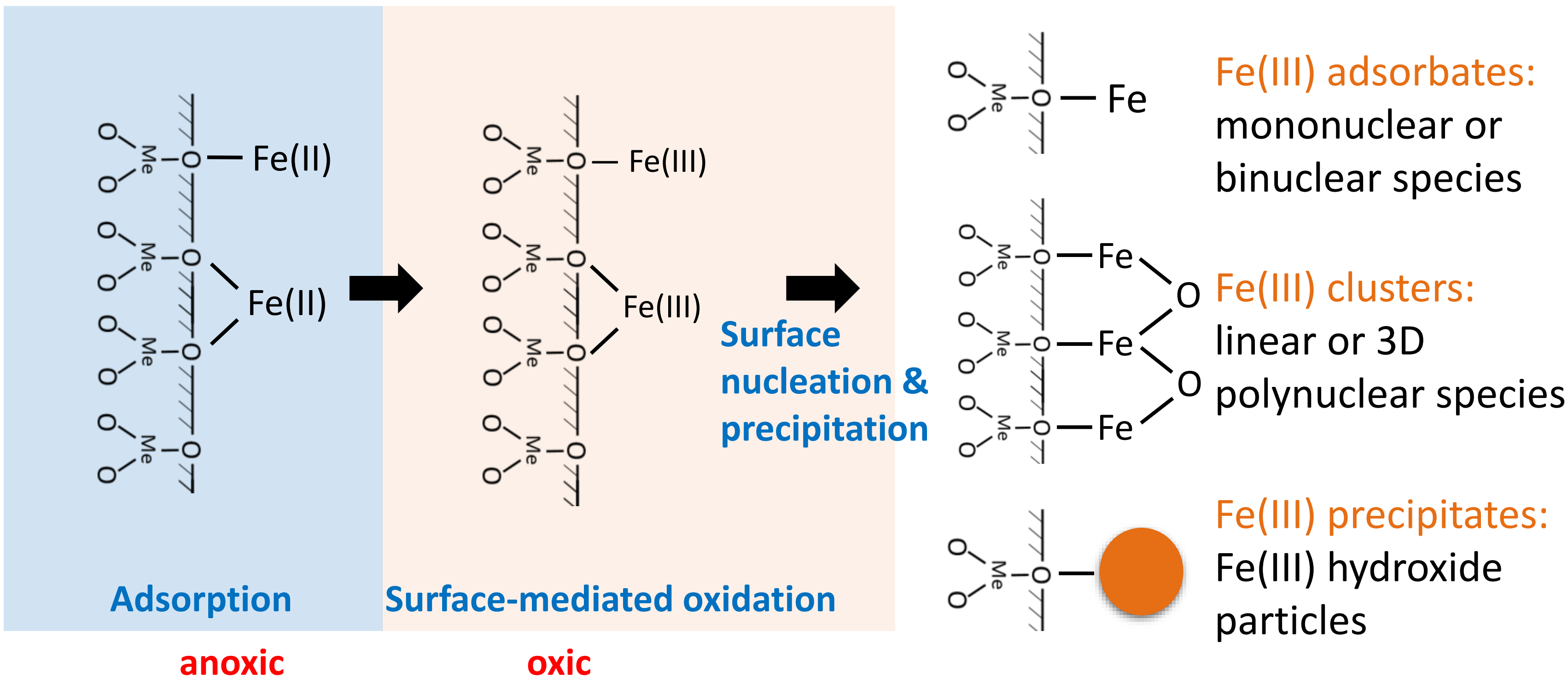
- Common oxidants used in hydrocarbon sites: hydrogen peroxide (H_2O_2), persulfate, and permanganate
- Many aquifer minerals may activate H_2O_2, generating reactive oxygen species (ROS) such as hydroxyl radical (•OH) or ferryl (>Fe^{IV}) that are capable of degrading contaminants.
- Minerals serve as heterogeneous Fenton catalysts:
  - Iron Oxides (e.g., goethite, ferrihydrite)
  - Iron-coated Mineral Colloids (e.g., Fe deposited on silica, alumina, aluminosilicates, etc)



Haber and Weiss (1934)

Iron-coated Mineral Colloids

In subsurface, aqueous Fe may immobilize onto natural mineral colloids through multiple pathways, forming iron-laden mineral colloids. This surface-residing Fe is known as *Interfacial Iron Species.*



