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

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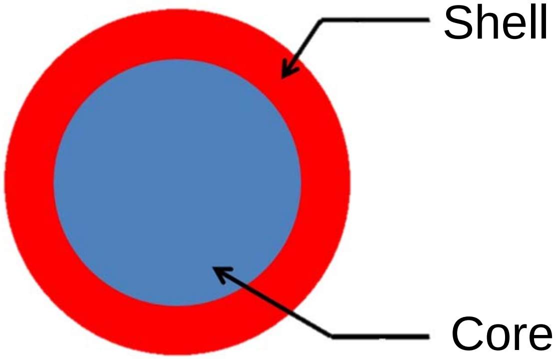
Background

- Core-shell structure exhibits high surface area and catalytic-like properties



- Conventional coating techniques for core-shell particles require both high capital and operating cost
- Some coating techniques involve toxic solvent.

Proposed Synthetic Methods

- Metal Organic Chemical Vapor Deposition
  - Utilize a low cost hot walled reactor as an alternate route for the preparation of core-shell structures.
- Ionic Diffusion via Redox Cycles
  - Utilize the movement of atoms during redox, forming a core-shell like structure
  - OSU has rich experience with particle development for chemical looping system
    - In depth testing of different metal oxides particles under redox environment

Potential Significance

- Reduce the cost of synthesis
- Improve the performance of catalytic fossil fuel conversion, chemical looping combustion/gasification and sorbent-based fossil fuel applications
- Environmental friendly since no solvent is required for ionic diffusion

Chemical Looping

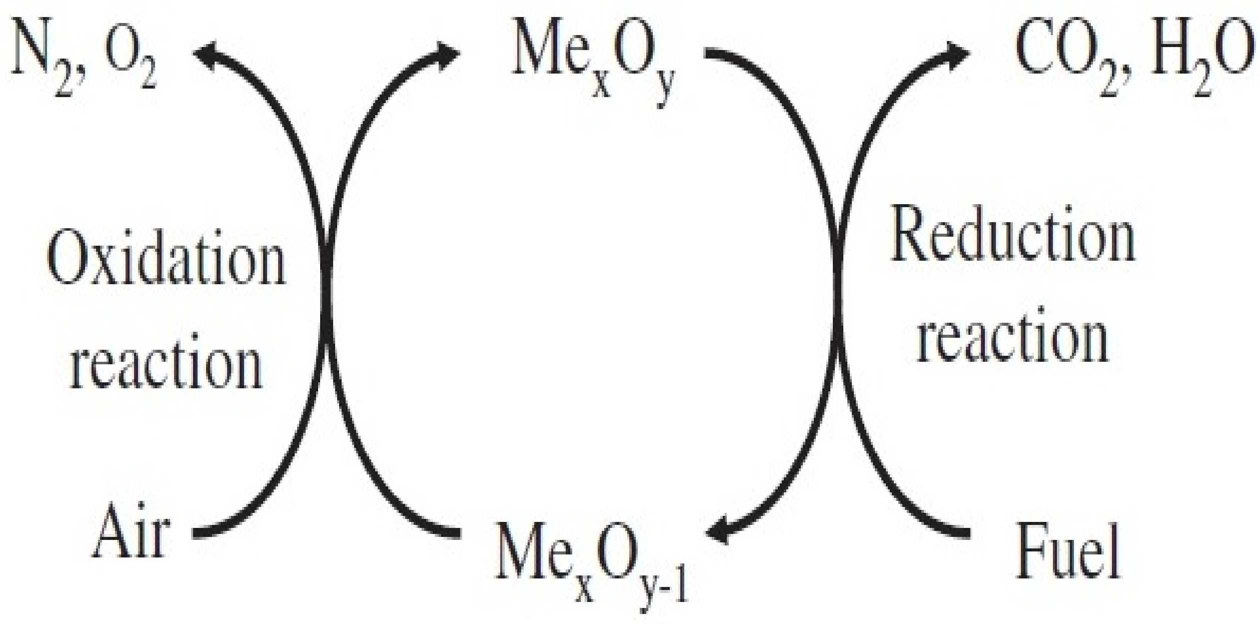


Fig. 1. General scheme of a Chemical-Looping Combustion system for gaseous fuels.

Statement of Project Objectives

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

- Synthesize and characterize Fe_2O_3-shell/Al_2O_3-core micro-particles prepared via the cyclic ionic diffusion and 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

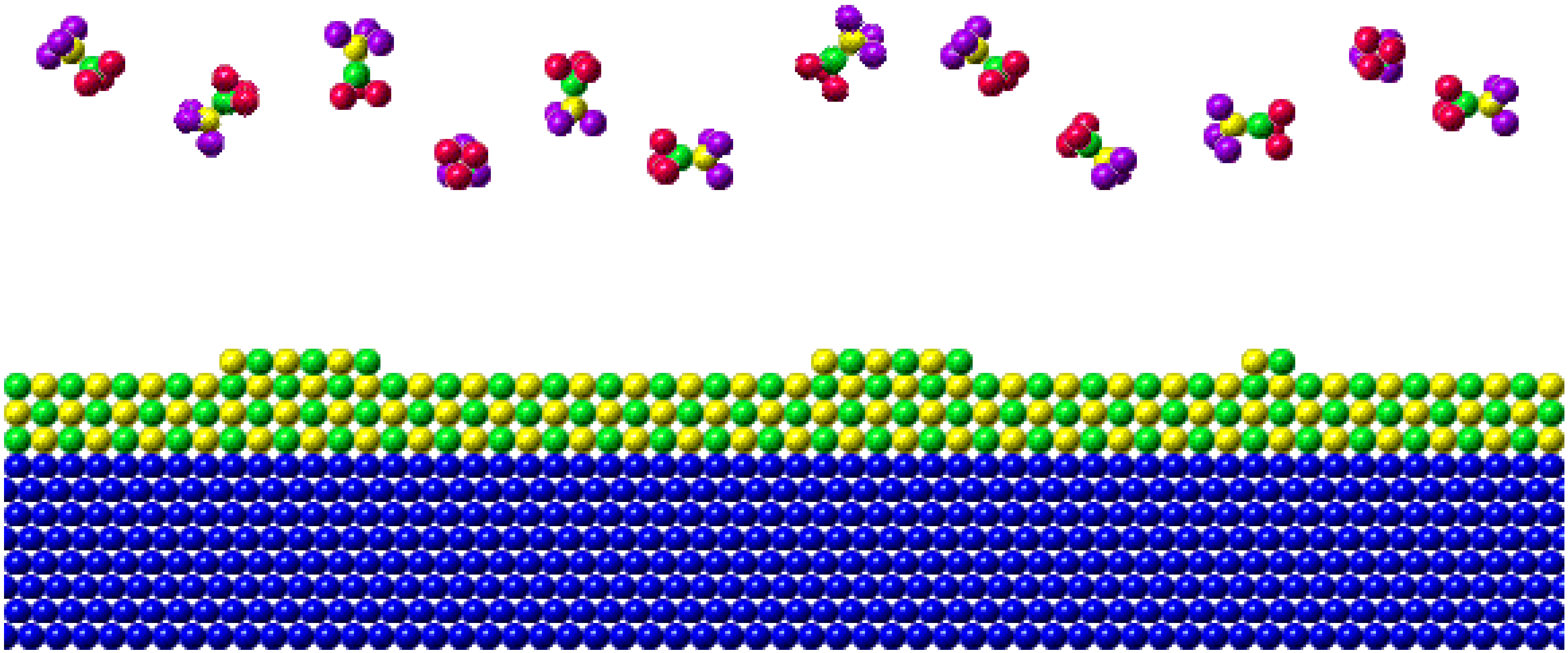
- Demonstrate the applicability of proposed method by preparing and test a CaO-core/Fe_2O_3-shell particle

Metal-Organic Chemical Vapor Deposition (MOCVD)

