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

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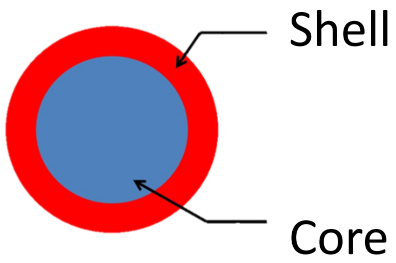
OUTLINE

- 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

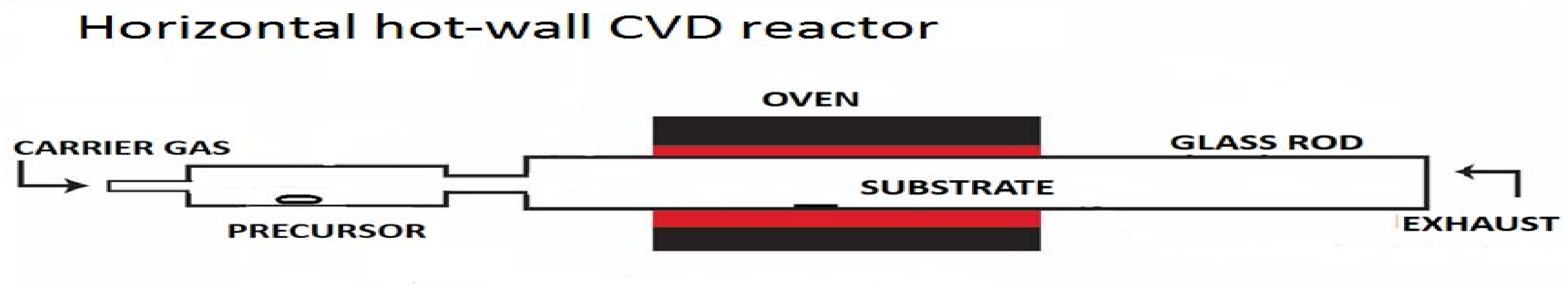
Proposed Synthetic Methods

- 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

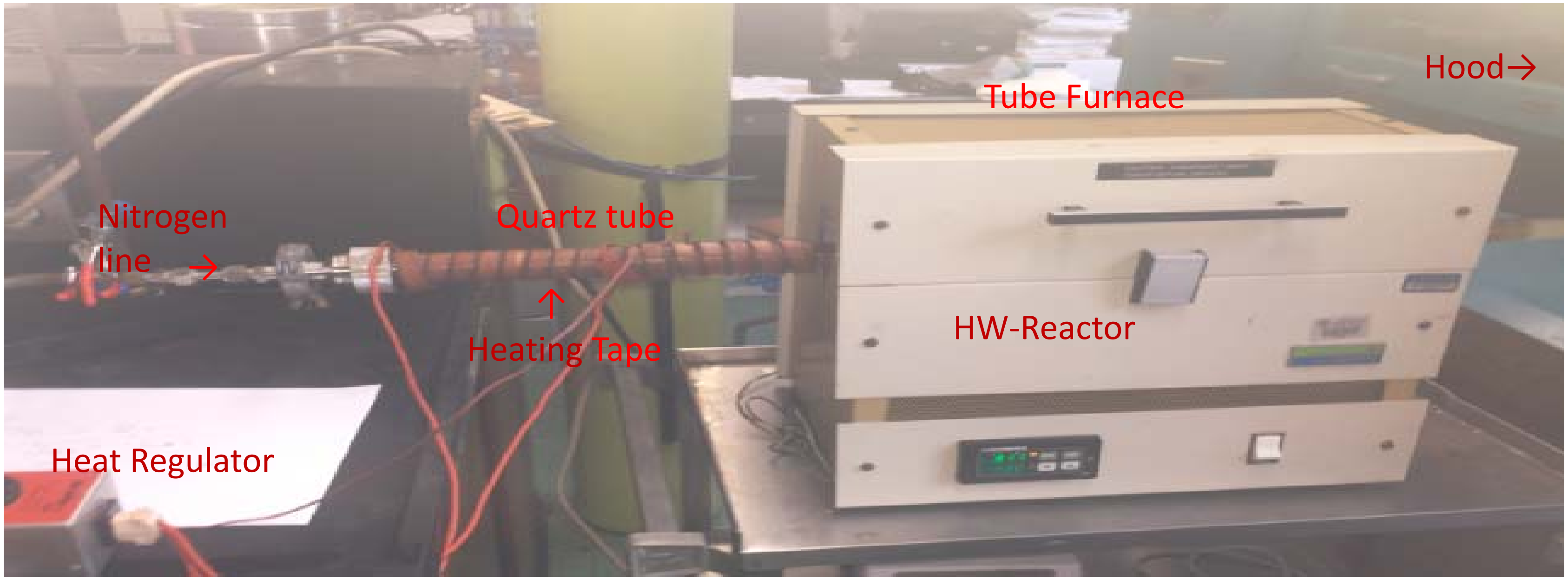
Potential Significance

- Cost effective method
- Improved catalytic activity
- Potential application in Chemical looping combustion/gasification, and sorbent-based fossil fuel

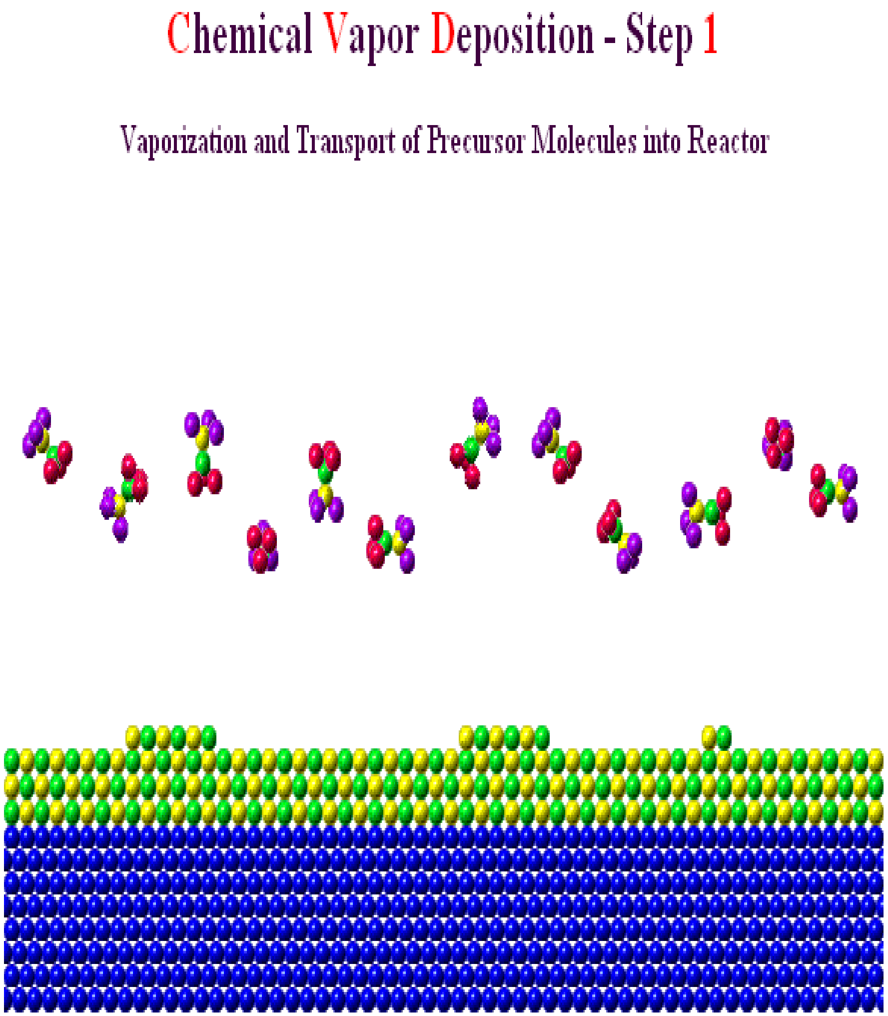
Metal Organic Chemical Vapor Deposition (AP-MOCVD)



Schematic illustration of a horizontal CVD hot-wall reactor

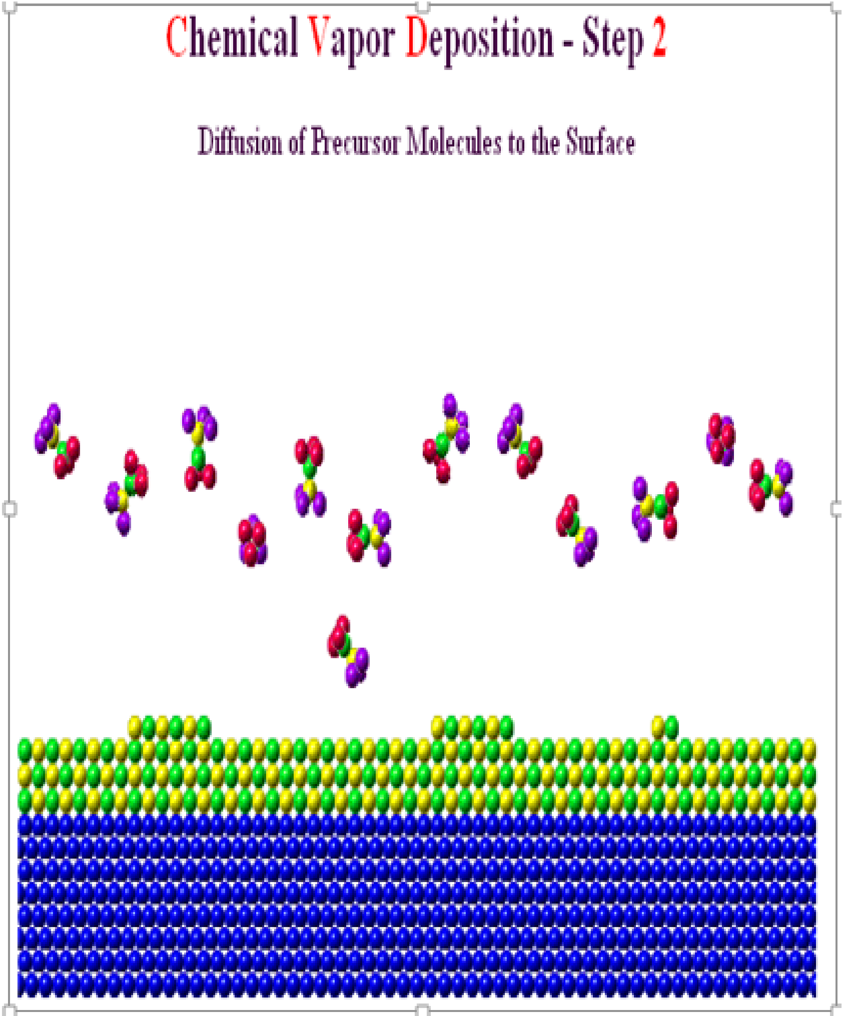


Physicochemical reactions processes in the CVD Reactor : STEP (1&2)