Intro · Objectives · Methods · Results

Motivation of Study

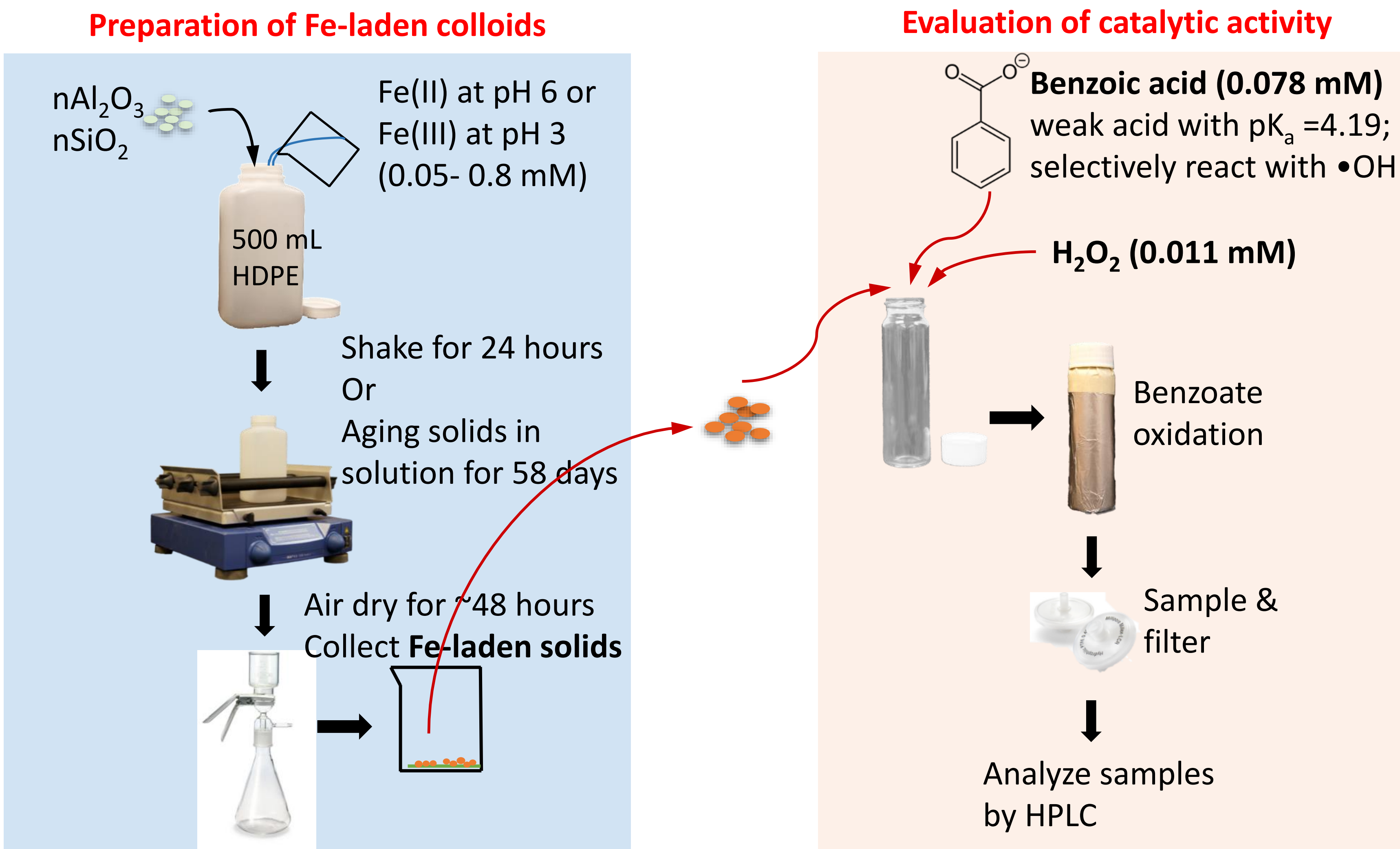
- Many studies have focused on iron oxides as catalysts for peroxide activation.
- Few research has assessed the activity of iron-laden mineral colloids.
- Understanding the catalytic activity of these ubiquitous mineral particles will allow:
  - Quantification of oxidant dosage
  - Prediction of contaminant degradation rates
  - Possible engineering of site geochemistry for optimal remediation outcome

Objectives

1. Characterize the **physical and chemical properties** of interfacial Fe species on iron-laden mineral colloids.
2. Examine the **catalytic activity** of interfacial Fe for H_2O_2 activation and the oxidation of organic compounds.
3. Investigate the **changes in structure and reactivity** of interfacial Fe during aging in aqueous media.

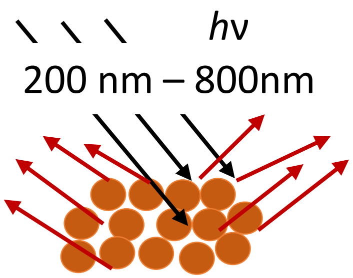
Methodology

Aqueous Experiments



Surface and Solid Phase Characterization

- **HR-TEM, BET, XRD**
- **UV-Vis Diffuse Reflectance Spectroscopy (DRS)**
  - measures reflectance of light (R_∞) by densely-packed particulate material
  - R_∞ of pristine materials serves as the "blank", so the spectra reflect the feature of the iron immobilized on the materials.
  - R_∞ is related to Schuster-Kubelka–Munk (SKM) function ($F(R_\infty)$),



$$F(R_\infty) = \frac{(1 - R_\infty)^2}{2R_\infty} = \frac{K}{S} \Rightarrow F(R_\infty) \propto K$$

Varied little in 200-800 nm

Diff. species → diff. K

Kortüm (2012); Torrent and Barrón (2002); Klier (1972)