Horizontal hot-wall CVD reactor

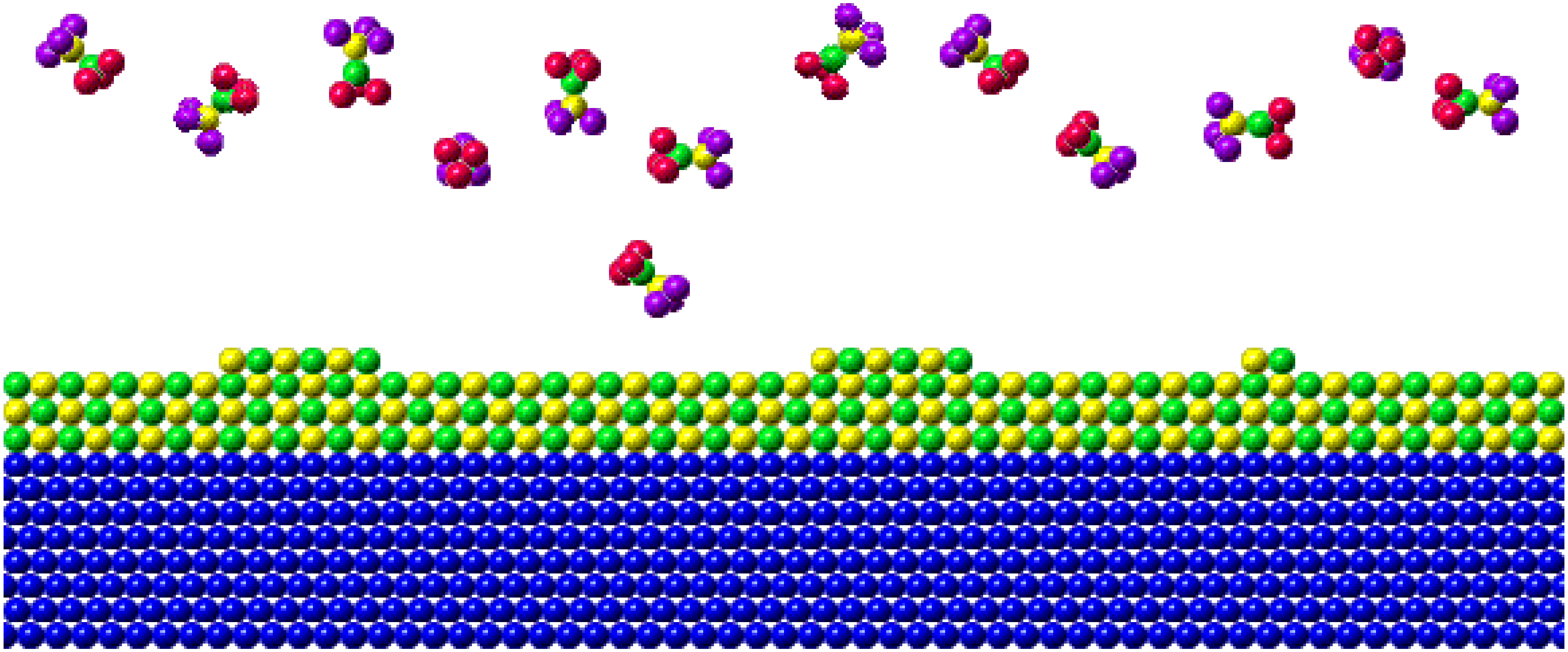
Chemical Vapor Deposition - Step 1

Vaporization and Transport of Precursor Molecules into Reactor



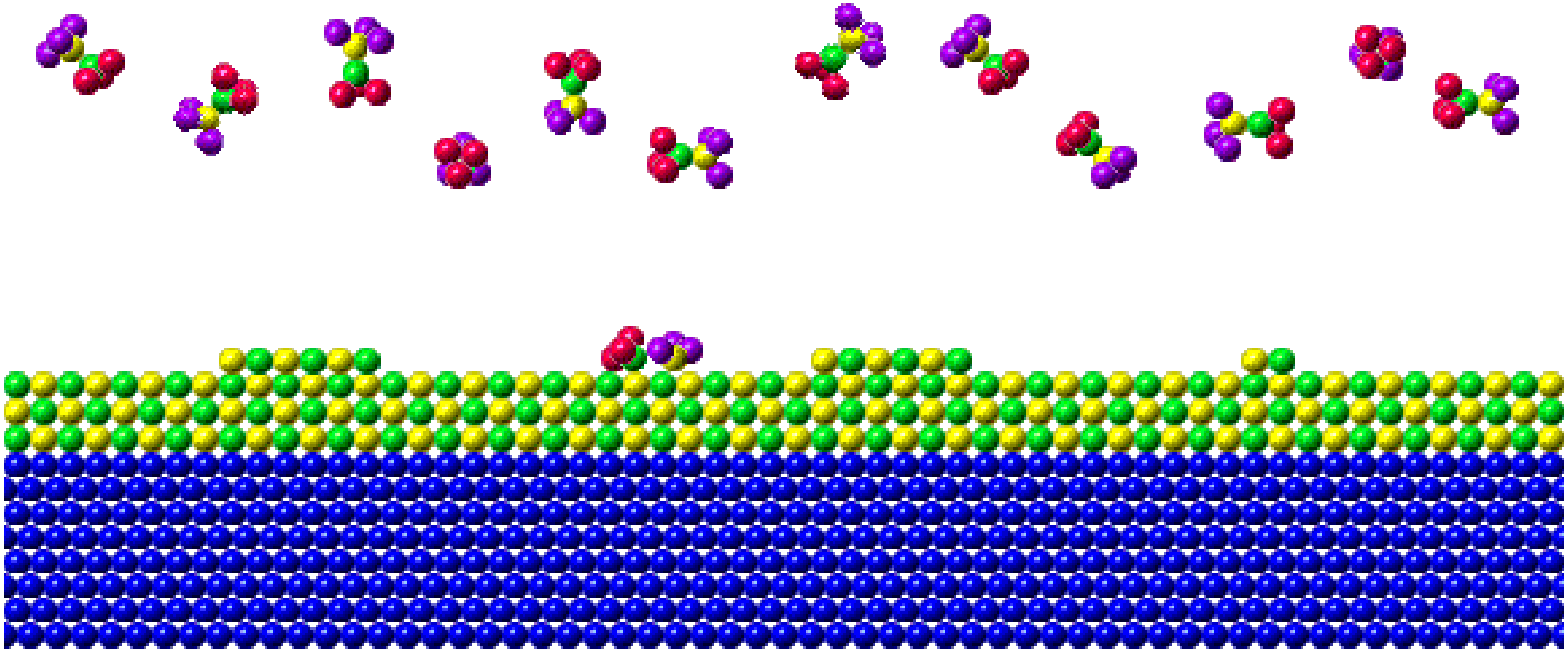
Chemical Vapor Deposition - Step 2

Diffusion of Precursor Molecules to the Surface



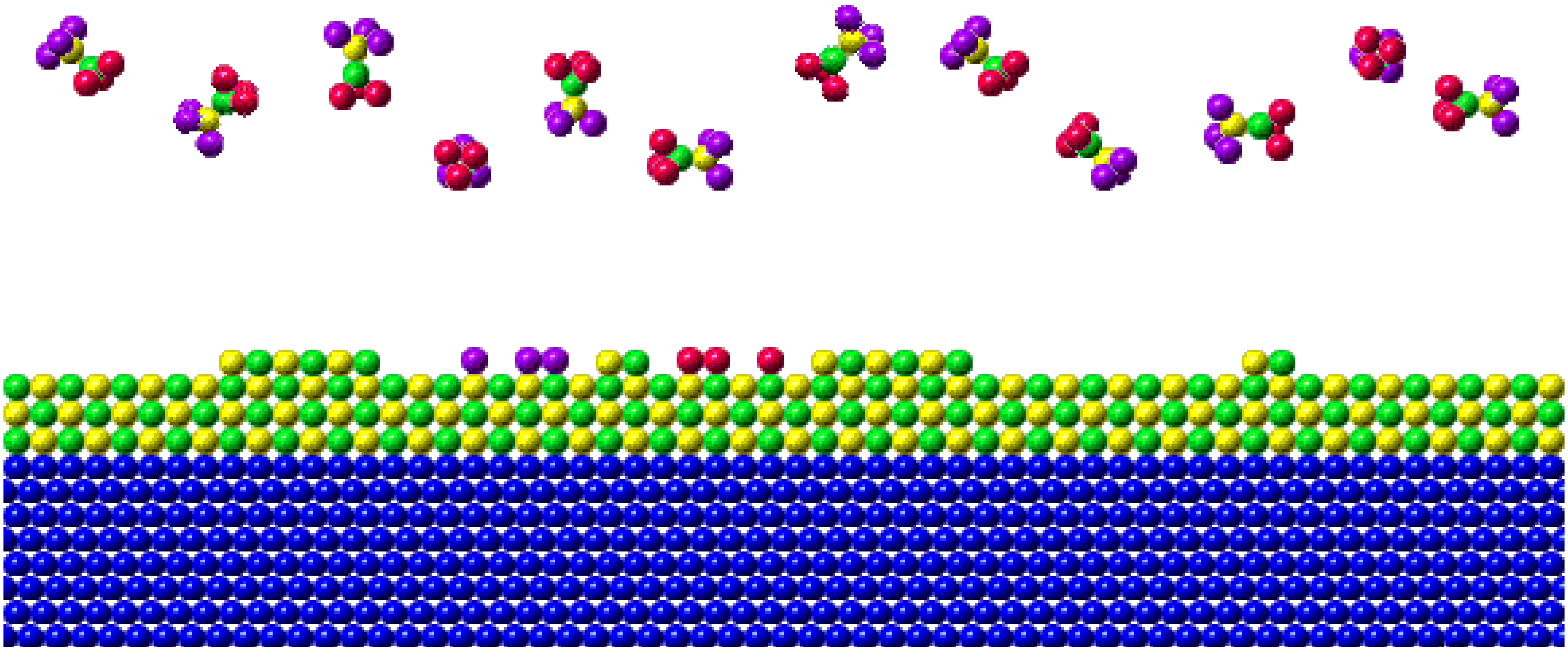
Chemical Vapor Deposition - Step 3

Adsorption of Precursor Molecules to Surface



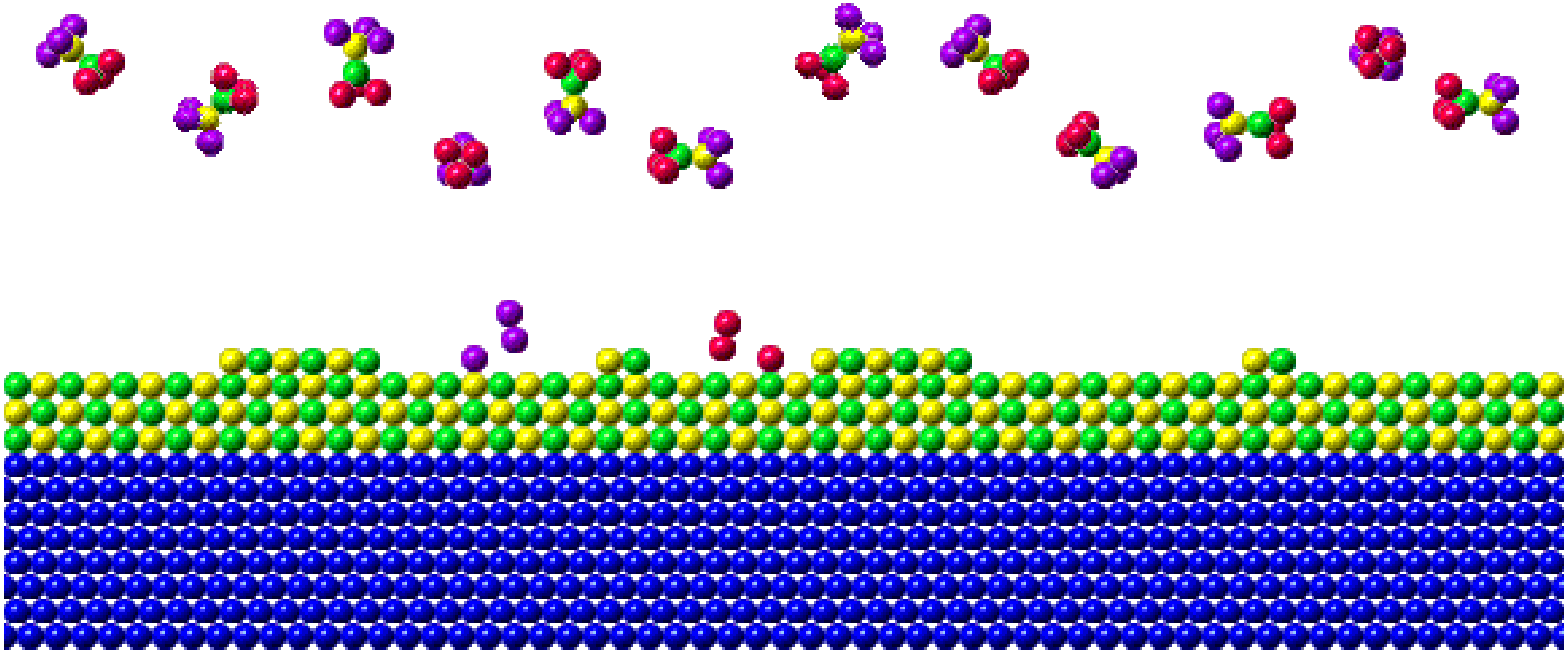
Chemical Vapor Deposition - Step 4

Decomposition of Precursor and Incorporation into Solid Films

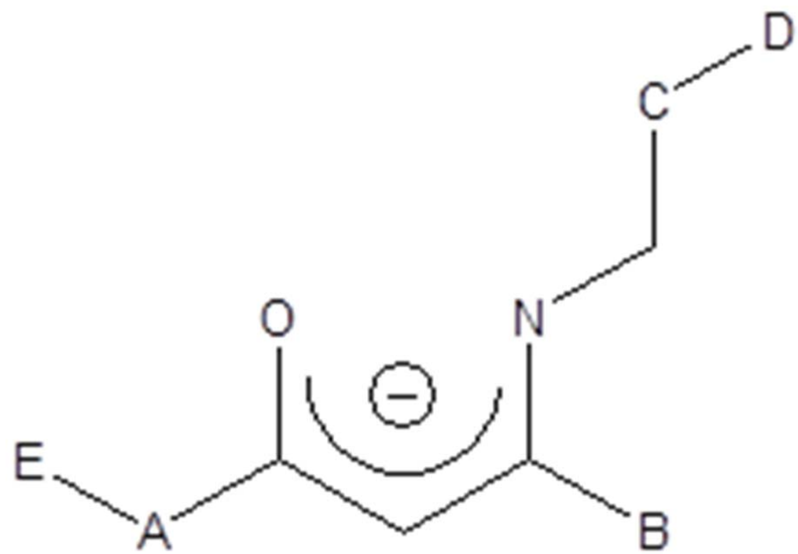


Chemical Vapor Deposition - Step 5