Chemical Vapor Deposition - Step 1

Vaporization and Transport of Precursor Molecules into Reactor

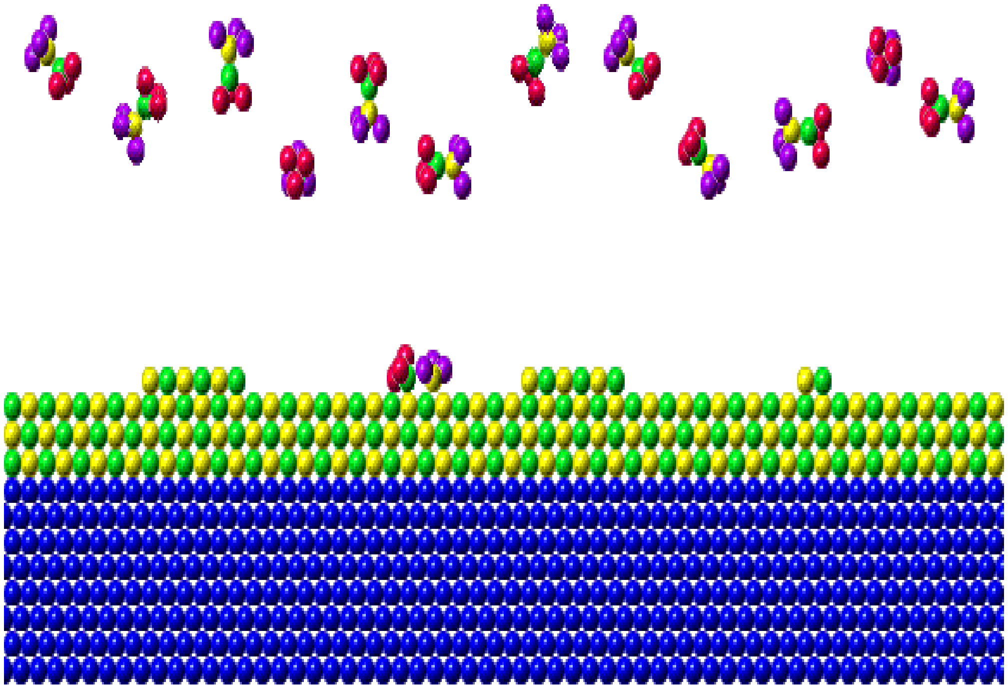


Chemical Vapor Deposition - Step 2

Diffusion of Precursor Molecules to the Surface

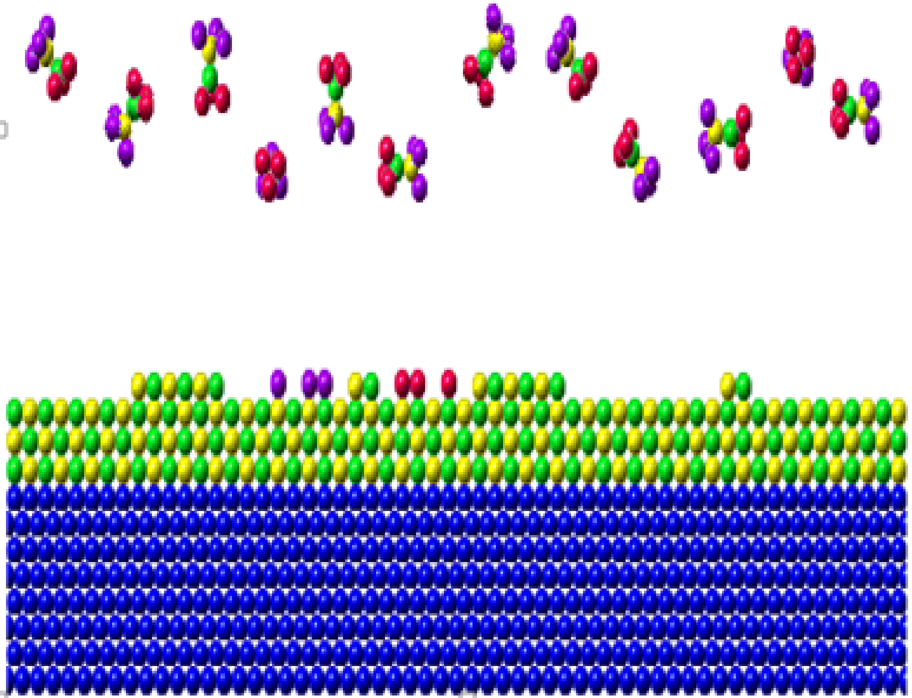
Chemical Vapor Deposition - Step 3

Adsorption of Precursor Molecules to Surface



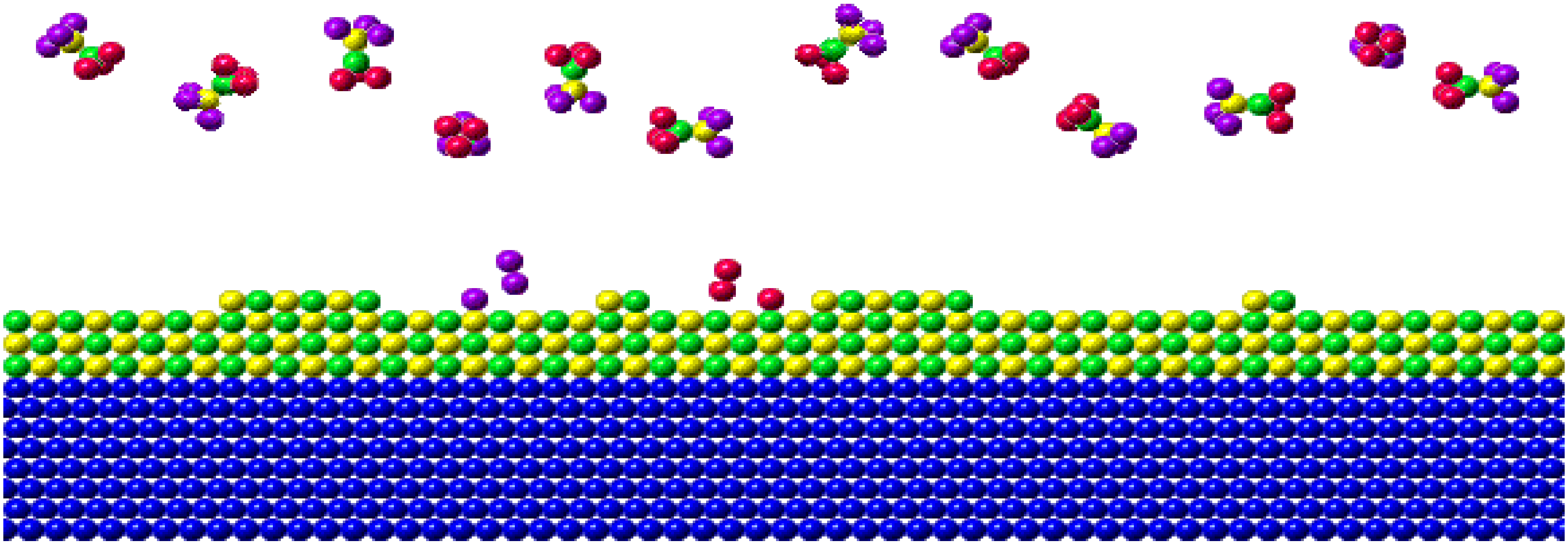
Chemical Vapor Deposition - Step 4

Decomposition of Precursor and Incorporation into Solid Films



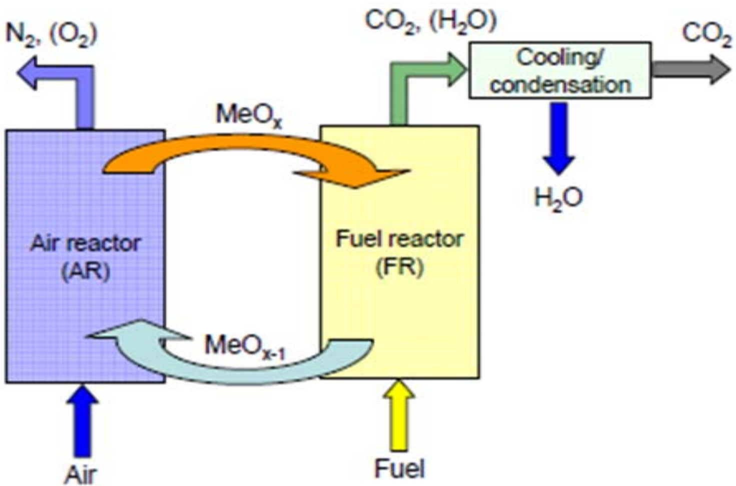
Chemical Vapor Deposition - Step 5

Recombination of Molecular Byproducts and Desorption into Gas Phase

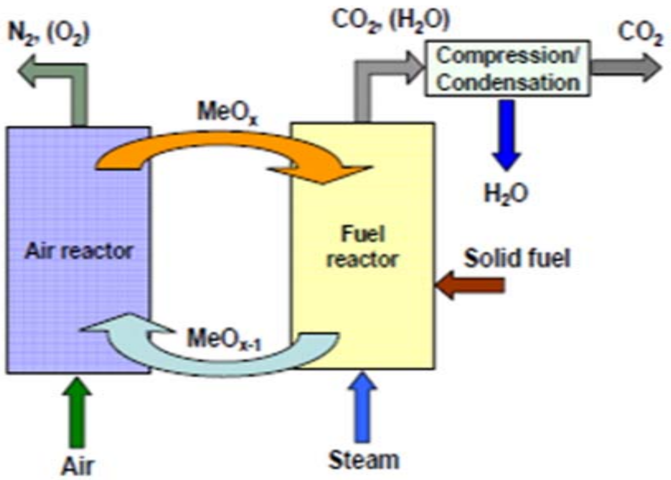


Chemical Looping Technology

Catalytic process that converts fossil fuels into energy and CO_2 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

$$(2n+m)Me_xO_y + C_nH_{2n} \rightarrow (2n+m)Me_xO_{y-1} + nCO_2 + mH_2O \quad (1)$$

$$(n+m)Me_xO_y + nCO + mH_2 \rightarrow (n+m)Me_xO_{y-1} + nCO_2 + mH_2O \quad (2)$$