Results and Discussion

Properties of Mineral Colloids

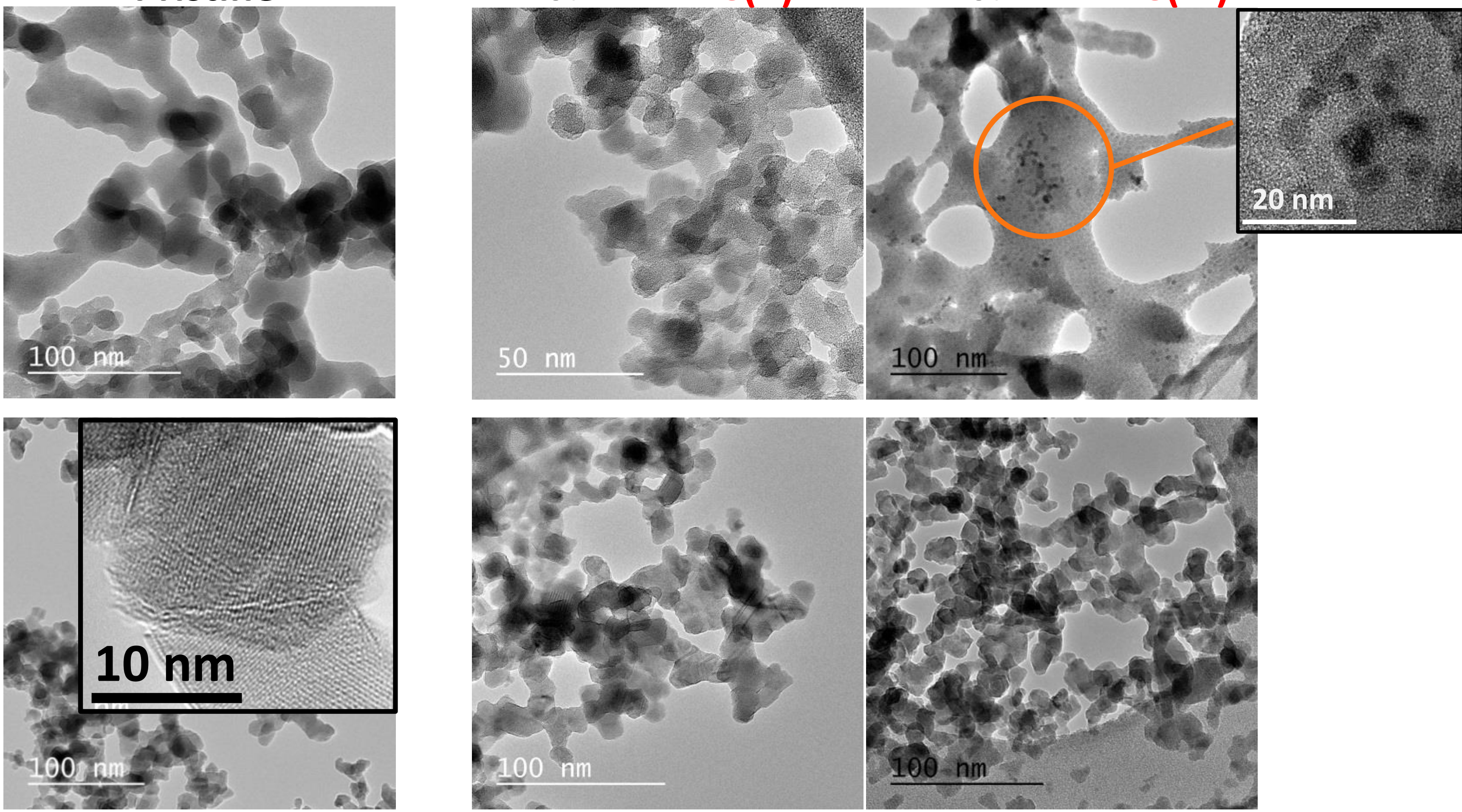
[a] Particle size info was provided by vendor and was verified qualitatively with TEM characterization.
[b] Identified with X-ray diffraction analysis.
[c] Particles immersed in 0.2 mM Fe(III) for $nSiO_2$ and nAl_2O_3 for 24 h.

HR-TEM Images

Pristine | Impregnated In 0.2 mM Fe(II) | Impregnated In 0.2 mM Fe(III)

