Structure and Reactivity of Nano-Particles Containing Zero-Valent Iron: Bridging the Gap Between Ex Situ Properties and In Situ Performance

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THE REACTION SPECIFICITY OF NANOPARTICLES IN SOLUTION

Application to the Reaction of Nanoparticulate Iron and Iron-Bimetallic Compounds with Chlorinated Hydrocarbons and Oxyanions

- Synthesis and characterization of Fe and Fe-Oxide nanoparticles
- Measurements solution and gas reactivity with Fe nanoparticles
- Vacuum based studies of supported Fe nanoparticles
- Models of particle structure and effects of structure on reactivity

Oregon Health & Science University: P. Tratnyek, J. Nurmi, V. Sarathy
University of Minnesota: L. Penn and M. Driessen
## Iron and Iron Oxides Studied

<table>
<thead>
<tr>
<th>Name</th>
<th>Source</th>
<th>Method</th>
<th>Particle Size (dia.)</th>
<th>BET Surface Area</th>
<th>Major Phase</th>
<th>Minor Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(^{H2})</td>
<td>Toda Americas, Inc.</td>
<td>High temp. reduction of oxides with H(_2)</td>
<td>70 nm</td>
<td>29 m(^2)/g</td>
<td>(\alpha)-Fe(^0)</td>
<td>Magnetite</td>
</tr>
<tr>
<td>Fe(^{BH})</td>
<td>W.-X. Zhang, Lehigh Univ.</td>
<td>Precip. w/ NaBH(_4)</td>
<td>10-100 nm</td>
<td>33.5 m(^2)/g</td>
<td>Fe(^0)</td>
<td>Goethite, Wustite</td>
</tr>
<tr>
<td>Fe(^{EL})</td>
<td>Fisher Scientific</td>
<td>Electrolytic</td>
<td>150 (\mu)m</td>
<td>0.1-1 m(^2)/g</td>
<td>99% Fe(^0)</td>
<td></td>
</tr>
<tr>
<td>Fe(_3)O(_4)</td>
<td>PNNL</td>
<td>Precip from FeSO(_4) w/ KOH</td>
<td>30-100 nm</td>
<td>4-24 m(^2)/g</td>
<td>Fe(_3)O(_4)</td>
<td></td>
</tr>
<tr>
<td>Fe(_2)O(_3)</td>
<td>Nanotek, Corp.</td>
<td>Physical Vapor Synthesis (PVS)</td>
<td>23 nm</td>
<td>50 m(^2)/g</td>
<td>(\gamma)-Fe(_2)O(_3)</td>
<td></td>
</tr>
</tbody>
</table>

Structure from TEM

Fe$^{\text{H}_2}$ (Toda)  Fe$^{\text{BH}}$ (Zhang)

Particle Size from TEM

Composition from XPS

Fe$^{H2}$ (Toda)  
Fe$^{BH}$ (Zhang)

## Summary of Structure/Composition

<table>
<thead>
<tr>
<th>Name</th>
<th>Sample History</th>
<th>Mean Particle Size from TEM (nm)</th>
<th>Shell Thickness (nm)</th>
<th>TEM Structure</th>
<th>XRD (Grain Size nm)</th>
<th>XPS</th>
<th>STXM</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Fe}^{\text{H}2} )</td>
<td>As-received</td>
<td>(~38 \text{ Fe}^0) (\geq 60) nm oxide plates</td>
<td>Fe-Oxide (~3.4)</td>
<td>“large” plates (oxide) and smaller Fe(^0) irregularly shaped particles with crystalline oxide shell</td>
<td>Fe(^0) (~30) oxide (~60)</td>
<td>Fe(^0)+Fe(^{+3})</td>
<td>Fe(^0) + oxide</td>
</tr>
<tr>
<td>( \text{Fe}^{\text{H}2} )</td>
<td>Flash-dried</td>
<td>(~44 \text{ Fe}^0)</td>
<td></td>
<td>As above with more large plates</td>
<td></td>
<td>Less Fe(^0)</td>
<td></td>
</tr>
<tr>
<td>( \text{Fe}^{\text{BH}} )</td>
<td>As-received</td>
<td>(~59) (20-100)</td>
<td>(~2.3)</td>
<td>Three levels of structure: i) small crystallites (&lt;1.5 nm), ii) 20-100 nm spherical aggregates with an amorphous coating, and iii) chains of 20-100 nm particles</td>
<td>Mostly Fe(^0) (&lt;1.5)</td>
<td>Fe(^0)+Fe(^{+3}) + B and Na</td>
<td>Mostly Fe(^0)</td>
</tr>
<tr>
<td>( \text{Fe}^{\text{BH}} )</td>
<td>Flash-dried</td>
<td>(~67) (20-100)</td>
<td>(~3.2)</td>
<td>As above with thicker coating</td>
<td></td>
<td>Less Fe(^0) + B and Na</td>
<td></td>
</tr>
</tbody>
</table>