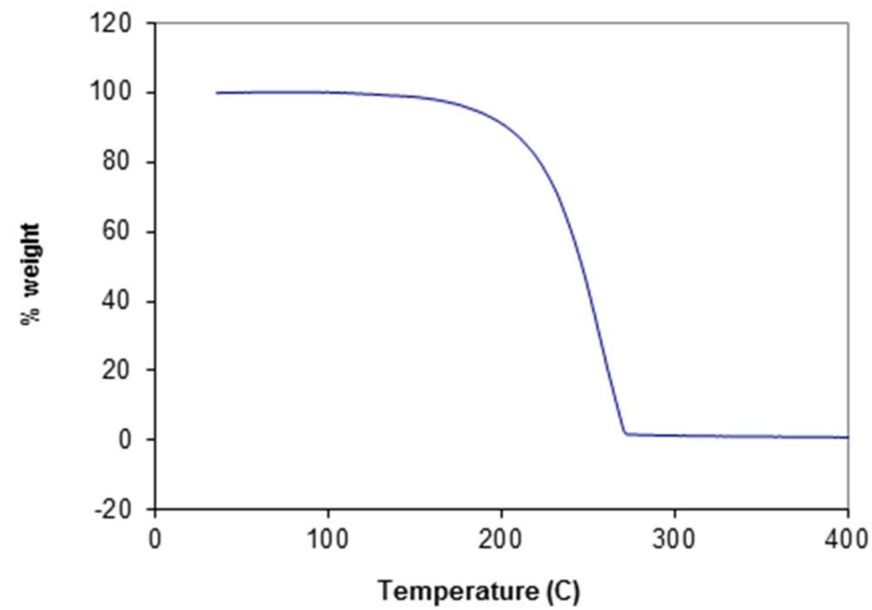
Recombination of Molecular Byproducts and Desorption into Gas Phase



MOCVD



Tunable β-ketoiminate ligand backbone



TGA Analysis of a MOCVD Precursor

Advantages of MOCVD

- Films with uniform thickness under mild conditions (<700°C)

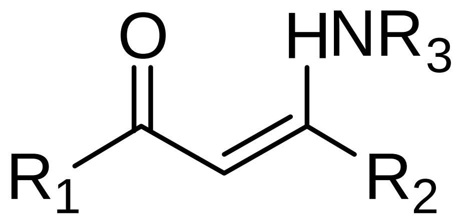
- High quality thin films with less impurities

- High growth rate

- Highly crystalline films

MOCVD
Precursor Requirements

- ❑ Volatile and thermally stable
- ❑ Produce uniform and reproducible coatings
- ❑ Decompose to afford high purity material
- ❑ No premature decomposition of the precursor prior to reaching the substrate