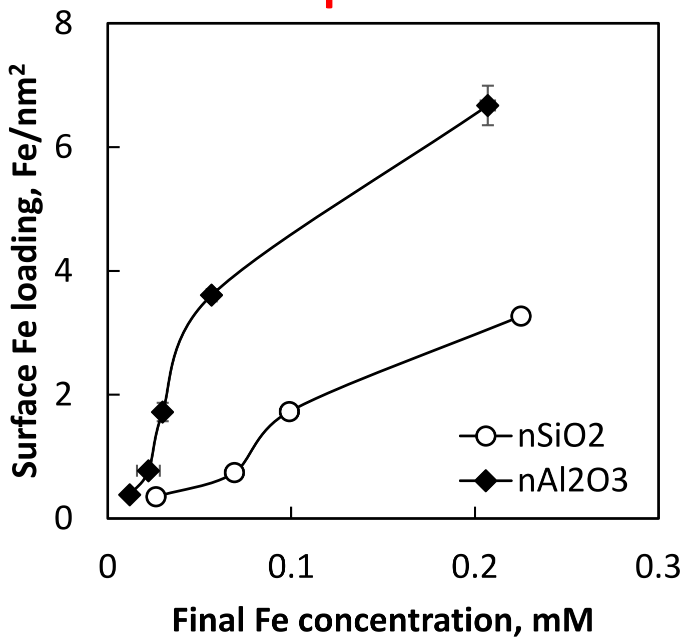
nSiO$_2$

nAl$_2$O$_3$

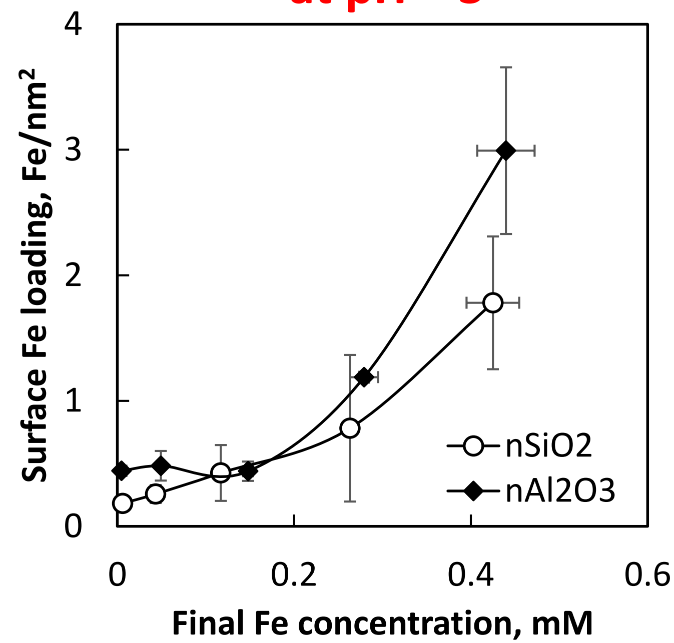


Uptake of Dissolved Fe by Mineral Colloids

Impreg. in Fe(II) solution at pH = 6

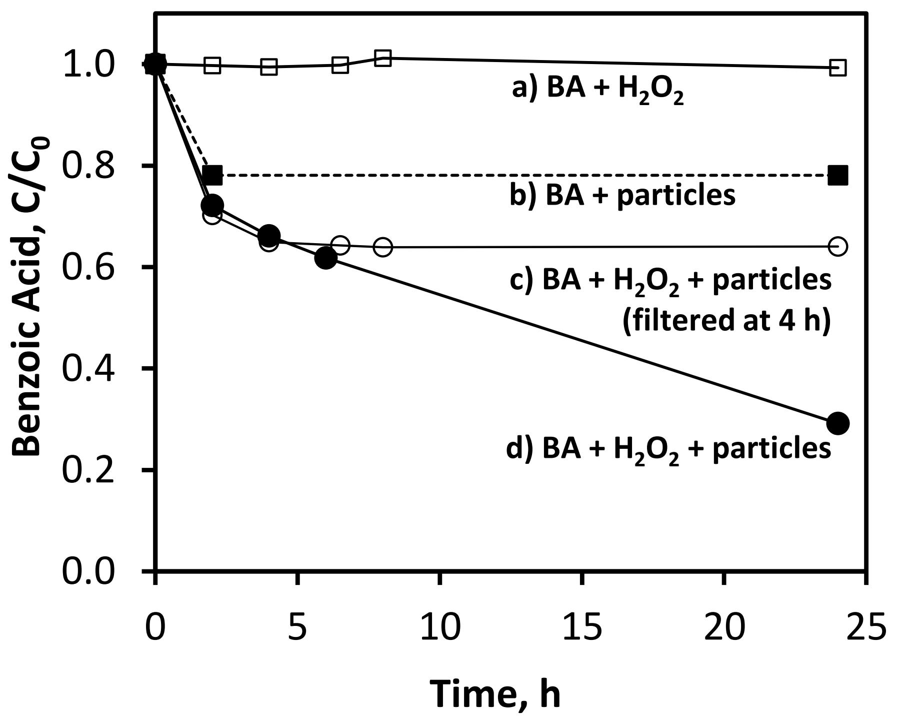


Impreg. in Fe(III) solution at pH = 3



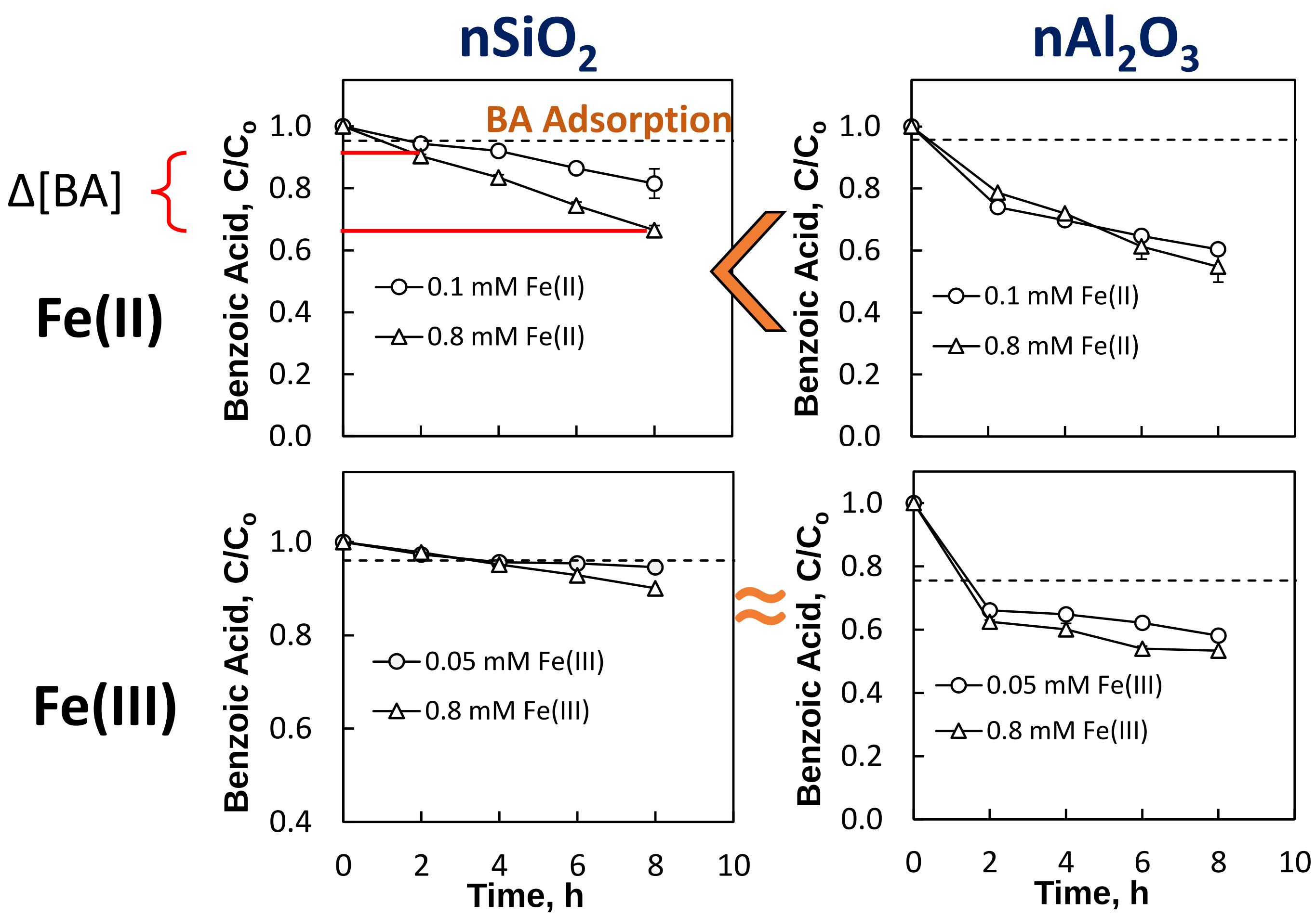
Data do not conform to Langmuir adsorption isotherm, suggesting surface precipitation occurred in addition to adsorption.

