Nanoparticle preparation

**Ball Milling Method**

Physically grind micron size feedstock down to the nanoscale regime using planetary ball milling with WC balls

Particles are coated with various ligands/capping agents to promote suspension in a variety of fuels and/or to protect them from unwanted oxidation

**Particle Characterization**

Chemical composition: XPS, FTIR, TGA

Particle Size: DLS, SEM, TEM
~50 nm particles separated by settling big particles

SEM image of <100 nm particles

Boron Nanoparticle Size distribution
Unoxidized Boron Nanoparticles

- Elemental B1s peak observed at ~188 eV, B$^{3+}$ at ~193 eV
- Nanosized boron immediately formed oxide upon exposure to air as the XPS samples were prepared.
- Oleic acid prevented oxidation of the fresh boron surfaces formed during the milling process.
CeO$_2$ catalyst

Boron core

Oleic Acid

XPS suggests the presence of a low binding energy boride species (Ce$_x$B$_y$)

CeO$_2$ exists as patch of island on a boron nanoparticle

Table 3. EDX Results Boron Milled with Ceria

<table>
<thead>
<tr>
<th>Element</th>
<th>area A atomic %</th>
<th>area A weight %</th>
<th>area B atomic %</th>
<th>area B weight %</th>
<th>area C atomic %</th>
<th>area C weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>27.8</td>
<td>23.0</td>
<td>30.4</td>
<td>26.1</td>
<td>37.4</td>
<td>33.0</td>
</tr>
<tr>
<td>Ce</td>
<td>0.2</td>
<td>1.8</td>
<td>0.2</td>
<td>2.1</td>
<td>0.0</td>
<td>0.3</td>
</tr>
<tr>
<td>O</td>
<td>4.8</td>
<td>5.8</td>
<td>2.5</td>
<td>3.2</td>
<td>1.1</td>
<td>1.5</td>
</tr>
<tr>
<td>C</td>
<td>65.4</td>
<td>60.3</td>
<td>65.7</td>
<td>62.7</td>
<td>60.2</td>
<td>59.0</td>
</tr>
<tr>
<td>Cu</td>
<td>1.9</td>
<td>9.0</td>
<td>1.2</td>
<td>5.9</td>
<td>1.2</td>
<td>6.2</td>
</tr>
</tbody>
</table>

STEM

XPS
Boron Nanoparticles with Polar Surfactants

Boron Powder + ⅛” WC balls
80:1 BPR

3 hrs dry milling

+ Surfactant (Ionic Liquid, Et₂NH, Et₃N, Ethanolamine)
~10% total volume

3 hrs milling

+ Solvent (Ethanol)

18 hrs milling

Samples washed with EtOH to remove excess surfactant

4 x 250 ml capacity
Method of Preparation: Ball Milling

Solubility /Dispersibility in Ethanol (polar solvent)

Characterize size of particles using:
SEM, DLS

Characterize chemical composition using:
EDX-STEM, XPS, FTIR
Boron-Ionic Liquid Particle Size

SEM Image of Boron Nanoparticles on TEM Grid

DLS Measurement of Particle Size

Size weighted

- 79 nm (41%)
- 209 nm (59%)

Number weighted

- 78 nm (93%)
- 201 nm (7%)
Boron, Nitrogen Species

**B1s Region** XPS of Boron milled with Ionic Liquid in EtOH

- \( B^0 = 188 \text{ eV} \)
- \( B-N = 191 \text{ eV} \)

**N1s Region** XPS of Boron milled with Ionic Liquid in EtOH

- \( N-B = 398 \text{ eV} \)
- \( 400 \text{ eV} \) Organic N?
Boron, Nitrogen Species

\[ B - N = 191 \text{ eV} \]

\[ B_0 - N = 188 \text{ eV} \]

\[ N - B = 398 \text{ eV} \]

N1s Region XPS of Boron milled with Ionic Liquid in EtOH

400 eV

Organic N?
Diethylamine Surfactants

- Size Weighted
  - 86 nm (57%)
  - 189 nm (43%)

- Number Weighted
  - 81 nm (93%)
  - 178 nm (7%)
**B1s Region XPS of Boron milled with Et₂NH in EtOH**

- $B^0 = 188$ eV
- $B-N = 192$ eV
- Light sputter
- Unsputtered

**N1s Region XPS of Boron milled with Et₂NH in EtOH**

- $N-B = 398$ eV
- 400 eV
- Organic N?

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**Note:**

- The graphs show the XPS spectra for the B1s and N1s regions of Boron milled with Et₂NH in EtOH.
- The energy levels and peak positions are indicated for both the light sputter and unsputtered conditions.
Triethylamine Surfactants

![Image of nanoscale structures with labeled sizes]

- **Size Weighted**
  - 59 nm (59%)
  - 176 nm (41%)

- **Number Weighted**
  - 57 nm (97%)
  - 165 nm (3%)

[Bar charts showing size and number distributions]
B\text{1s} Region XPS of Boron milled with Et\textsubscript{3}N in EtOH

N\text{1s} Region XPS of Boron milled with Et\textsubscript{3}N in EtOH
Combustion testing in a turbulent flame calorimeter

~3% Boron Loaded Ethanol vs. Pure Ethanol

Boron loaded Etoh $\Delta T = 27.45 ^\circ C$
Temperature Increase = 1.18 $^\circ C$
A 4.49% increase

Increase is consistent with complete combustion of the boron. Burner has difficulties with higher loadings.
Boron nanoparticles functionalized with ionic liquid

Dynamic Light Scattering (DLS) of particles suspended in EtOH
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