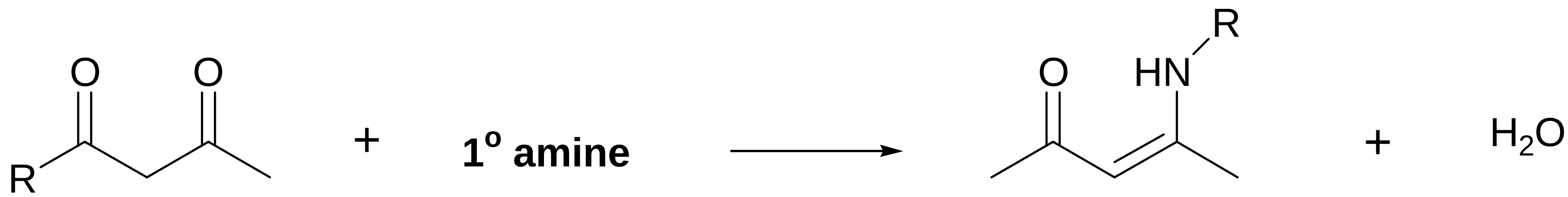


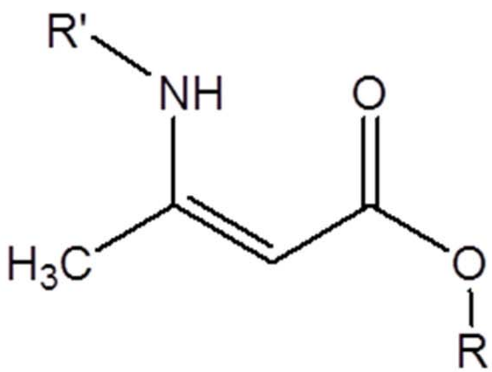
β-Ketoimines

More attractive than their β–diketonate analogs:

- Volatile and thermally stable
- Ability to tune the volatility and thermal stability by varying the R groups

β-Ketoimine Synthesis





$R = CH_2CH_3$

R'

5 - isopropyl

6 - isobutyl

7 - t-butyl

8 - sec-butyl

9 - methoxypropyl

$R = CH_3$

R'