Importance of Heterogeneous Reactions

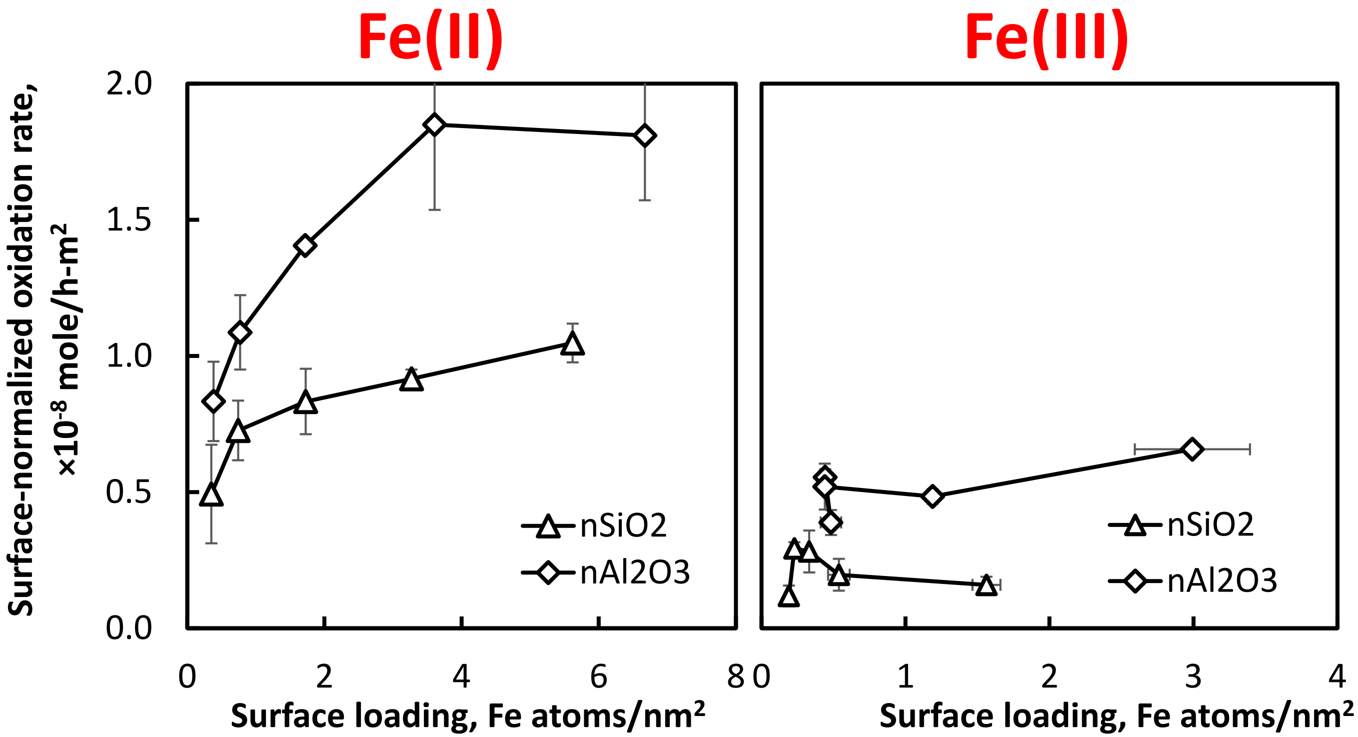


Activation of H_2O_2 is mediated by Fe-laden mineral surfaces.
No significant H_2O_2 decomposition in aqueous solution only.