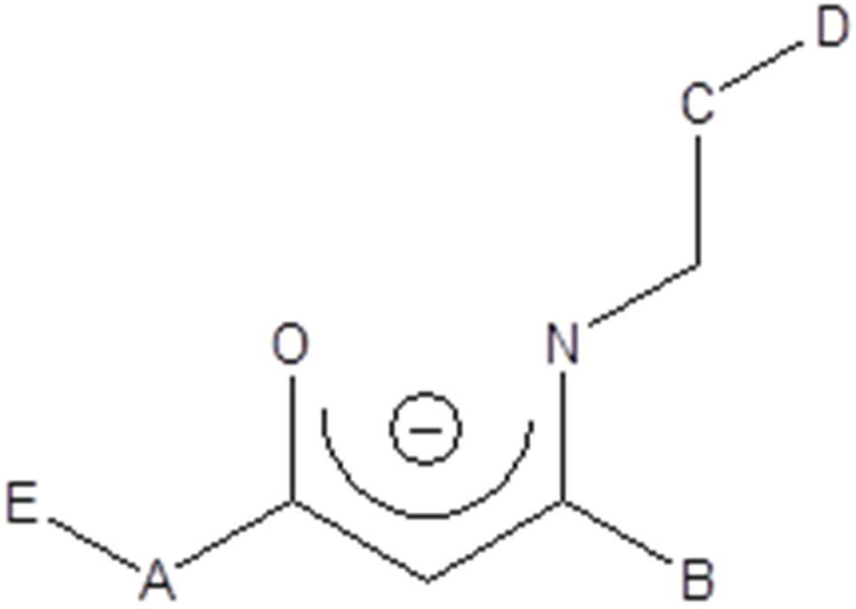
$$2Me_xO_{y-1} + O_2 \rightarrow 2Me_xO_y \quad (3)$$

$$(2n+1)H_2 + nCO \rightarrow C_nH_{2n+2} + nH_2O \quad (4)$$

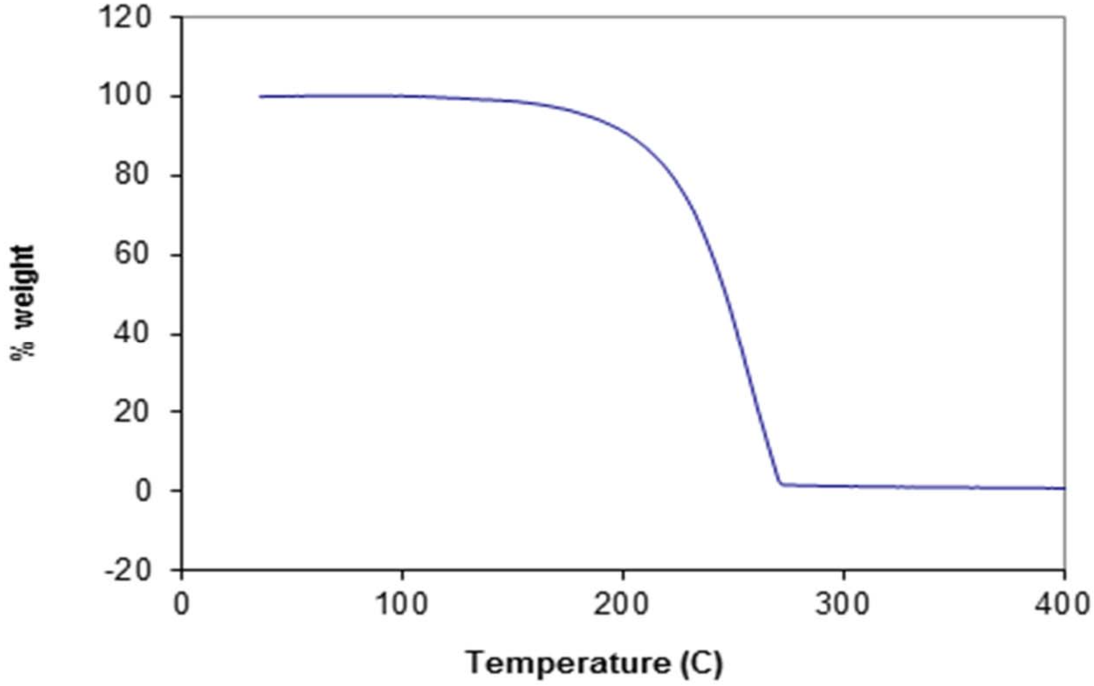
Statement of Project Objectives

- 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 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

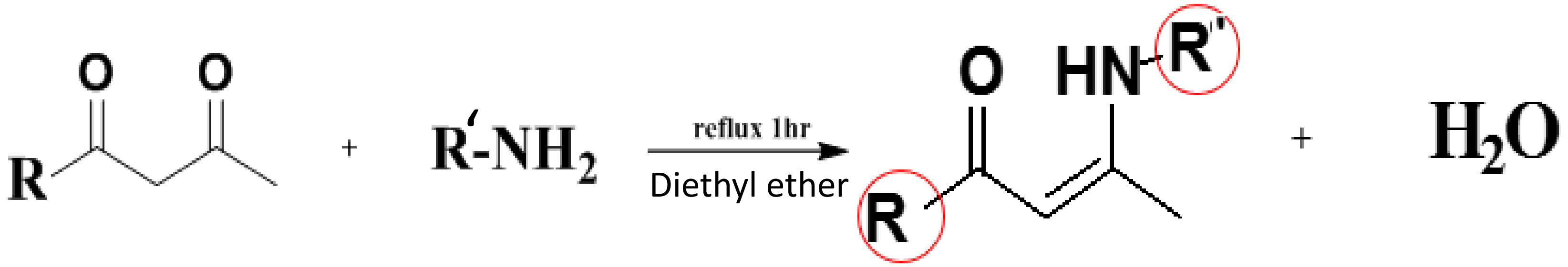
MOCVD-Precursor Requirements

- 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

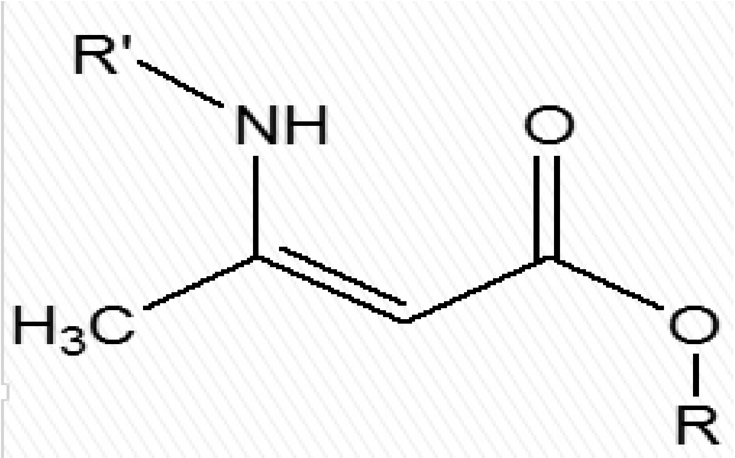
Synthesis and Characterization of β- Ketoimines



β-diketone

Amine

Synthesized Free ligands



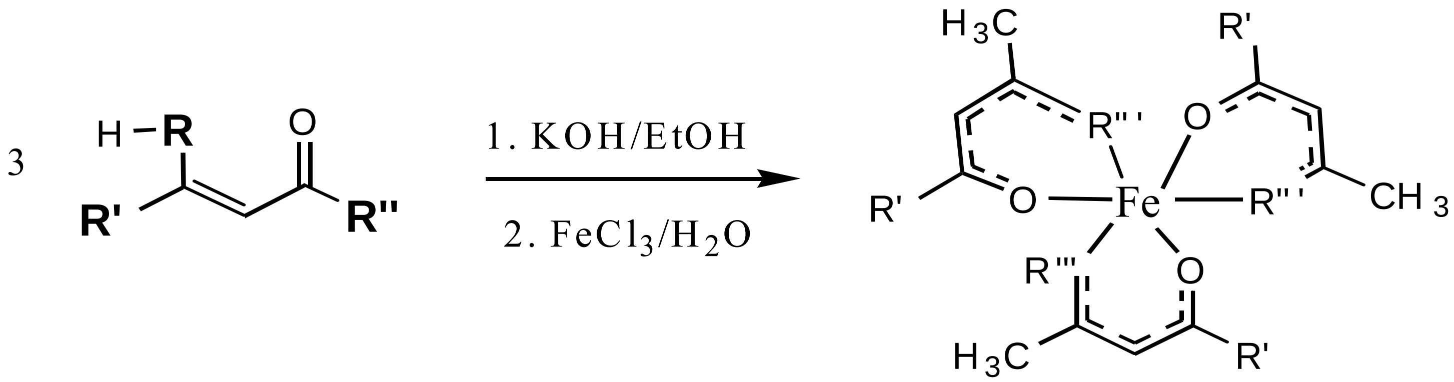
R’ =

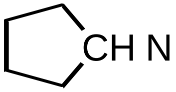
1. Isopropyl
2. Isobutyl
3. Butyl
4. Cyclopentyl
5. Cyclohexyl
6. Methoxypropyl
7. t-butyl
8. Propyl

R =

1. CH_2CH_3
2. CH_3

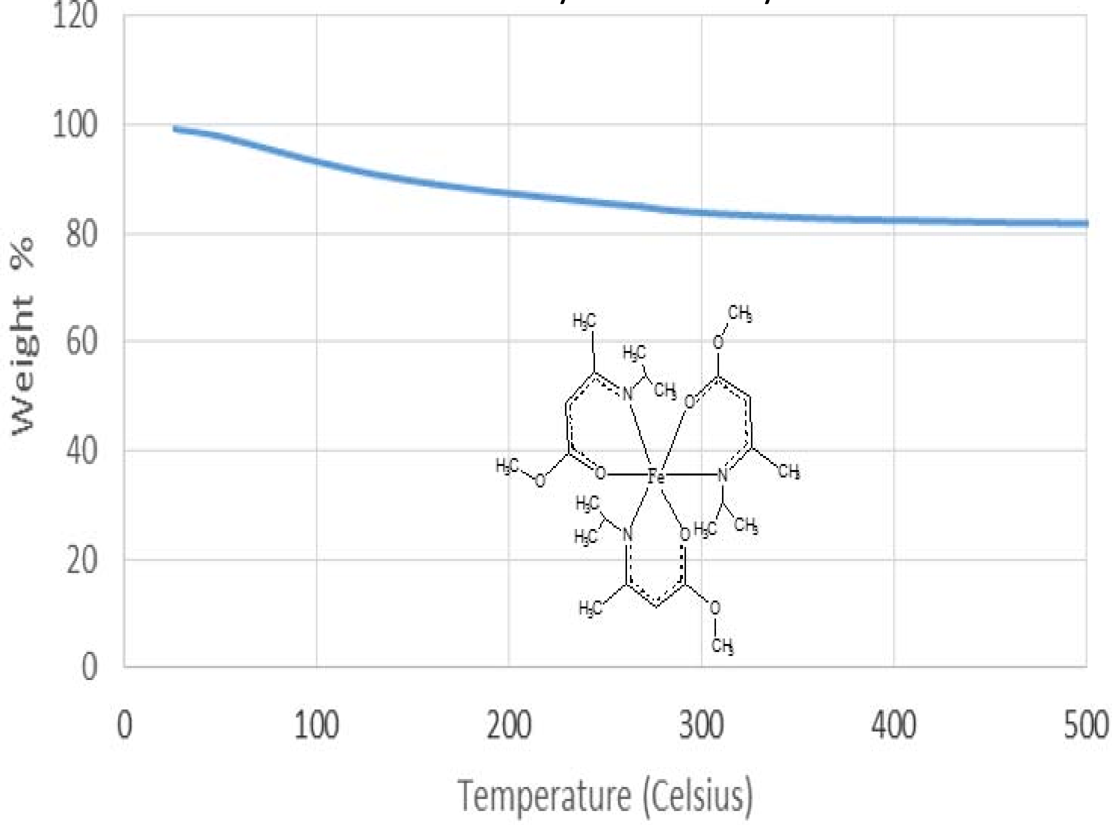
Synthesis of Fe(III) Complex



	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	
30	CH_3	CH_3O	$CH_3OCH_2CH_2CH_2N$
31	CH_3	CH_3	O