10 - cyclopentyl

11 - cyclohexyl

12 - propyl

13 - butyl

14 - isopropyl

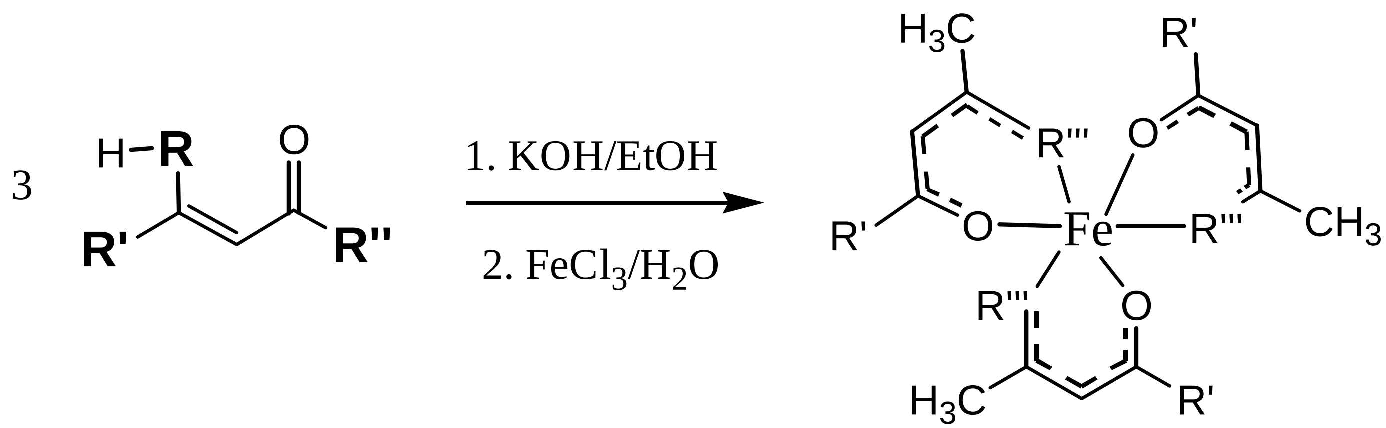
15 - isobutyl

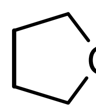
16 - t-butyl

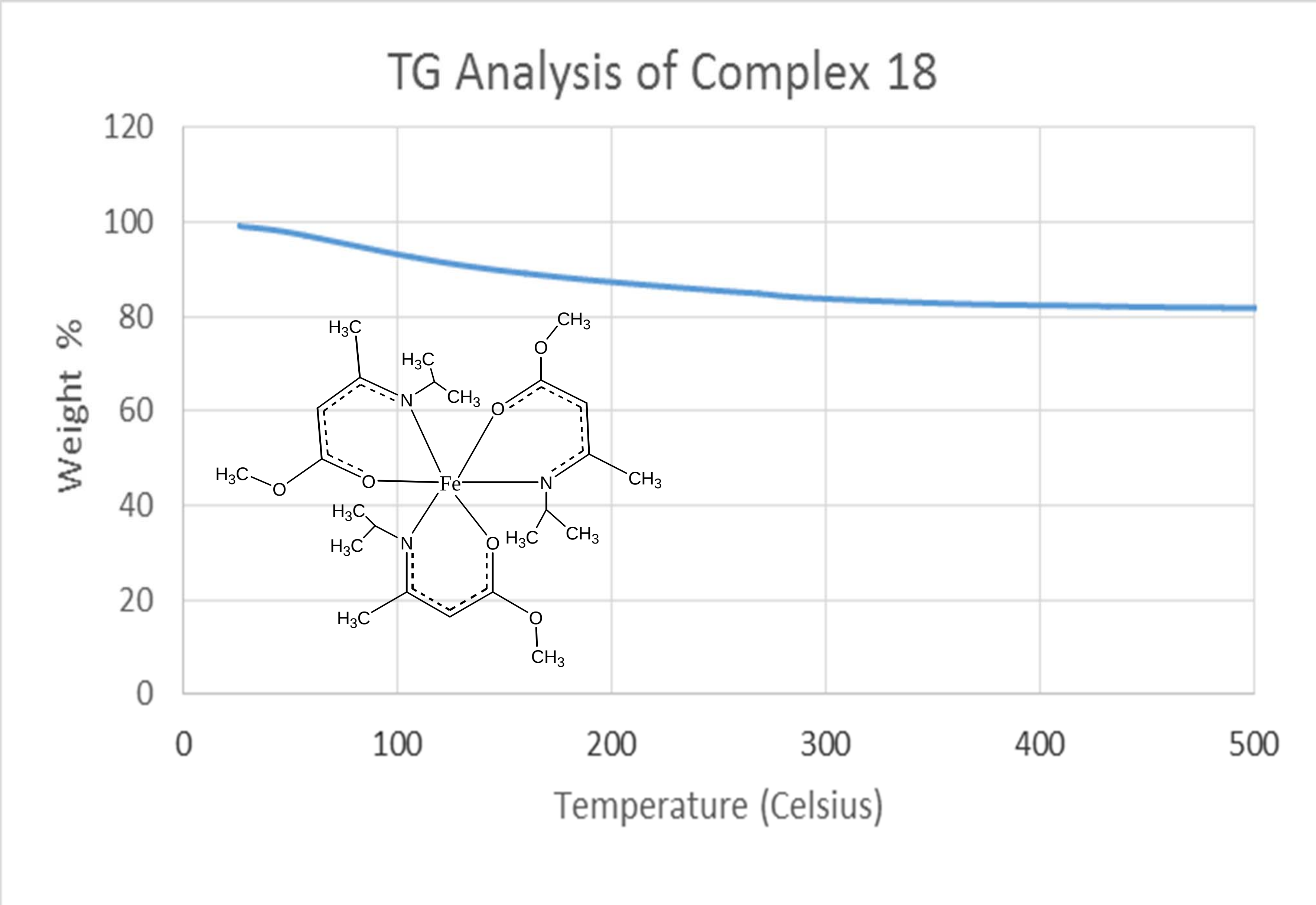
17 - sec-butyl

18 - methoxypropyl

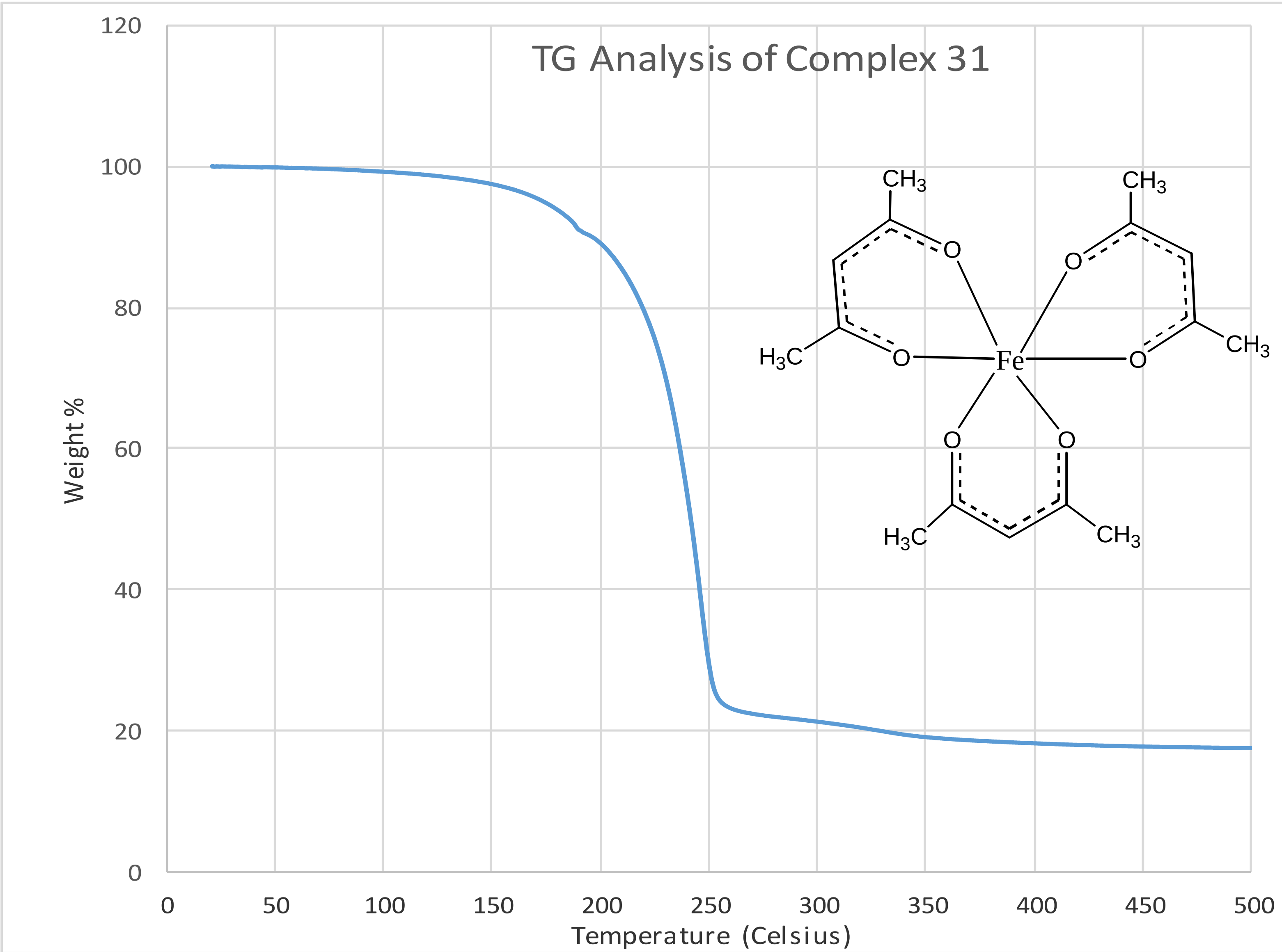
Synthesis of Fe(III) Complex



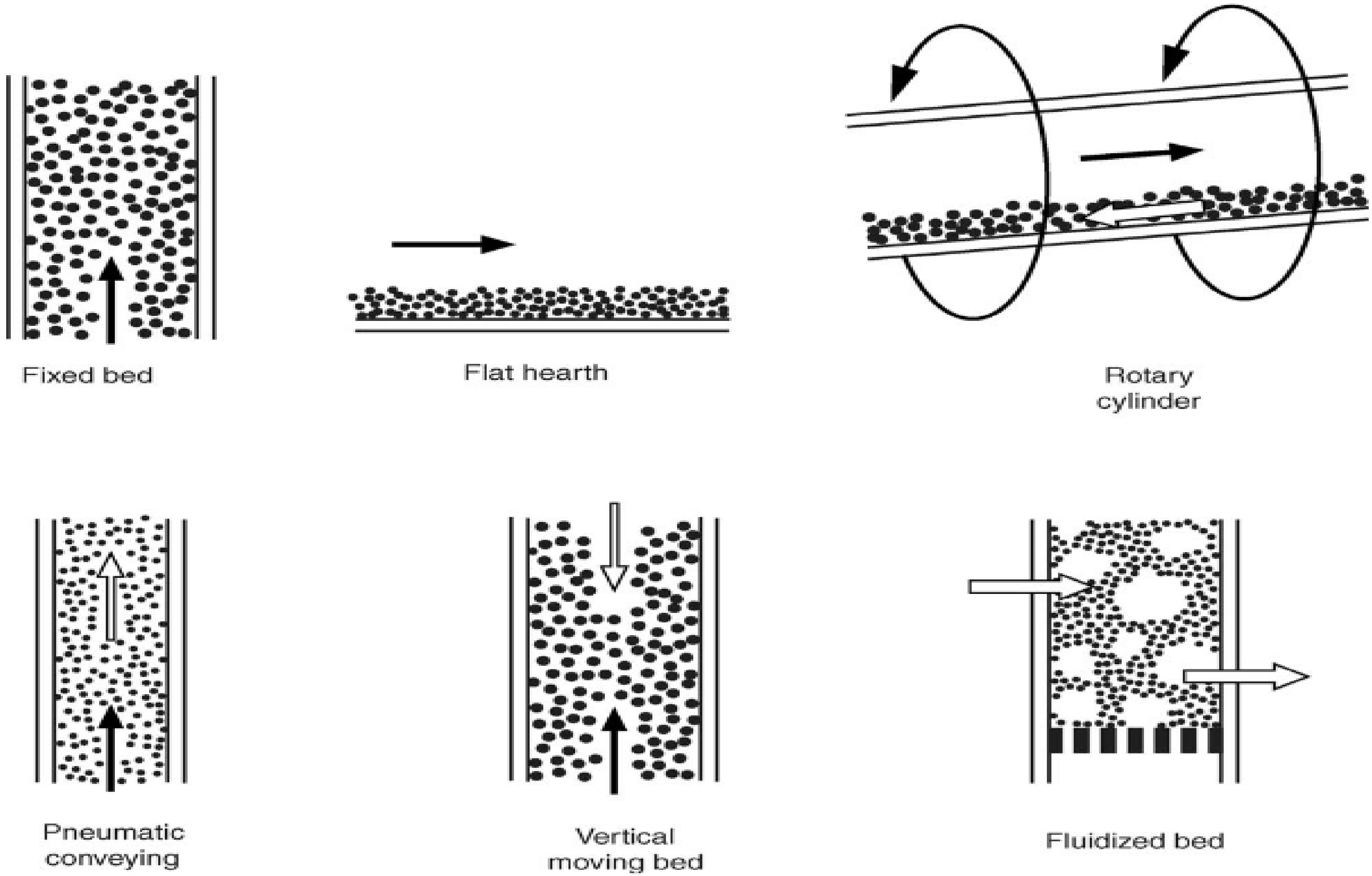
	R'	R''	R'''
17	CH_3	CH_3CH_2O	$(CH_3)_2CHN$
18	CH_3	CH_3O	$(CH_3)_2CHN$
19	CH_3	CH_3O	$CH_3CH_2CH_2N$
20	CH_3	CH_3CH_2O	$(CH_3)_2CHCH_2N$
27	CH_3	CH_3CH_2O	 CHN
30	CH_3	CH_3O	$CH_3OCH_2CH_2CH_2N$
31	CH_3	CH_3	O



TG Analysis of Complex 18
120
100
80
60
40
20
0
Weight %
0
100
200
300
400
500
Temperature (Celsius)
H3C
CH3
O
N
Fe
O
N
O
N
O
CH3
H3C


TG Analysis of Complex 31
Weight %
Temperature (Celsius)
0
20
40
60
80
100
120
0
50
100
150
200
250
300
350
400
450
500
CH3
CH3
H3C
CH3
Fe
O
O
O
O
O
O
H3C
CH3