Catalytic Oxidation of Benzoate

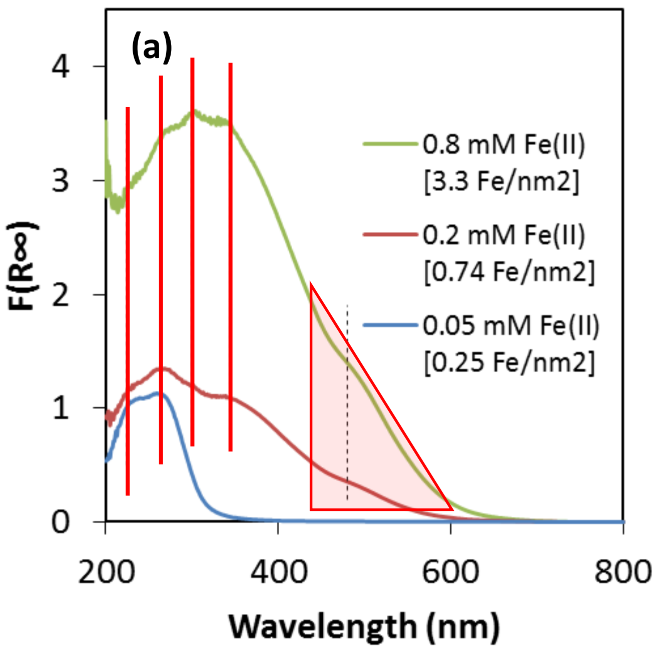


Dependence of Oxidation Rate on Surface Fe Loading



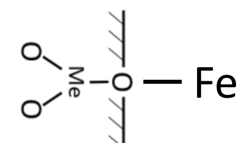
- Oxidation rate increases with surface Fe density at low Fe loading.
- Above a critical Fe loading, surface activity approaches a plateau (or increases marginally)
- Solids derived from Fe(II) precursor have higher reactivity.

Characterization of Fe speciation by DRS UV-Vis



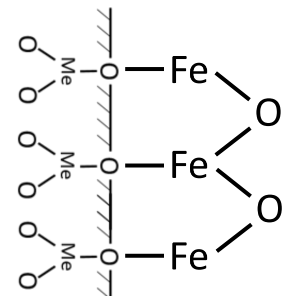
225 & 265 nm :