TGA- thermogram of complex 18

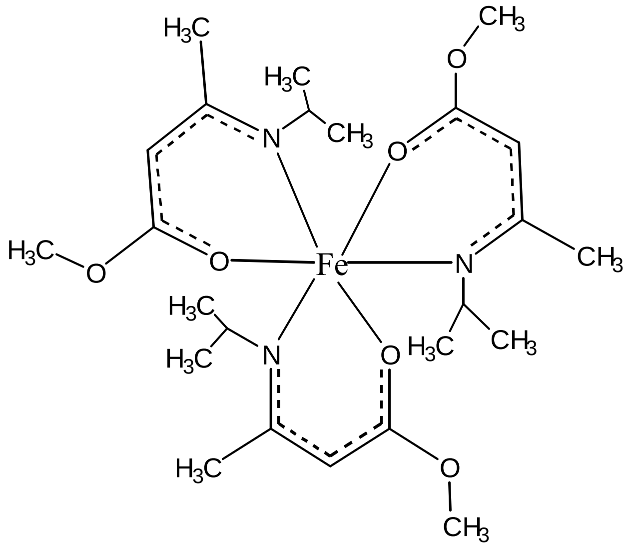
exhibit less volatility and stability



TGA: of complex of complex 18

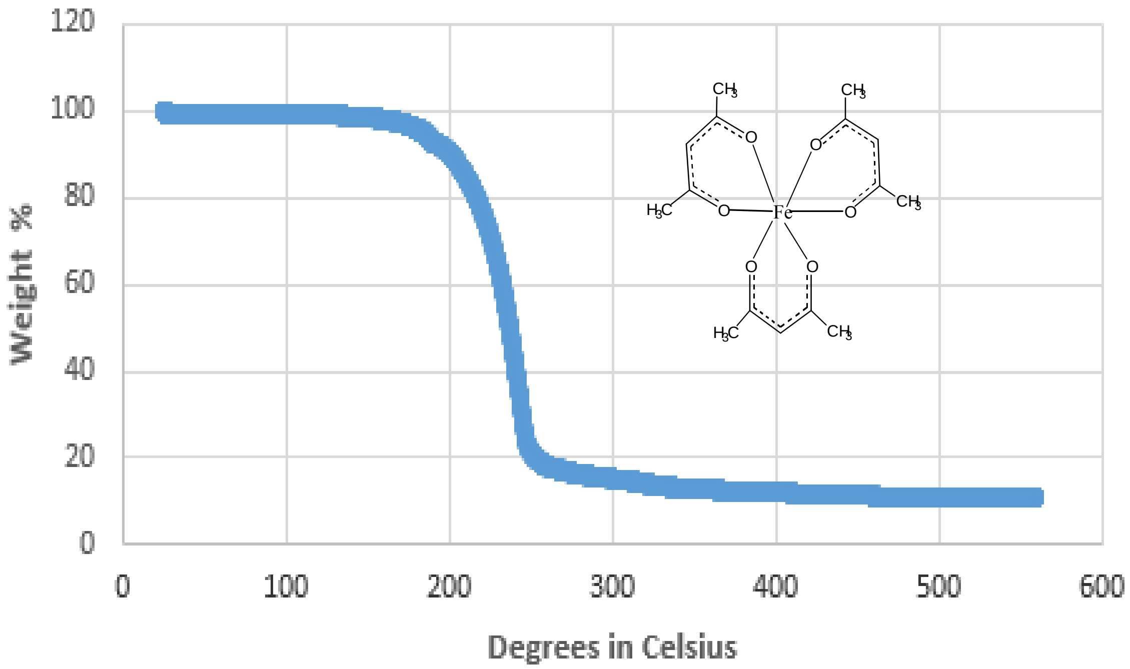
Structure of complex 18

Tris(methyl-3-(isopropyl)amino-2-butenoato)iron(III)



TGA- thermogram of complex 31

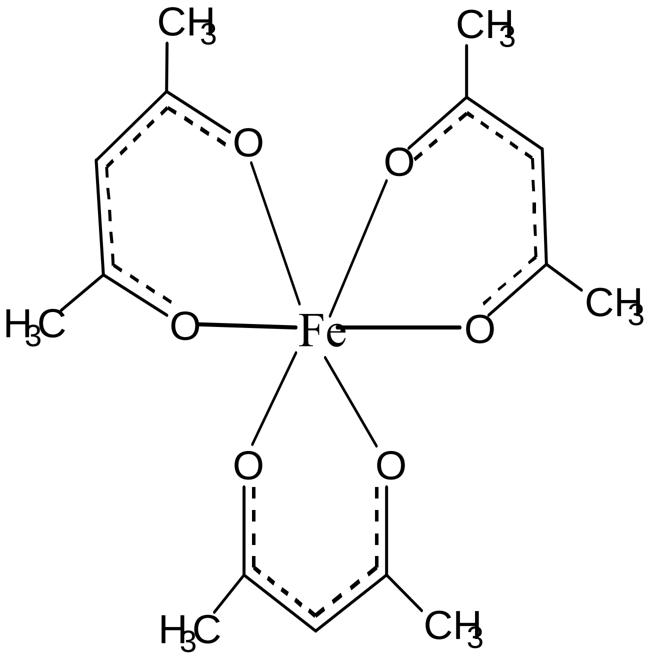
exhibit higher volatility and minimal decomposition



TGA: of recrystallized iron complex 31

Structure of complex 31

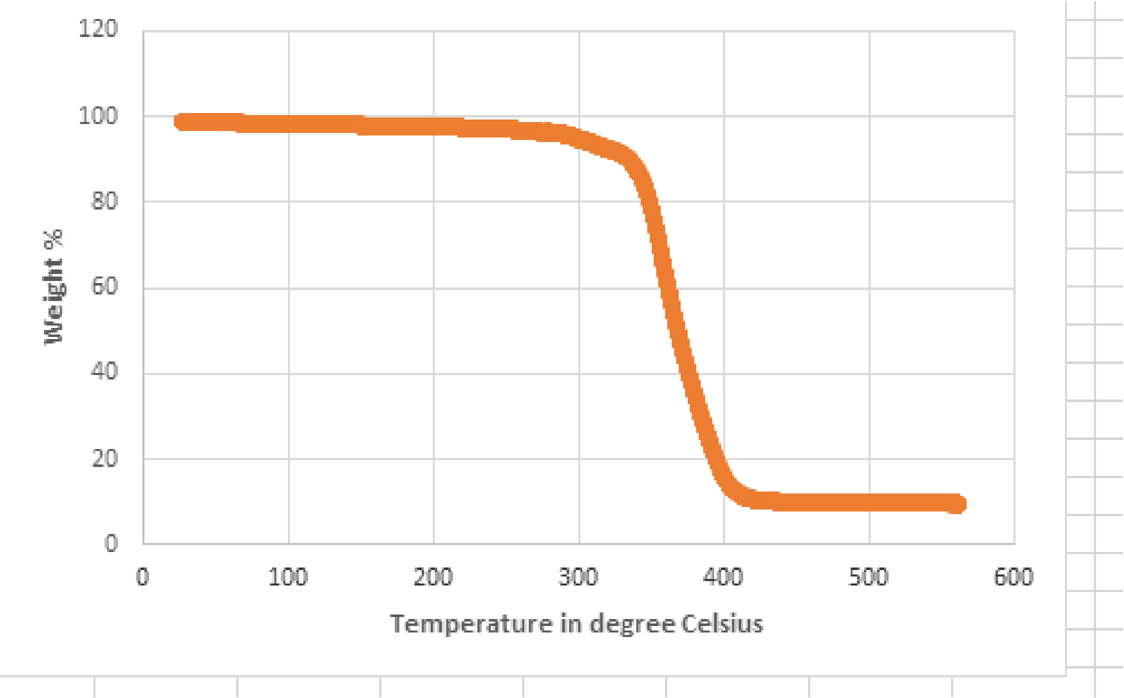
Tris(2,4-pentanedionato)iron(III)



Fe(acac)$_3$

TGA- thermogram of Iron (III) oxide precursor 33

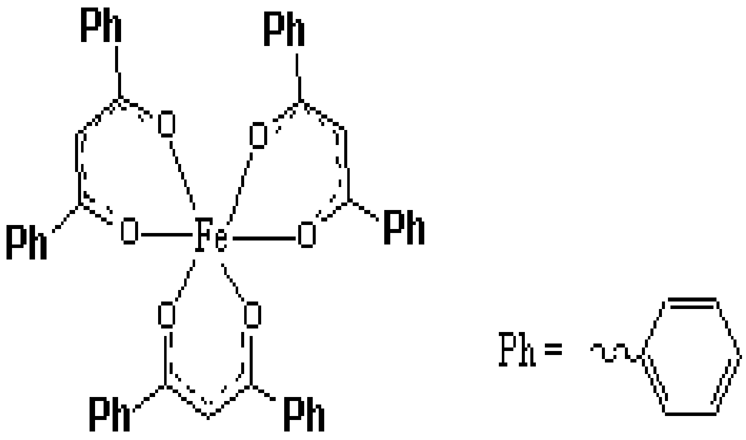
exhibit higher volatility and minimal decomposition.