MOCVD Coating of Particles



Future Work

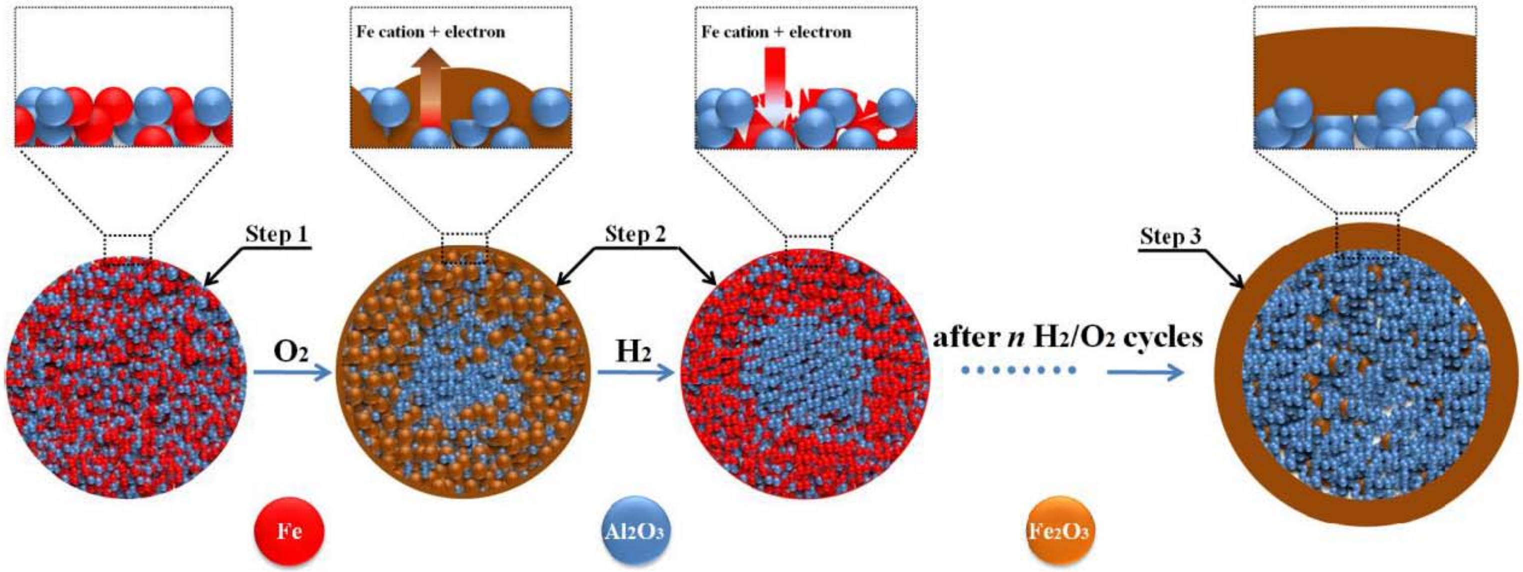
- Continued preparation of volatile and thermally stable precursors.

- Growth and characterization of core shell particles via MOCVD.

- Defining the relationship between CVD reaction time and shell thickness.

Technical Approach: Synthesis

- Ionic Diffusion via Cyclic Redox Cycles

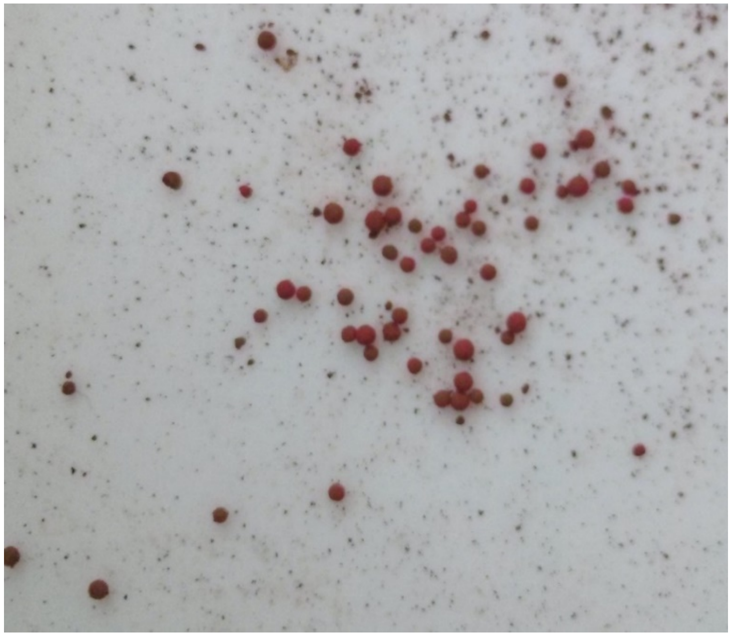


Technical Approach - OSU

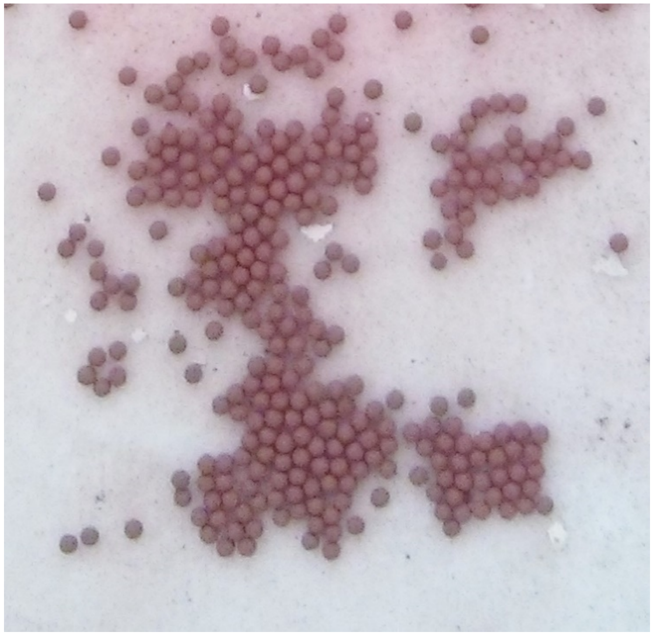
- Synthesis of Fe_2O_3 $Shell/Al_2O_3$ $Core$ via cyclic redox reaction
  - Confirmation from SEM and EDX analysis ← Completed
- Application of 2-D diffusion model and diffusion mechanism study
- Control of shell thickness and synthesis optimization
  - Amount of iron loading ←
  - Number of cycles required ← In Progress
- Performance characterization for both synthesis method (Fe_2O_3/Al_2O_3)
  - Reactivity comparison via TGA
  - Mechanical Strength measurement
  - Surface Area comparison
- Synthesis of Fe_2O_3 $Shell/CaO$ $Core$ particle
  - Universal application of the redox cycle synthesis method

