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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DOE BES/EMSP Project

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 µm</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$^{H_2}$ (Toda)

Fe$^{BH}$ (Zhang)

Particle Size from TEM

Composition from XPS

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

<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>FeH₂ As-received</td>
<td>~38 Fe₀</td>
<td>≥60 nm oxide plates</td>
<td>Fe-Oxide</td>
<td>“large” plates (oxide) and smaller Fe₀ irregularly shaped particles with crystalline oxide shell</td>
<td>Fe₀ (~30) oxide (~60)</td>
<td>Fe₀+Fe⁺³</td>
<td>Fe₀ + oxide</td>
</tr>
<tr>
<td>FeH₂ Flash-dried</td>
<td>~44 Fe₀</td>
<td></td>
<td></td>
<td>As above with more large plates</td>
<td></td>
<td>Less Fe₀</td>
<td></td>
</tr>
<tr>
<td>FeBH As-received</td>
<td>~59 (20-100)</td>
<td>~2.3</td>
<td></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 Fe₀ (&lt;1.5)</td>
<td>Fe₀+Fe⁺³  + B and Na</td>
<td>Mostly Fe₀</td>
</tr>
<tr>
<td>FeBH Flash-dried</td>
<td>~67 (20-100)</td>
<td>~3.2</td>
<td></td>
<td>As above with thicker coating</td>
<td></td>
<td>Less Fe₀ + 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

- Adding deox. DI water
- Spiking
  - Time = \( t_0 \)
- Mixing
- Sampling
  - Time = \( t_1, t_2, t_3 \ldots \)
- 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 Fe⁰ has a shell of Fe₃O₄, other oxides, and impurities.
• Specific surface area is an important and challenging property.
• Nano Fe⁰ gives greater $k_m$, but not necessarily greater $k_{SA}$.
• Some nano Fe⁰ gives more favorable products (low $Y_{CF}$).
• Low $Y_{CF}$ and injectability offer prospects for remediation.

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