Novel Low-Cost and Environmentally-Friendly Synthesis of Core-Shell Structured Micro-Particles for Fossil Energy Applications

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OUTLINE

• Introduction
• Background
• Methodology
• Results
• Conclusion
Introduction

- Core-shell structured particles
  - Energy, Catalysis, Pharmaceutical Science and Physics
  - Nano-and biomaterial applications
- Synthetic approach
  - Coating Process – Application of shell material onto the core
- Core-shell structure exhibits high surface area and catalytic-like properties

Simplified illustration of a typical core-shell structured particle
Proposed Synthetic Methods

• **Metal Organic Chemical Vapor Deposition (AP-MOCVD)**
  • Utilize a low cost hot walled reactor as an alternate route for the preparation of core-shell structures.
  • Metal organic precursors

• **Ionic Diffusion via Redox Cycles**
  • Utilize the movement of atoms during redox, forming a core-shell like structure
  • In depth testing of different metal oxides particles under redox environment

Potential Significance

• Cost effective method
• Improved catalytic activity
• Potential application in Chemical looping combustion/gasification, and sorbent-based fossil fuel
Metal Organic Chemical Vapor Deposition (AP-MOCVD)

Schematic illustration of a horizontal CVD hot-wall reactor

- Carrier gas
- Precursor
- Oven
- Glass rod
- Exhause
- Nitrogen line
- Heating tape
- Quartz tube
- Heat regulator
- Tube furnace
- Hood
- HW-Reactor
Physicochemical reactions processes in the CVD Reactor: STEP (1&2)

Chemical Vapor Deposition - Step 1
Vaporization and Transport of Precursor Molecules into Reactor

Chemical Vapor Deposition - Step 2
Diffusion of Precursor Molecules to the Surface
Chemical Vapor Deposition - Step 3

Adsorption of Precursor Molecules to Surface

Chemical Vapor Deposition - Step 4

Decomposition of Precursor and Incorporation into Solid Films
Chemical Vapor Deposition - Step 5

Recombination of Molecular Byproducts and Desorption into Gas Phase
Chemical Looping Technology
Catalytic process that converts fossil fuels into energy and CO₂ without extra energy consumption

Chemical looping combustion – gaseous fuel. Solid fuels in CLC with steam as gasification agent.

Proceedings from AIChE Meeting 2010, Salt Lake City, Utah, U.S.A., November 7-12, 2010

Chemical Reactions

\[(2n+m)\text{Me}_x\text{O}_y + C_n\text{H}_{2n} \rightarrow (2n + m)\text{Me}_x\text{O}_{y-1} + n\text{CO}_2 + m\text{H}_2\text{O}\]  \((1)\)

\[(n + m)\text{Me}_x\text{O}_y + n\text{CO} + m\text{H}_2 \rightarrow (n + m)\text{Me}_x\text{O}_{y-1} + n\text{CO}_2 + m\text{H}_2\text{O}\]  \((2)\)

\[2\text{Me}_x\text{O}_{y-1} + \text{O}_2 \rightarrow 2\text{Me}_x\text{O}_y\]  \((3)\)

\[(2n + 1)\text{H}_2 + n\text{CO} \rightarrow C_n\text{H}_{2n+2} + n\text{H}_2\text{O}\]  \((4)\)
Statement of Project Objectives

• Synthesize stronger and more chemically reactive particles for use in fossil energy applications

• Synthesize and characterize Fe$_2$O$_3$-shell/Al$_2$O$_3$-core micro-particles prepared via the cyclic ionic diffusion and AP-MOCVD methods.