Parametric Study

- Percent Iron Loading



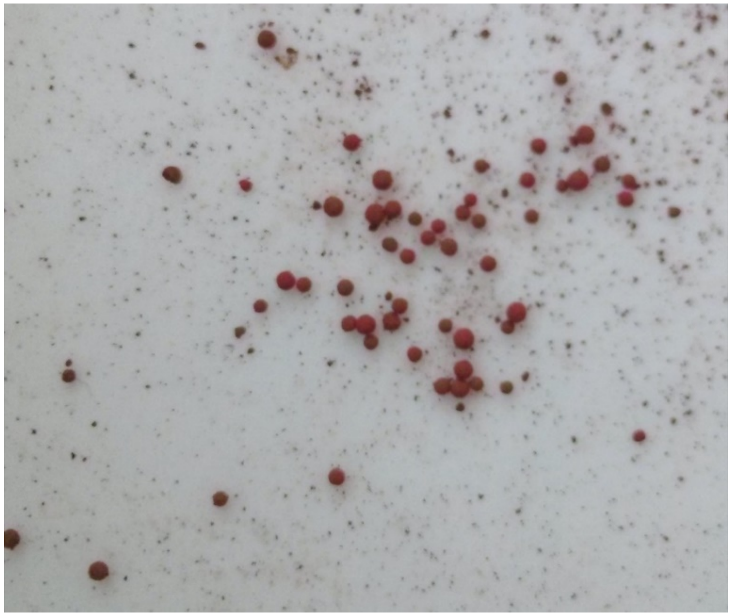
Homogeneous 20/80 Fe/Al Particle



Homogeneous 40/60 Fe/Al Particle

Parametric Study

- Particle Size



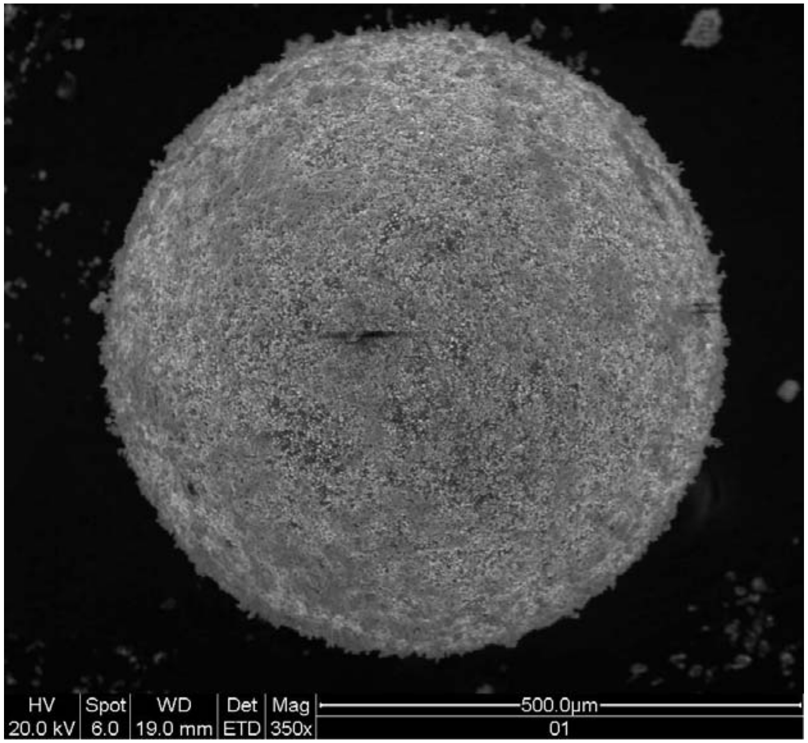
D = 0.35mm

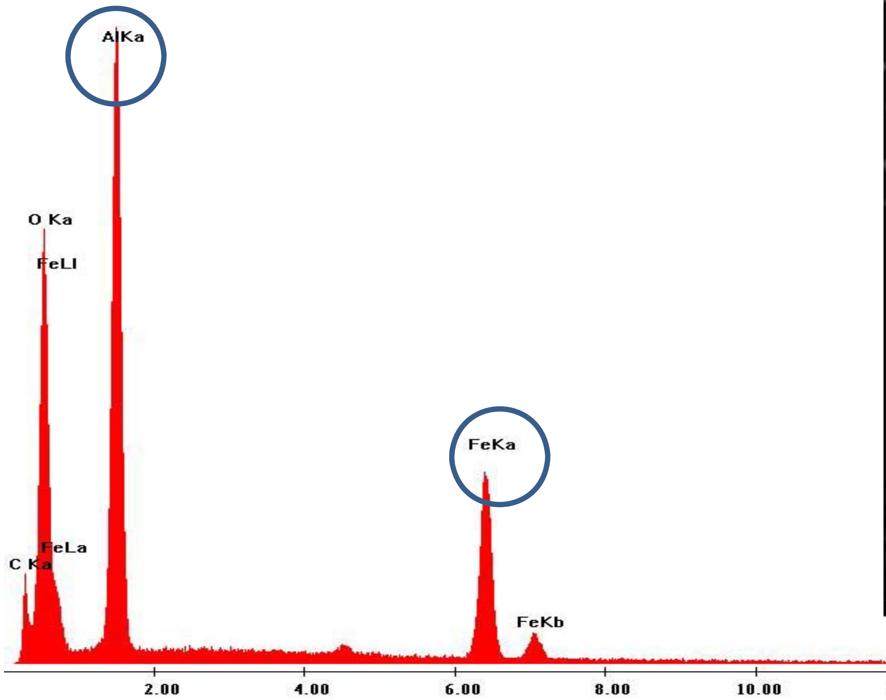
D = 2.00 mm

Characterization

SEM Analysis

- 40/60 Fe/Al

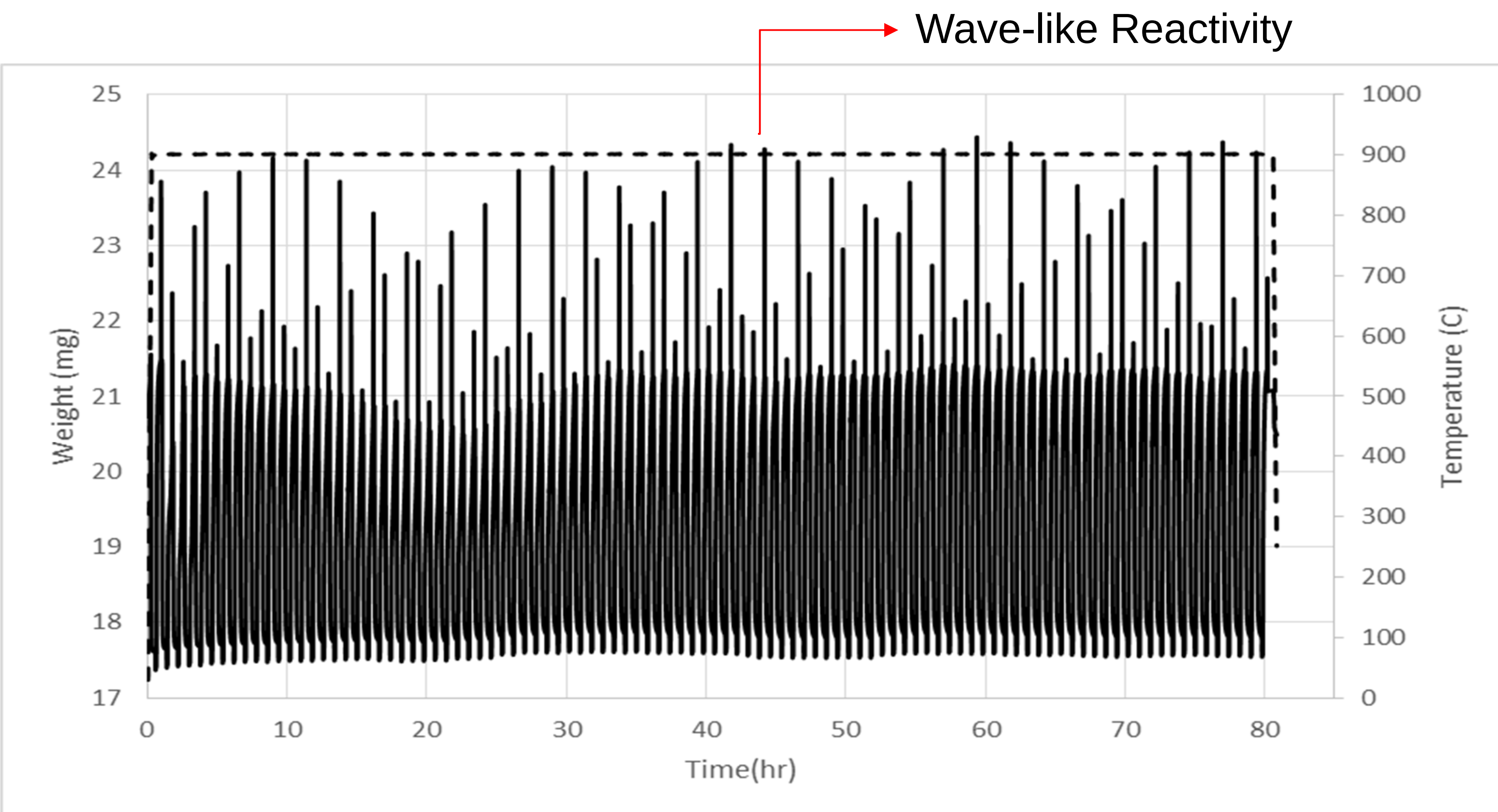




EDAX Analysis

Both Fe and Al are detected

Cyclic Redox via TGA



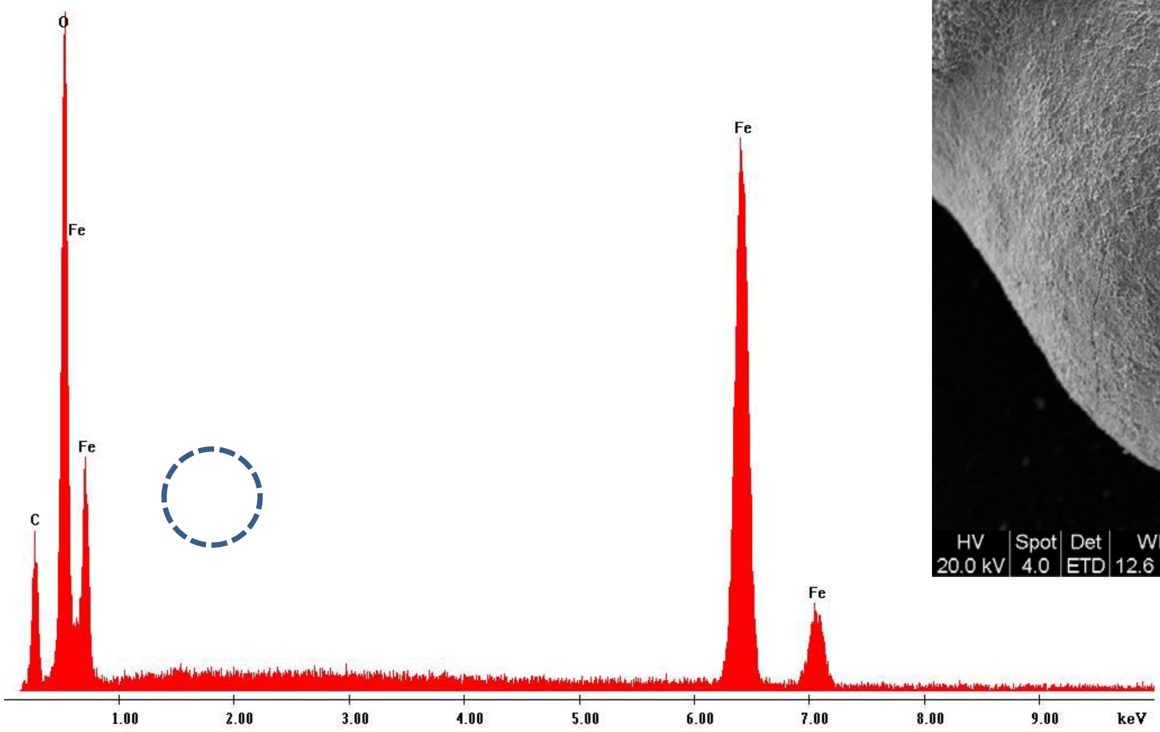
Condition: 100 cycles. Reduction under Hydrogen. Oxidation under Air.

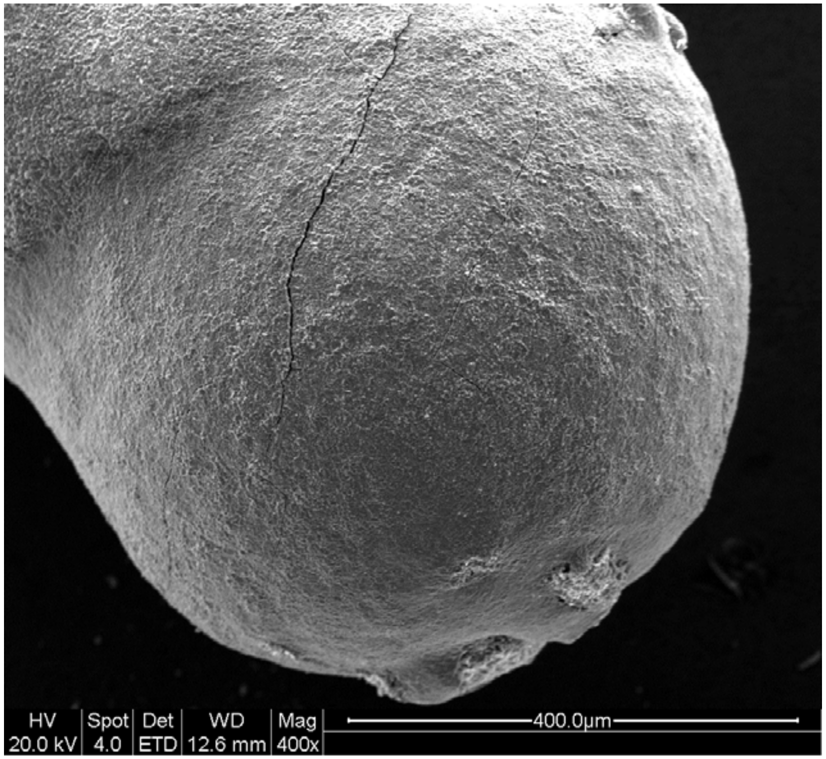
Cyclic Redox via TGA

- Wave-like Profile
  - Increased Reactivity
    - Migration of iron atoms toward the surface
  - Decrease in Reactivity
    - Sintering of surface iron oxide

Characterization

- Post Cyclic Redox