TGA: of recrystallized iron complex 33

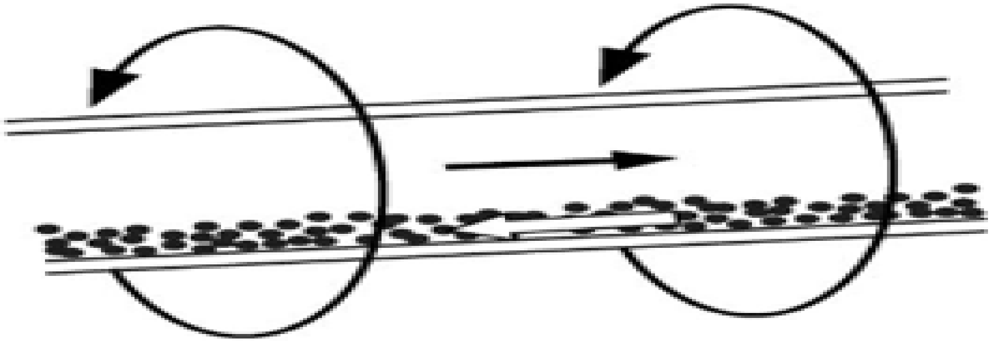
Structure of complex 33

Tris(1,2-diphenylpropane-1,2-dionato)iron(III)



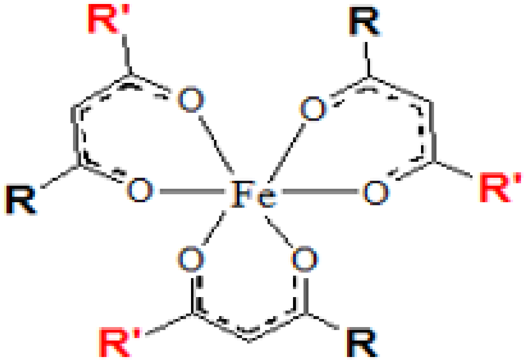
Coating mode of Particle

- **Gas-solid contact in the CVD Reactor**



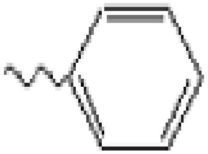
Rotary Bed

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



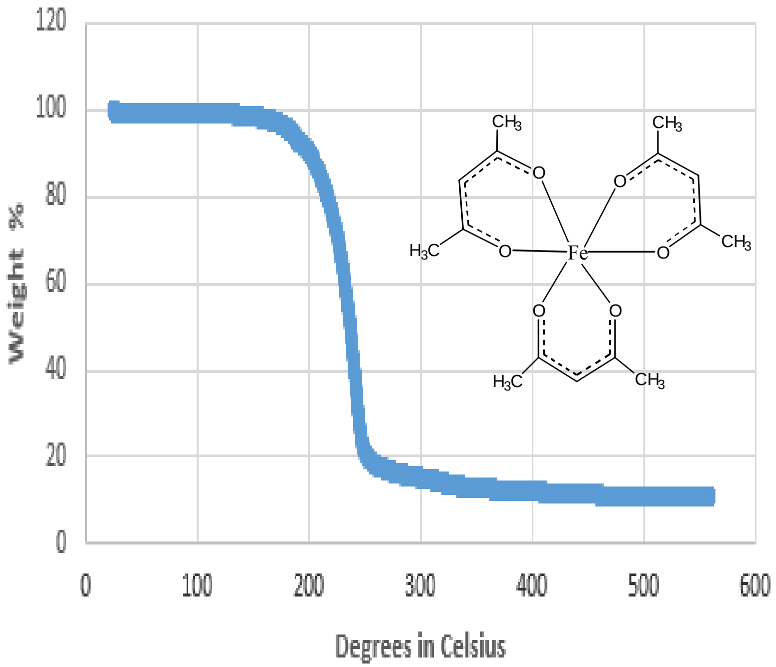
	R	R'
31	CH_3	CH_3
32	CH_3	Ph
33	Ph	Ph
34	CH_3	OCH_3
35	CH_3	OCH_2CH_3
36	OCH_2CH_3	OCH_2CH_3

Ph =

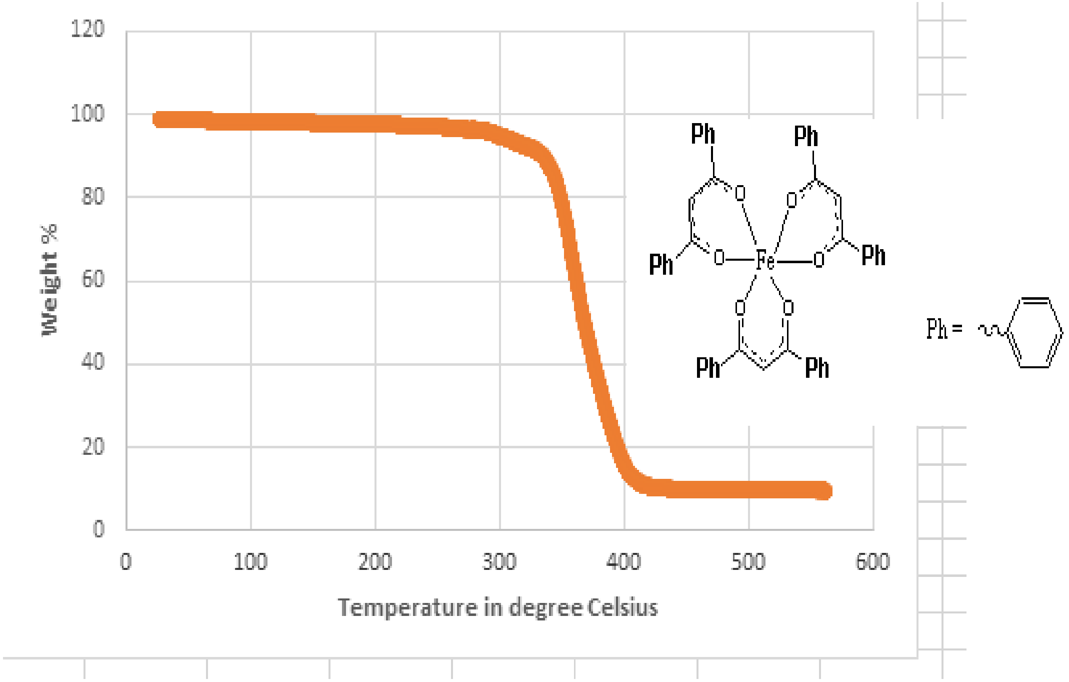


Evaluated TGA thermogram of Iron (III)oxide precursor

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

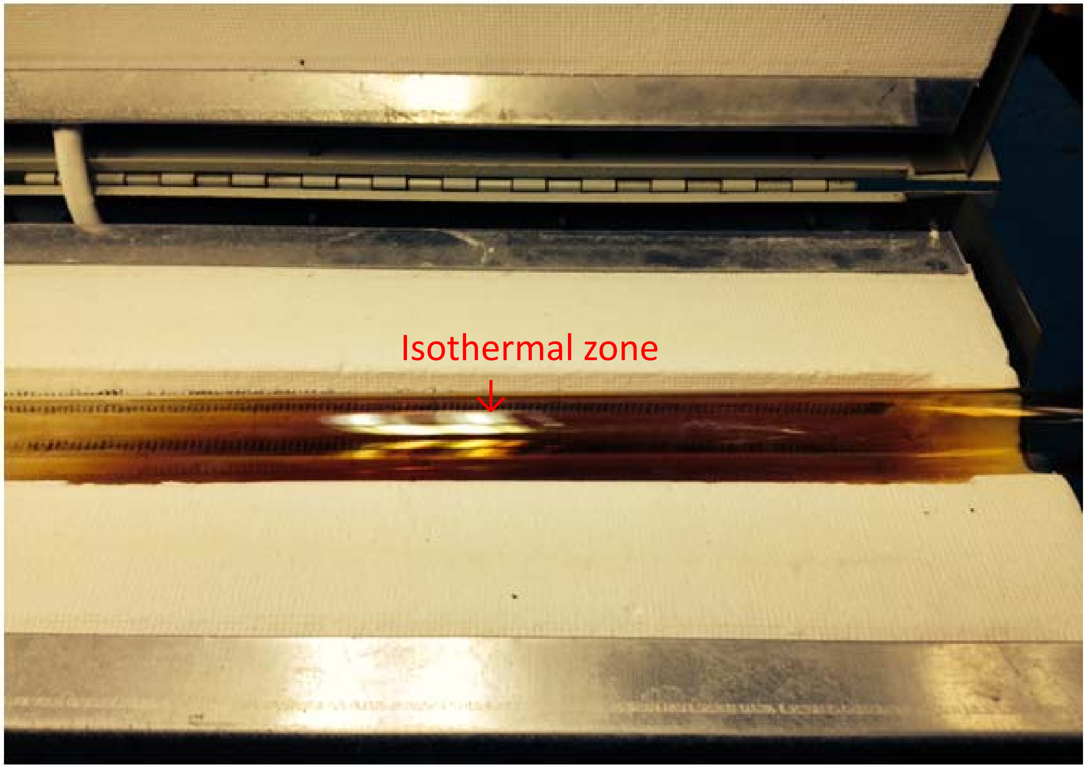


TGA: of complex 31



TGA: of complex 33

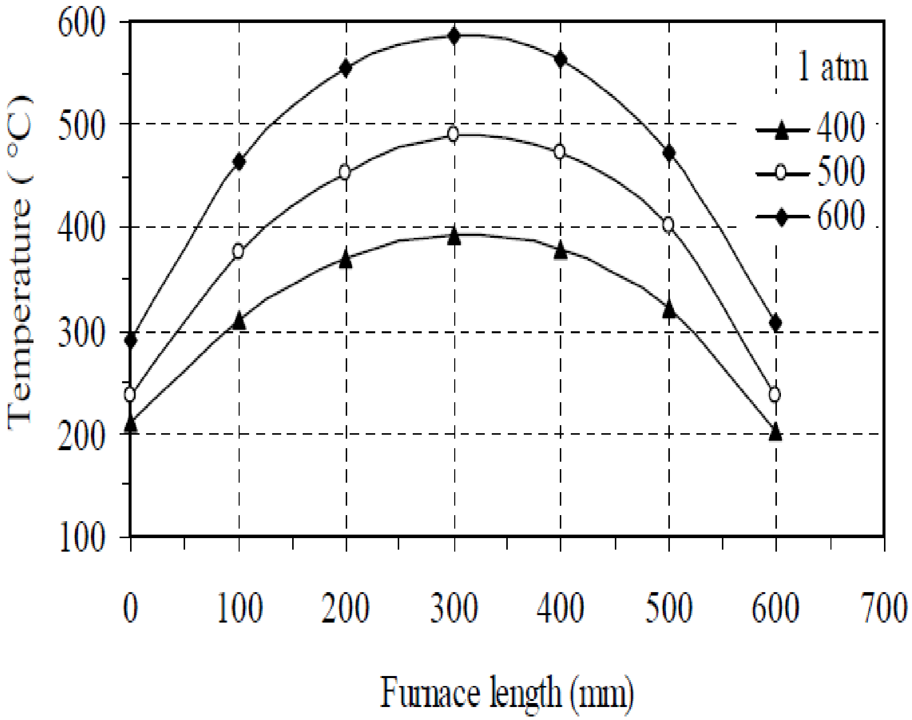
Determination of Source and Decomposition Temperatures