• Gain control of shell thickness

• Comparison of morphology, mechanical strength, and reactivity of synthesized core-shell structured particles synthesized via vapor deposition and ionic diffusion
Platform of β-ketoiminate ligand for the synthesis of the precursor

Tunable β-ketoiminate ligand backbone

TGA- bench mark thermogram for precursor synthesis
MOCVD-Precursor Requirements

- Volatile and thermally stable
- Inexpensive and simple to synthesize
- No premature decomposition of the precursor prior to reaching the substrate

Advantages of AP–MOCVD

- Films with uniform thickness under mild conditions (<700°C)
- High quality thin films with less impurities
- High growth rate
- Highly crystalline films
Synthesis and Characterization of β- Ketoimines

\[
\begin{align*}
\text{β-diketone} & \quad + \quad \text{R’-NH}_2 \\
& \quad \xrightarrow{\text{reflux 1hr}} \quad \text{Diethyl ether} \\
& \quad \quad \xrightarrow{\text{}} \quad \text{β-Ketoimine} \\
& \quad + \quad \text{H}_2\text{O}
\end{align*}
\]
Synthesized Free ligands

$R' =$
1. Isopropyl
2. Isobutyl
3. Butyl
4. Cyclopentyl
5. Cyclohexyl
6. Methoxypropyl
7. t-butyl
8. Propyl

$R =$
1. $\text{CH}_2\text{CH}_3$
2. $\text{CH}_3$
Synthesis of Fe(III) Complex

R' R'' R'''

1. KOH/EtOH
2. FeCl₃/H₂O

R' R'' R'''
17 CH₃ CH₃CH₂O (CH₃)₂CHN
18 CH₃ CH₃O (CH₃)₂CHN
19 CH₃ CH₃O CH₃CH₂CH₂N
20 CH₃ CH₃CH₂O (CH₃)₂CHC H₂N
27 CH₃ CH₃CH₂O CHN
30 CH₃ CH₃O CH₃OC H₂CH₂CH₂N
31 CH₃ CH₃ O
TGA- thermogram of complex 18
exhibit less volatility and stability

Structure of complex 18
Tris(methyl-3-(isopropyl)amino-2-butenoato)iron(III)

TGA: of complex of complex 18
TGA- thermogram of complex 31 exhibit higher volatility and minimal decomposition

Structure of complex 31
Tris(2,4-pentanedionato)iron(III)

TGA: of recrystallized iron complex 31

Fe(acac)₃
TGA- thermogram of Iron (III) oxide precursor 33 exhibit higher volatility and minimal decomposition.

TGA: of recrystallized iron complex 33

Structure of complex 33
Tris(1,2-diphenylpropane-1,2-dionato)iron(III)
Coating mode of Particle
  • Gas-solid contact in the CVD Reactor

Rotary Bed

Evaluation of the synthesized Iron(III)oxide β-diketonate MOCVD precursor
Evaluated TGA thermogram of Iron (III)oxide precursor

Complexes 31 and 33 β-diketonate exhibit higher volatility and stability

TGA: of complex 31

TGA: of complex 33
Determination of Source and Decomposition Temperatures

AP-MOCVD hot wall reactor with deposited iron oxide at 220°C

Temperature distribution profile in the Hot-Wall Reactor
(Gas flow changes the temp. profile slightly)

Isothermal zone

Mushin E.A, chemical vap. Deposition 11.07.2007 p(23)
SEM micrograph of Fe$_2$O$_3$ coated Al$_2$O$_3$ particle at 220°C

(a) 50 x

(b) 200 x

(c) Fe$_2$O$_3$ coated Al$_2$O$_3$ at substrate temperature of 220°C.

(d) Fresh uncoated Al$_2$O$_3$
Elemental composition analysis of $\text{Fe}_2\text{O}_3$ coated $\text{Al}_2\text{O}_3$ particle determined by EDS

(a) Before Annealing

<table>
<thead>
<tr>
<th>Element</th>
<th>Relative atomic Percentage</th>
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<tbody>
<tr>
<td>Aluminum (Al)</td>
<td>31</td>
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<tr>
<td>Oxygen (O)</td>
<td>65</td>
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<tr>
<td>Iron (Fe)</td>
<td>3</td>
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</table>

(b) After Annealing at 300°C for 30 minutes

<table>
<thead>
<tr>
<th>Element</th>
<th>Relative atomic Percentage</th>
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<tbody>
<tr>
<td>Aluminum (Al)</td>
<td>42</td>
</tr>
<tr>
<td>Oxygen (O)</td>
<td>52</td>
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<tr>
<td>Iron (Fe)</td>
<td>6</td>
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MOCVD Growth Optimization and EDS Analysis