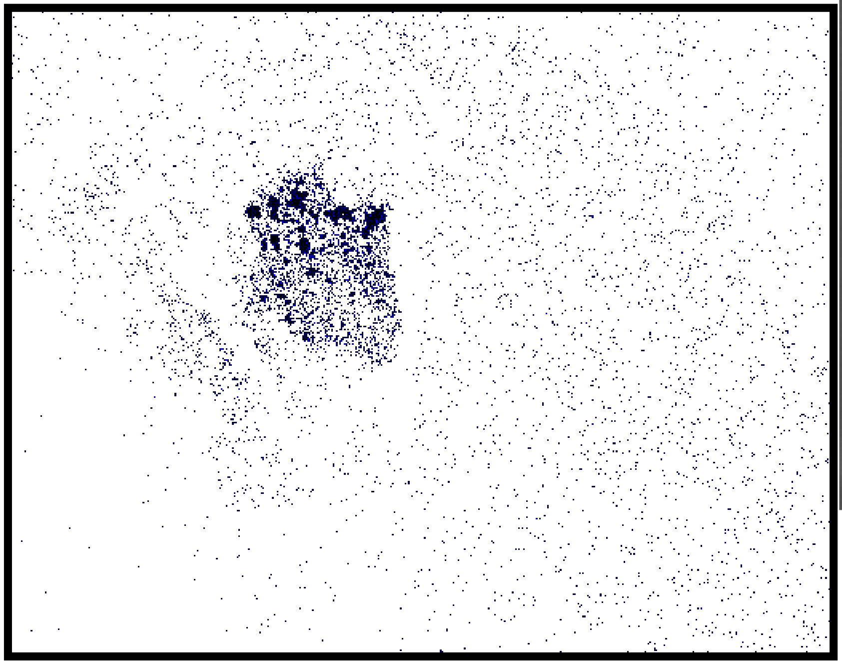


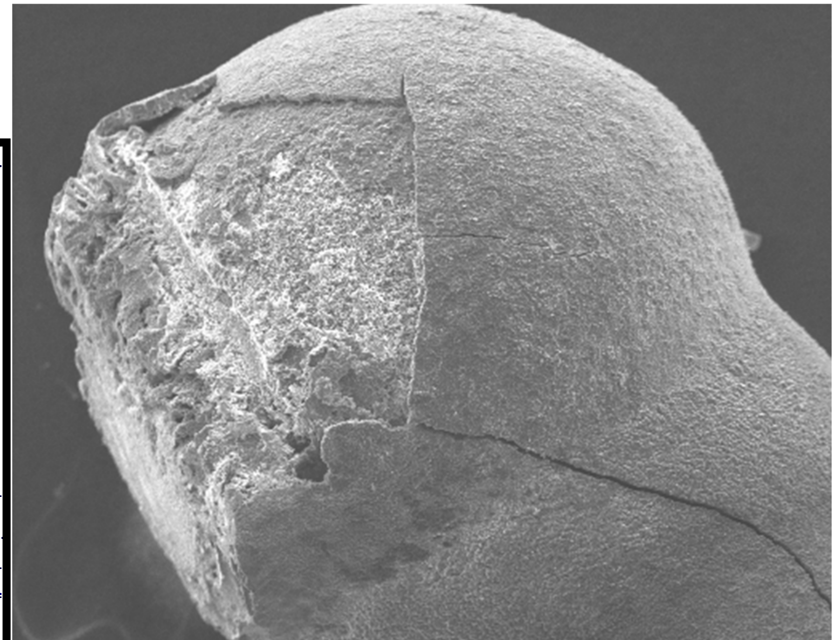


No Alumina is detected on the surface

Characterization

- Post Cyclic Redox





EDAX Mapping reveal concentrated Alumina under fractured shell

Summary-OSU

- Successful formation of core-shell particle via cyclic redox
- Homogeneous particles of various parameters have been prepared
- Two competing phenomenon has been proposed. Further investigation is needed

Future Work-OSU

- The competing phenomena during redox cycles will be examined by varying the number of cycles and end state.
- TGA profile for the larger particle will also be studied.
- Synthesis of varying degree iron loaded core-shell particles will continue in order to study the effect of iron loading.

Acknowledgements

- DOE-NETL DOE-FE0011515
- Howard University Graduate School
- Ohio State University