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

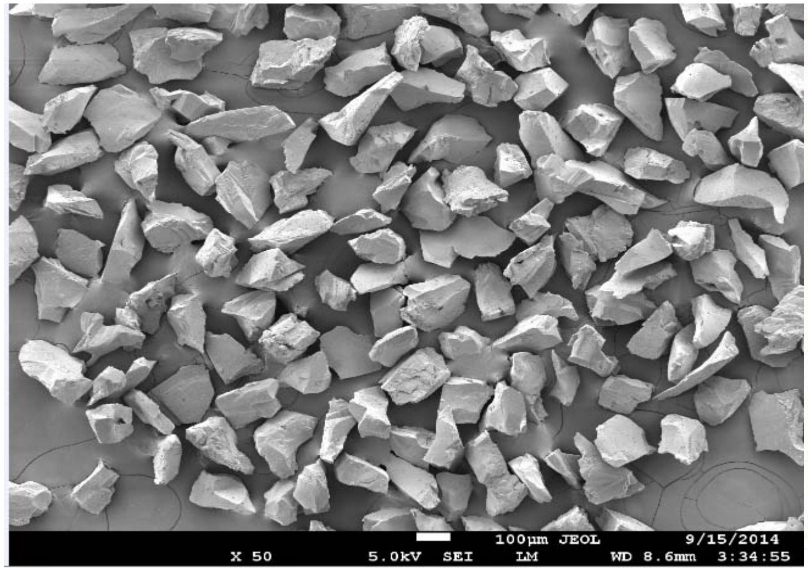
Temperature distribution profile in the Hot-Wall Reactor

(Gas flow changes the temp. profile slightly)

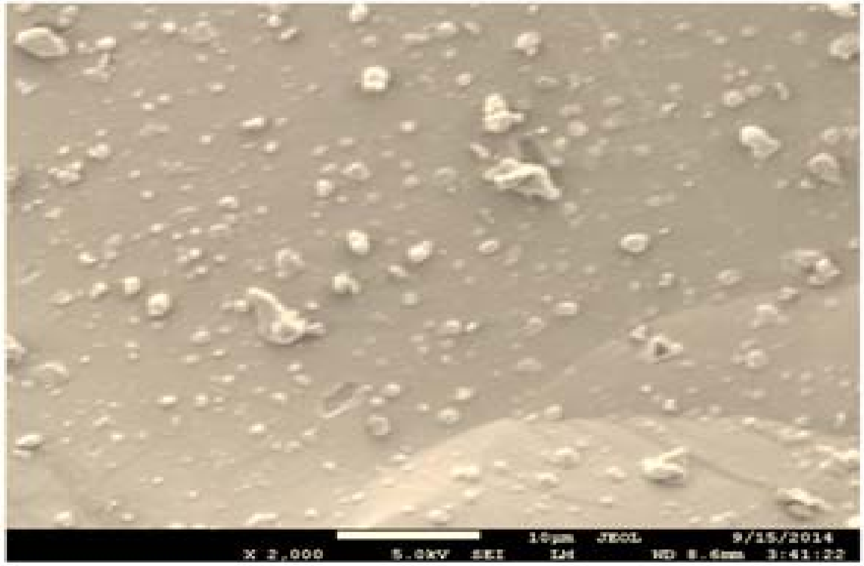


Mushin E.A, chemical vap. Deposition 11.07.2007 p(23)

SEM micrograph of Fe_2O_3 coated Al_2O_3 particle at 220°C



(a) 50 x



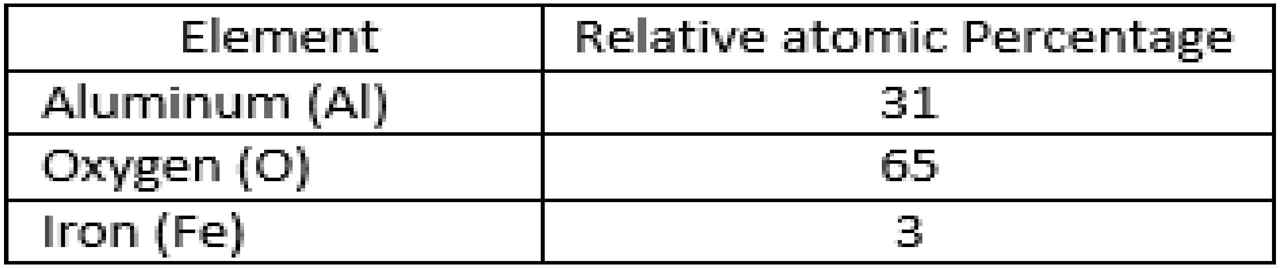
(b) 200 x

(c) Fe_2O_3 coated Al_2O_3 at substrate temperature of 220° C.

(d) Fresh uncoated Al_2O_3

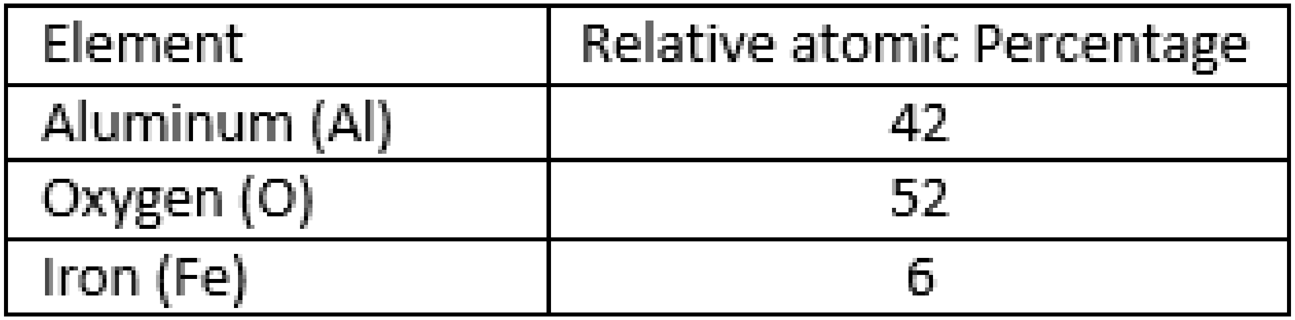
Elemental composition analysis of Fe_2O_3 coated Al_2O_3 particle determine by EDS

(a) **Before Annealing**



Element	Relative atomic Percentage
Aluminum (Al)	31
Oxygen (O)	65
Iron (Fe)	3

(b) After Annealing at 300^{o}C for 30 minutes



Element	Relative atomic Percentage
Aluminum (Al)	42
Oxygen (O)	52
Iron (Fe)	6

MOCVD Growth Optimization and EDS Analysis

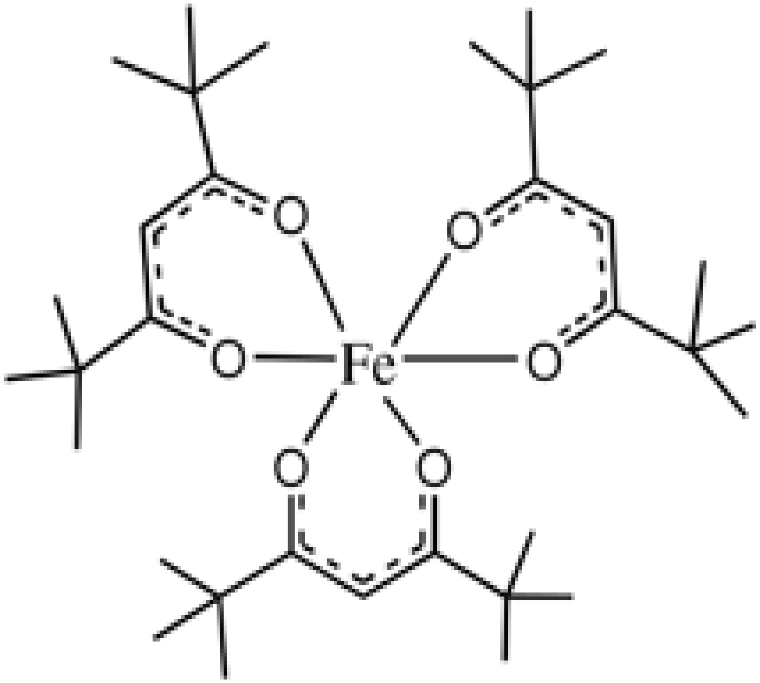
Four CVD growth cycles with deposition temperature 220° – 360°C at 20°C interval

annealed at 500°C for 30 minutes

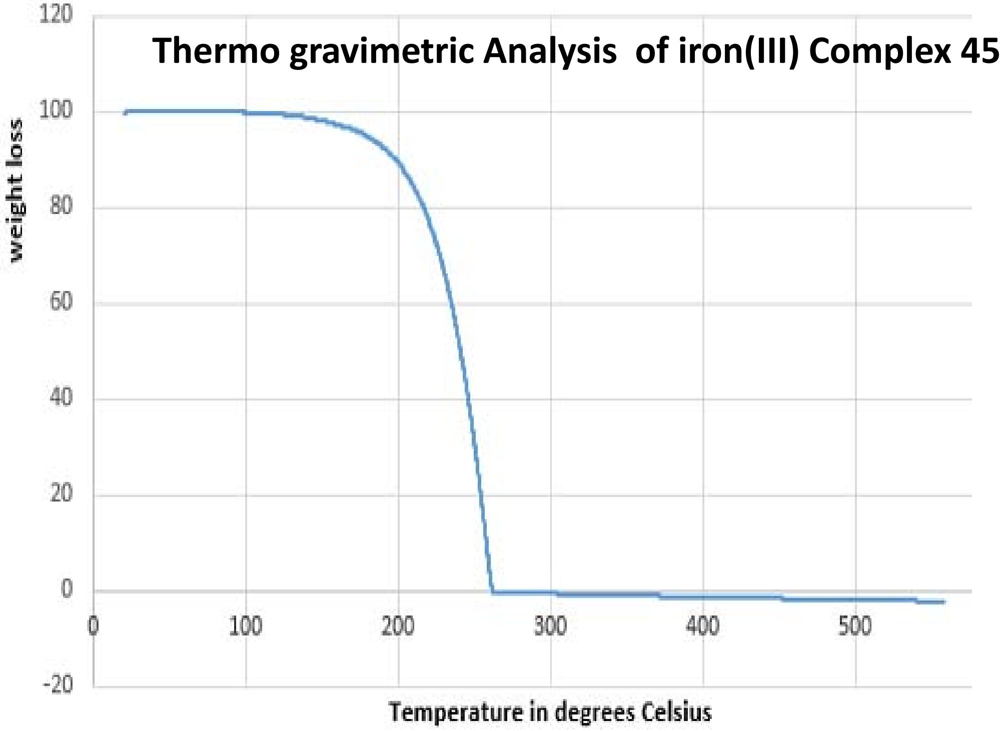
Sample	Iron	Oxygen	Aluminum
P(2)	1.91	58.41	36.64
P(3)	0.80	53.09	40.79
P(5)	3.13	63.71	29.71

Synthesized Iron(III)oxide Precursor 45

Tris(2,2,6,6-tetramethyl -3,5-heptanedionato)iron(III)