O → Fe^{3+} in octahedral coordination

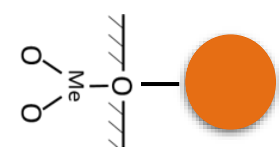


300 nm: dimer

350 nm - 480 nm:polymer

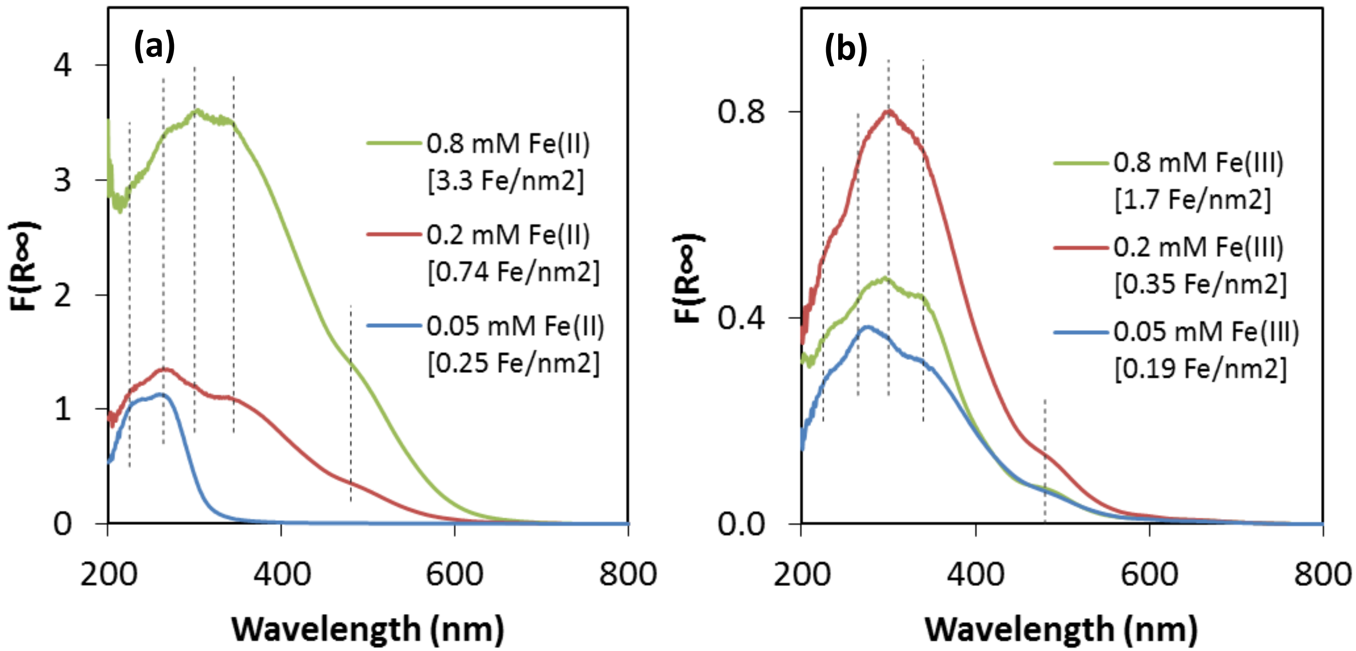


>480 nm: Fe(III) hydroxide nanoparticles



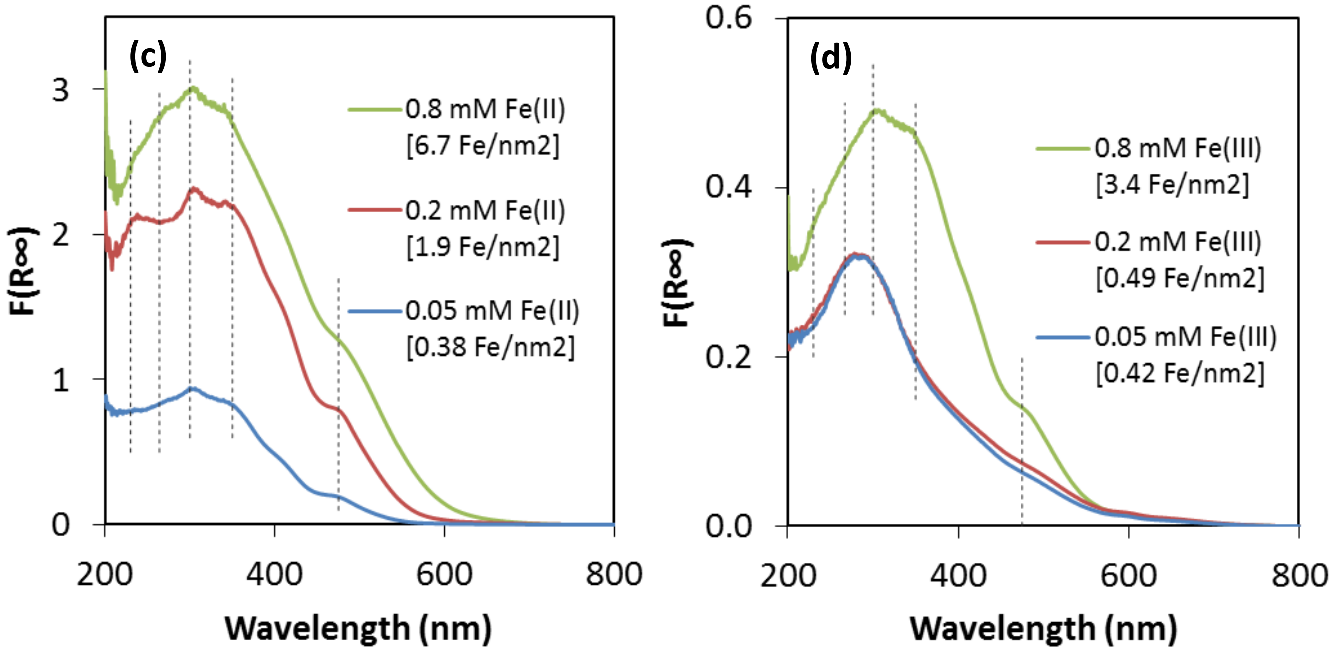
Perez-Ramirez, J, et. al (2005); Pirngruber, G. D., et.al (2006); Schwidder, M., et.al (2005); Kumar, M. S., et. al (2004)

DRS UV-Vis of Fe-loaded n-SiO_2



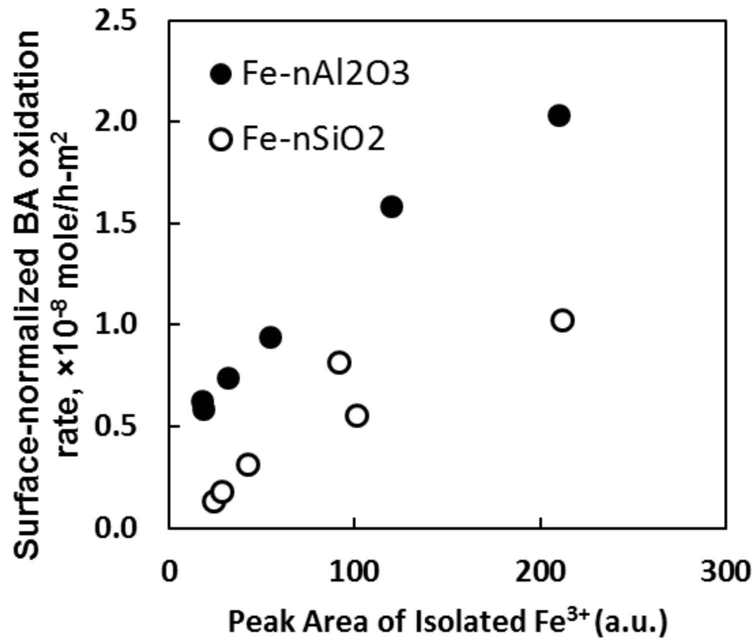
- Isolated Fe predominates on surface when immersed in low conc. Fe(II) solutions. Higher Fe(II) concentration gives rise to polymers and precipitates.
- Fe precipitates appear on n-SiO_2 even when exposed to low Fe(III) concentration.

DRS UV-Vis of Fe-loaded n-Al_2O_3



- Precipitates form on n-Al_2O_3 even when immersed in low conc. Fe(II) solution.
- Immersion in Fe(III) solution gives rise to predominantly Fe dimers and polymers. Surface precipitates emerge at higher surface Fe loading.

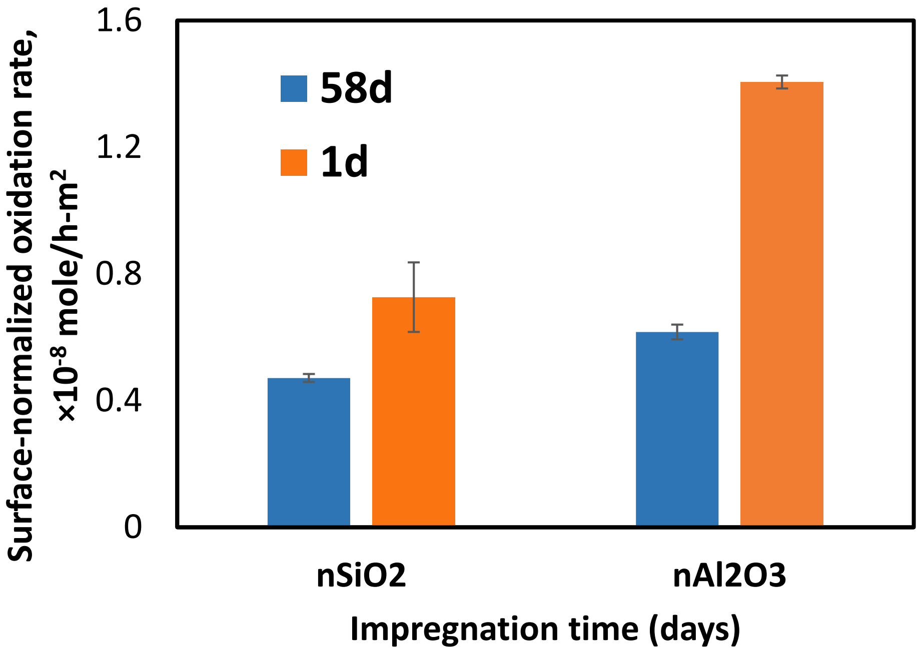
Correlation Between Surface Activity and Fe Molecular Structure