Four CVD growth cycles with deposition temperature 220° – 360°C at 20°C interval
annealed at 500°C for 30 minutes

<table>
<thead>
<tr>
<th>Sample</th>
<th>Iron</th>
<th>Oxygen</th>
<th>Aluminum</th>
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<tbody>
<tr>
<td>P(2)</td>
<td>1.91</td>
<td>58.41</td>
<td>36.64</td>
</tr>
<tr>
<td>P(3)</td>
<td>0.80</td>
<td>53.09</td>
<td>40.79</td>
</tr>
<tr>
<td>P(5)</td>
<td>3.13</td>
<td>63.71</td>
<td>29.71</td>
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</table>
Synthesized Iron(III)oxide Precursor 45
Tris(2,2,6,6-tetramethyl -3,5-heptanedionato)iron(III)

Molecular structure of Fe(thmd)$_3$
Iron(III) Complex 45

TGA: after recrystallization in acetone/ water solution
Elemental composition of $\text{Fe}_2\text{O}_3$ coated $\text{Al}_2\text{O}_3$ as determined by EDS after annealing at 500°C for 30 minutes

<table>
<thead>
<tr>
<th>Sample</th>
<th>Deposition temp. °C</th>
<th># cycles</th>
<th>Iron</th>
<th>Oxygen</th>
<th>Aluminum</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1</td>
<td>240</td>
<td>4</td>
<td>1.98</td>
<td>55.25</td>
<td>41.92</td>
</tr>
<tr>
<td>T2</td>
<td>280</td>
<td>4</td>
<td>14.61</td>
<td>57.41</td>
<td>27.98</td>
</tr>
<tr>
<td>T3</td>
<td>300</td>
<td>4</td>
<td>2.51</td>
<td>60.39</td>
<td>37.11</td>
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<td>T4</td>
<td>320</td>
<td>4</td>
<td>9.71</td>
<td>52.51</td>
<td>37.78</td>
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<td>T5</td>
<td>340</td>
<td>4</td>
<td>1.62</td>
<td>67.99</td>
<td>30.39</td>
</tr>
<tr>
<td>T03</td>
<td>360</td>
<td>10</td>
<td>75.53</td>
<td>18.0</td>
<td>6.47</td>
</tr>
</tbody>
</table>
SEM micrograph of Core-Shell particle derived from sample T03 after 10 CVD cycles

a) x10,000

b) x20,000

c) x30,000

d) x50,000
EDS Spectrum of Sample T03 after 10 CVD Cycles
Future work

• Increasing the number of CVD cycles utilizing the Fe(thmd)$_3$ precursor in order to form a high quality iron oxide shell.

• The synthesized particles will be evaluated for their catalytic activity.
Shell-Formation Mechanism

Ionic Diffusion via Cyclic Redox Cycles
Experimental Method

In Thermo-gravimetric Analyzer (TGA)

Reduction
- H2 balanced with N2

flushing
- Nitrogen

Oxidation
- Air

Complete Reduction and Oxidation during cyclic reaction at 900 Celsius. Dashed line represent temperature. Red double arrow represents reduction and blue double arrow represent oxidation.
Parametric Study

Particle Size
- 2 mm
- 0.35 mm

Number of cycles
- 40 cycles
- 100 cycles

Percent iron loading balanced with aluminum oxide
- 40% Iron Oxide
- 20% Iron Oxide

However, the iron-rich shells formed were too thin to be distinguished between different micro-particles. A better method is needed.
Improving Ionic Diffusion

- Reducing gaseous oxygen concentration during oxidation
  - Maintain reduced iron gradient in the particle and prevent iron from being oxidized before diffusion toward the surface

- Increasing nitrogen flushing time
  - Allowing more time for iron to diffuse per redox cycle before being oxidized
SEM and EDAX Analysis on a fractured micro-particle with longer flushing time

Distinguishable phases observed with SEM at the edge of the fractured micro-particle.
Summary and Future Work

- An improved method was developed to encourage iron diffusion toward the surface.

- SEM and EDAX spot analysis revealed observable phase separation on micro-particles with longer flushing time.

- Effect of lowering oxygen concentration during oxidation will be studied.
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