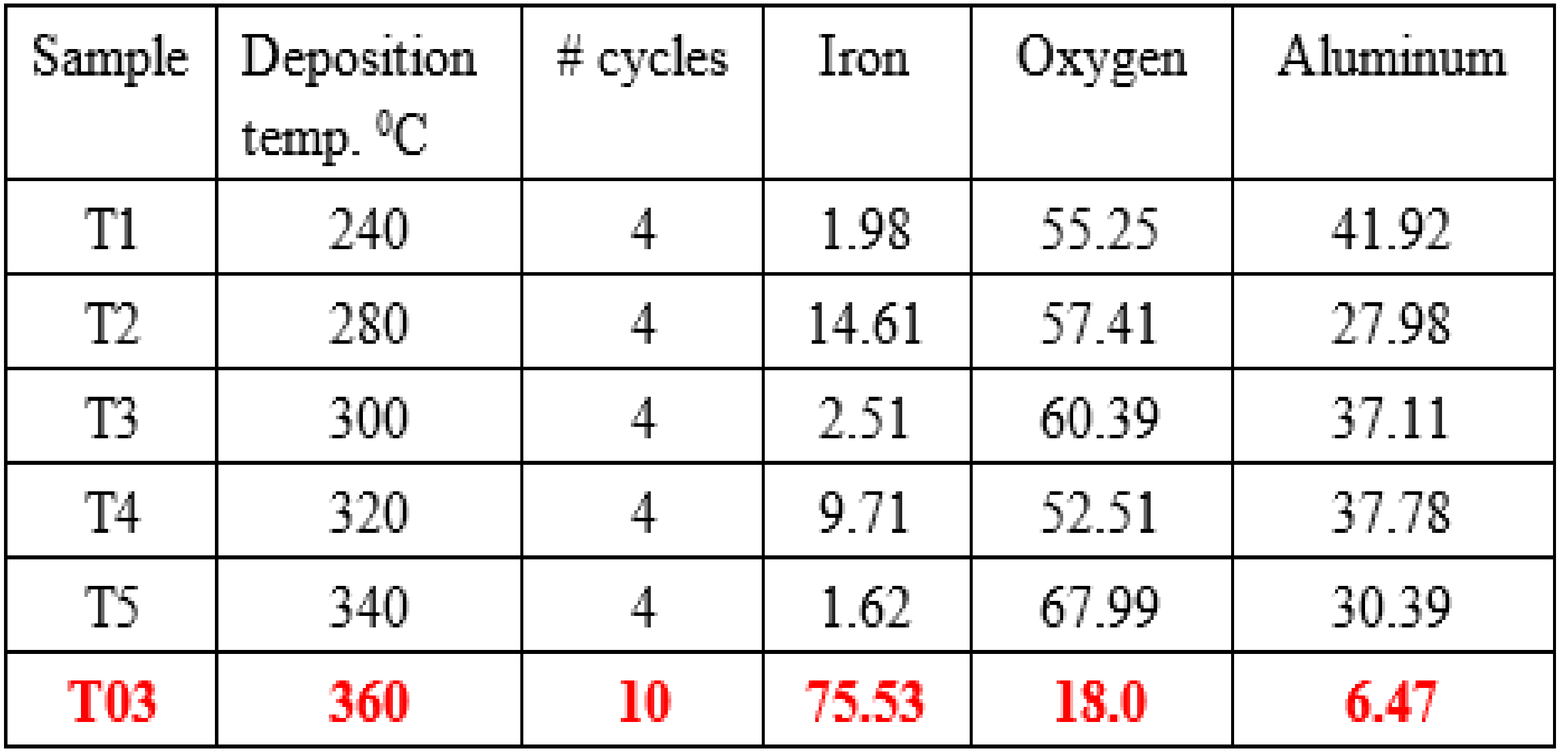


Molecular structure of Fe(thmd)$_3$
Iron(III) Complex 45



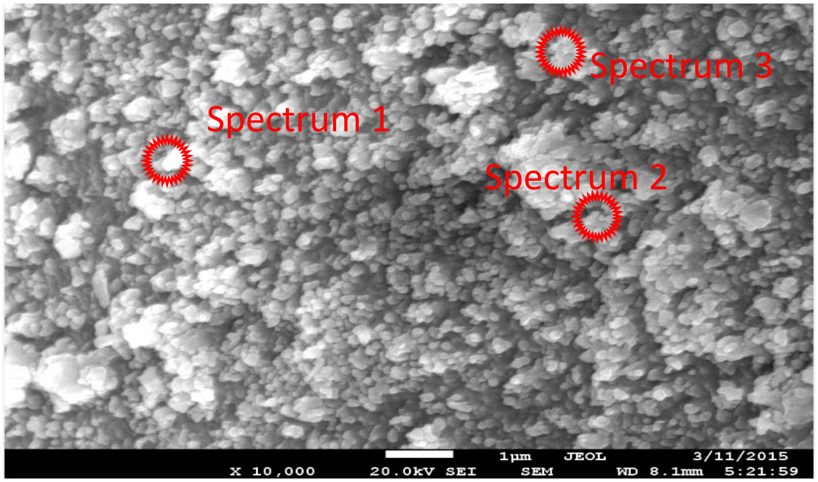
TGA: after recrystallization in acetone/ water solution

Elemental composition of Fe_2O_3 coated Al_2O_3 as determine by EDS after annealing at 500^0C for 30 minutes

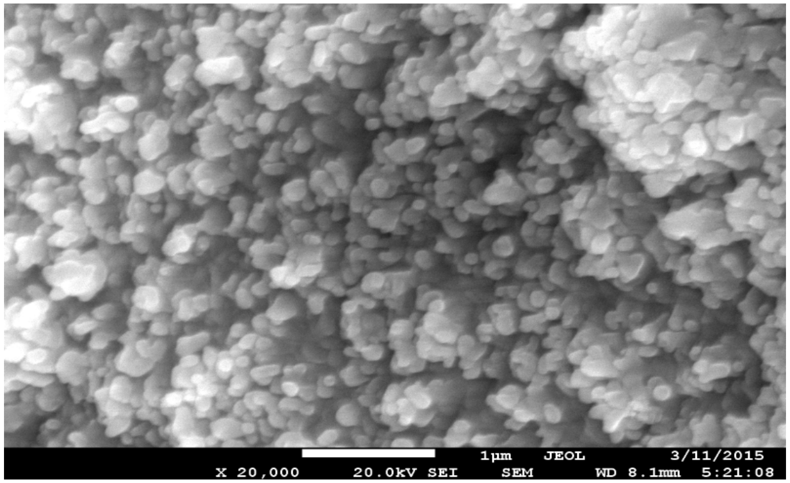


Sample	Deposition temp. ^{0}C	# cycles	Iron	Oxygen	Aluminum
T1	240	4	1.98	55.25	41.92
T2	280	4	14.61	57.41	27.98
T3	300	4	2.51	60.39	37.11
T4	320	4	9.71	52.51	37.78
T5	340	4	1.62	67.99	30.39
T03	**360**	**10**	**75.53**	**18.0**	**6.47**

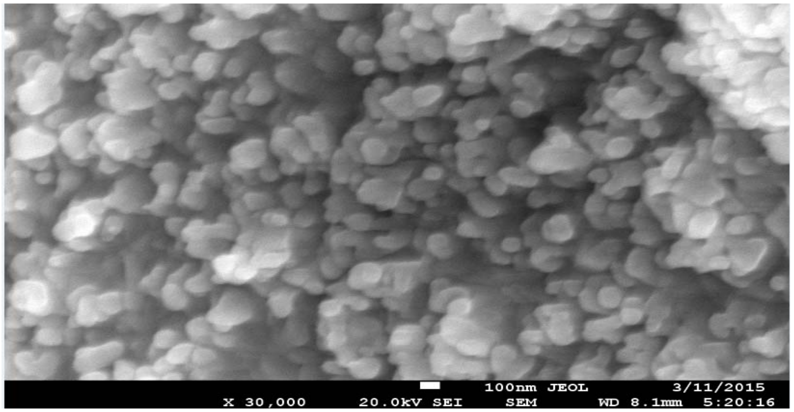
SEM micrograph of Core-Shell particle derived from sample T03 after 10 CVD cycles