Deconvulting DRS spectra reveal the linear correlation between density of isolated Fe and reactivity of iron-laden colloids.

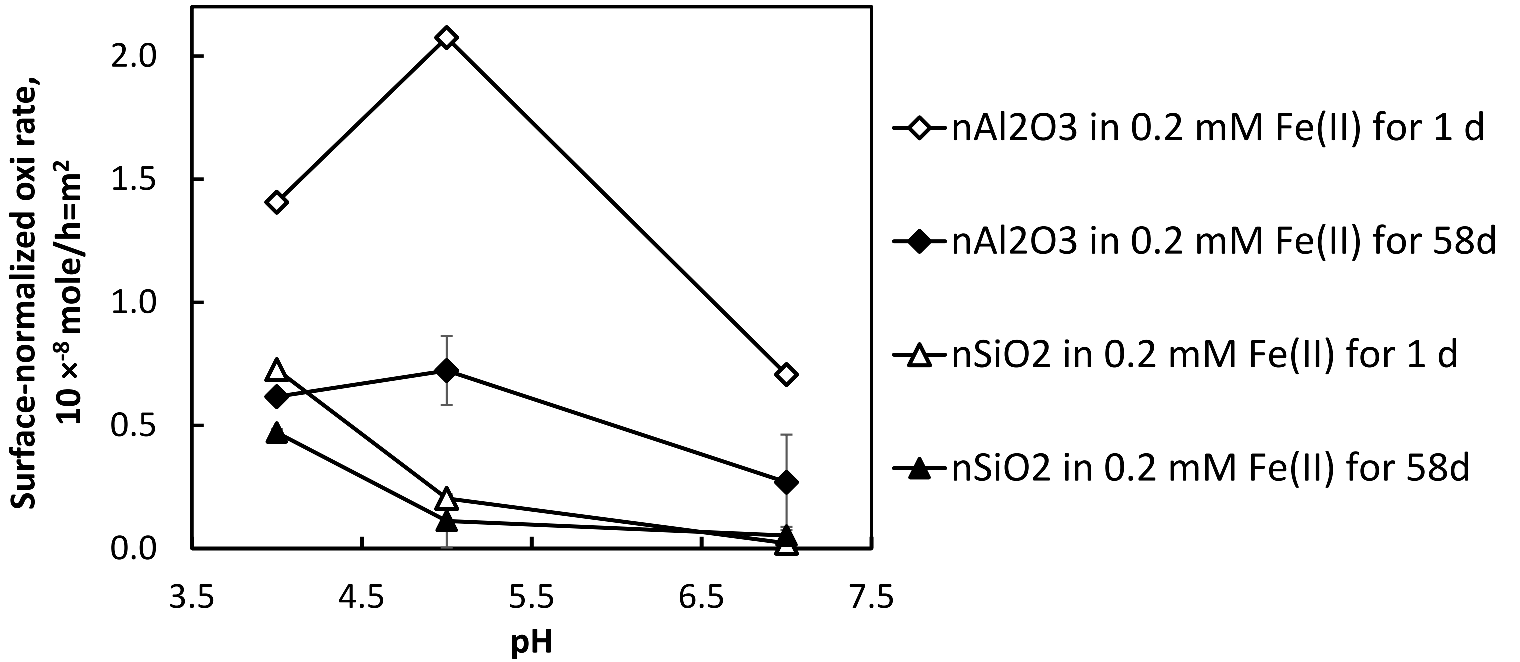
References on this slide: Perez-Ramirez, J, et. al (2005); Pirngruber, G. D., et.al (2006); Schwidder, M., et.al (2005); Kumar, M. S., et. al (2004)

Effect of Aging on Catalytic Activity



- Aging mineral colloids in the iron solution results in decrease in catalytic activity for interfacial iron species.
- Restructuring of interfacial Fe may occur during aging period. Characterization effort is on-going.

Effect of pH on catalytic reactivity



- For iron-laden $nSiO_2$, activity of solids decreases with increasing pH.
- For iron-laden nAl_2O_3, optimal catalytic activity is attained at circumneutral pHs.

Conclusions

- Interfacial iron species on silica and alumina colloids have considerable catalytic activity in activating H_2O_2 .
- Interfacial iron derived from aqueous Fe(II) has higher activity than those from Fe(III) ions.
- Surface activity is mainly contributed by well-dispersed isolated Fe species than Fe clusters or precipitates.
- The freshly formed interfacial iron species are more active than those aged in aqueous media.
- The effect of pH on reactivity of iron-laden minerals differs with different substrates.

Practical Implications

- Peroxide-based ISCO applications may be enhanced by:
  - engineering site geochemistry for formation of surfaces with active interfacial Fe species
  - introduction of reactive colloids as catalysts into source zones or hot-spots for increased degradation efficiency

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Questions?