Solution Chemistry—Methods

Electrochemical Cell
- Flash drying
- Packed powder electrode
  • Fabrication
  • Validation
- Data presentation
- Electrochemical model

Batch Reactor
- Flash drying
- Pre-exposure period
- Buffer selection
- Ox/Fe ratio
- Mixing rate
- Kinetic model
Protocol for Batch Experiments

1. Fe\textsuperscript{0} → Adding deox. DI water
2. Time = t\textsubscript{0}
3. Spiking
4. Mixing
5. Sampling
   Time = t\textsubscript{1}, t\textsubscript{2}, t\textsubscript{3}...
6. Analysis
   - HPLC
   - GC/ECD
   - UV/VIS

- Flash drying
- Pre-exposure period
- Buffer selection
- Ox/Fe ratio
- Mixing rate
- Kinetic model

Batch Experiments with CCl₄

CCl₄ (CT) + Fe(0) → CHCl₃ (CF) + Unk + Cl⁻ + Fe(II)

1. pH:
   - 7.3, 8.4, 9.0
2. Buffers:
   - Borate
   - EPPS
3. Type:
   - Fisher Electrolytic
   - Nano (Zhang, Toda)
4. Pretreatment:
   - Flash drying

$k_{sa}$ vs. $k_m$ plots

From:

$$k_M = k_{SA} a_s$$

It follows that:

$$\log k_{SA} = \log k_M - \log a_s$$

Plotting $\log k_{SA}$ vs. $\log k_M$ gives contours of constant $a_s$.

Cimitan et al. (2005) J. Med. Chem. ASAP

Effect of Surface Area—Our Data Only

- $k_M$ (Nano > Micro)
- $k_M$ (Fe$^{BH}$ ? Fe$^{H2}$)
- $a_s$ (TEM < BET)
- $k_{SA}$ (Nano ≈ Micro)
- $k_{SA}$ (Nano < Micro)

... Uncertainties in $a_s$ are important

... No “intrinsic” nano-size effect

Nurmi et al. (2005) ES&T 39: 1221-1230
Chloroform Yield

Nurmi et al. (2005) ES&T 39: 1221-1230. Sarathy et al. (in prep.)
Application to Site Remediation

- 200 W Area of Hanford
  - 750,000 kg spilled
  - Vadose and GW zones
  - 11 km² plume
  - up to 7000 ug/L

- ITRD TAG since 1999
  - Completed PITT
  - Reviewed Natural Attenuation
  - Modeled Reactive-Transport
  - Reviewed Treatment Options

- Status
  - Active intervention probably needed soon
  - “Critical” Need for Remediation Technology (TIP No. 0006)
Summary:
- Nano Fe\(^0\) has a shell of Fe\(_3\)O\(_4\), other oxides, and impurities.
- Specific surface area is an important and challenging property.
- Nano Fe\(^0\) gives greater \(k_m\), but not necessarily greater \(k_{SA}\).
- Some nano Fe\(^0\) gives more favorable products (low \(Y_{CF}\)).
- Low \(Y_{CF}\) and injectability offer prospects for remediation.

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