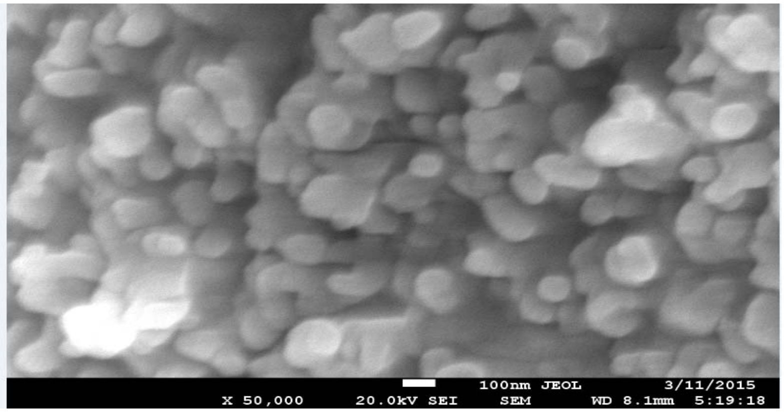
a) x10,000



b) x20,000

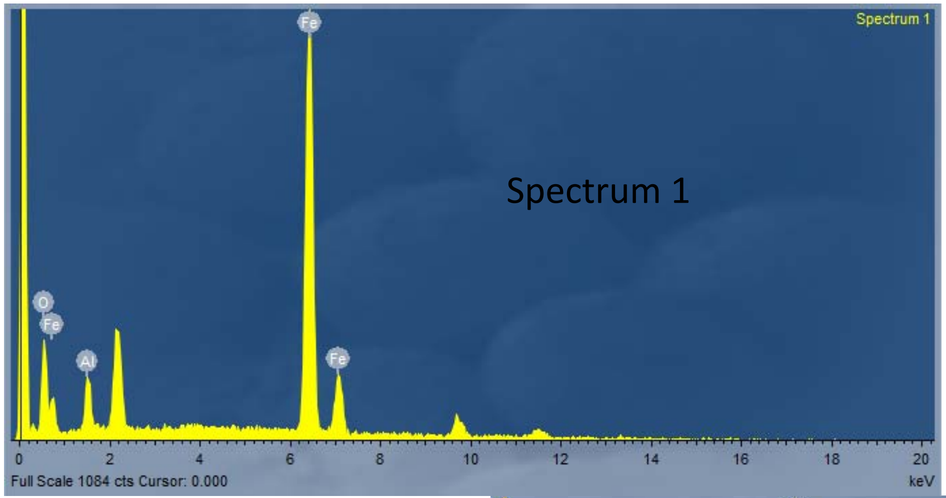


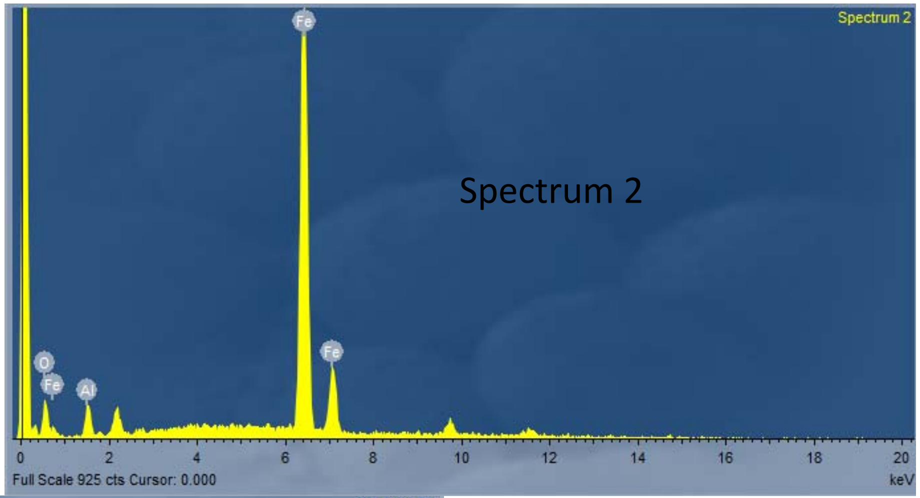
c) x30,000

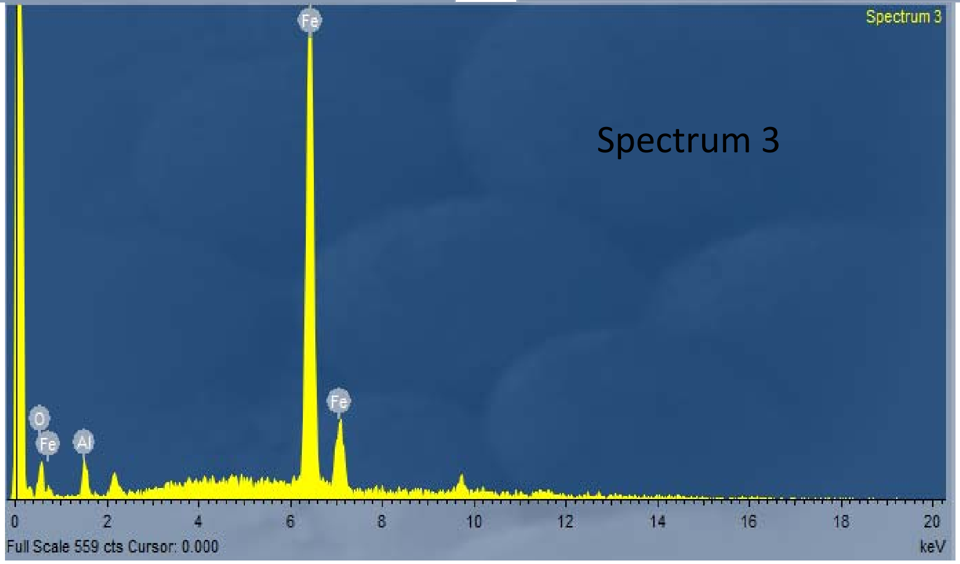


d) x50,000

EDS Spectrum of Sample T03 after 10 CVD Cycles





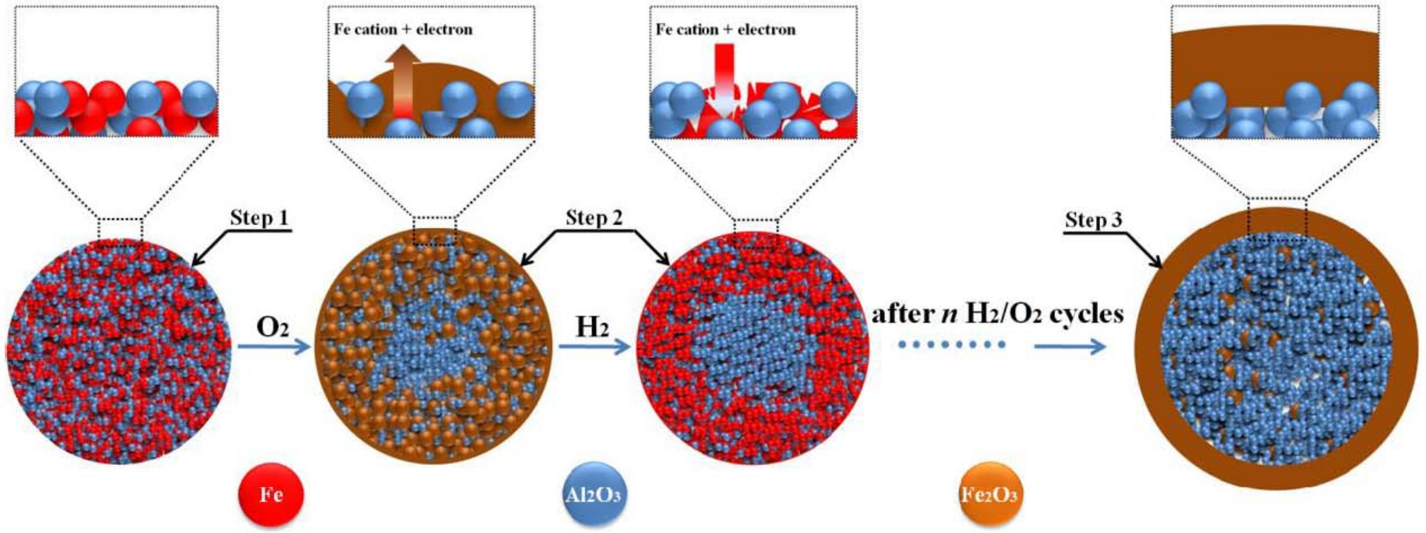


Future work

- 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

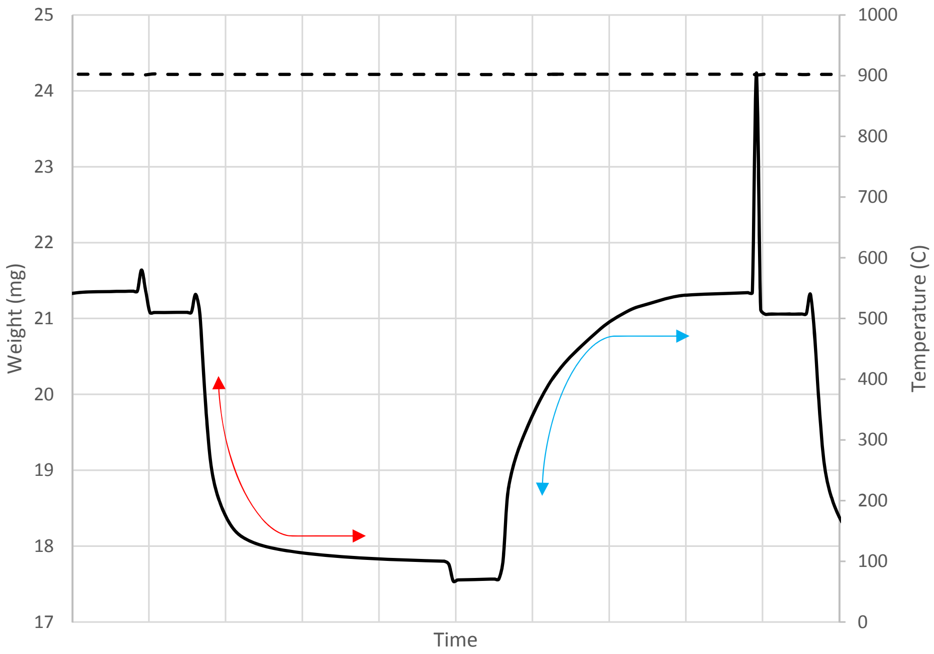
- H_2 balanced with N_2

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

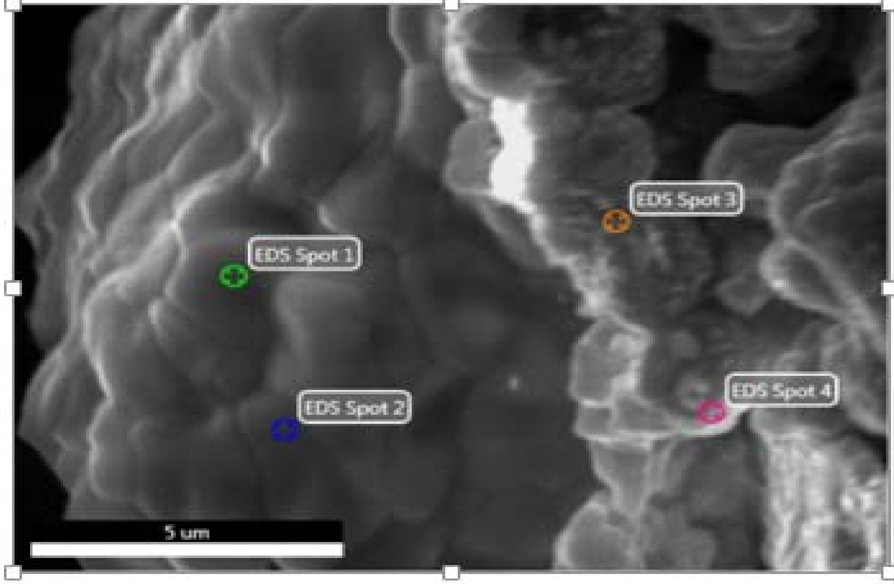
However, the iron-rich shells formed were too thin to be distinguished between different micro-particles. A better method is needed.

Improving Ionic Diffusion

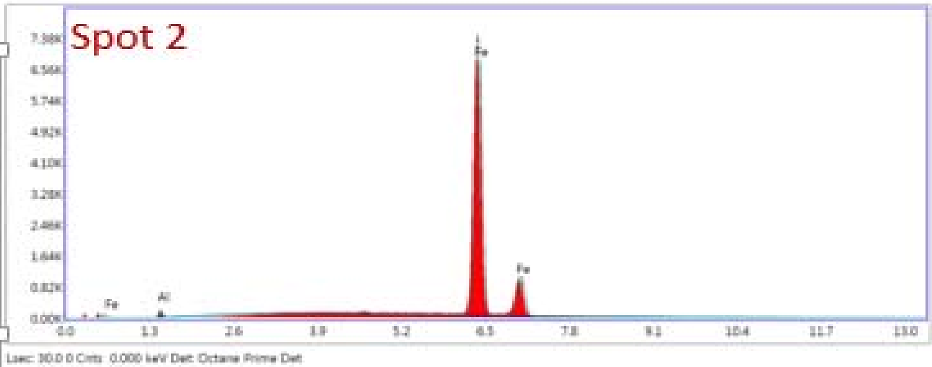
- Reducing gaseous oxygen concentration during oxidation
  - Maintain reduced iron gradient in the particle and prevent iron from being oxidized before diffusion toward the surface

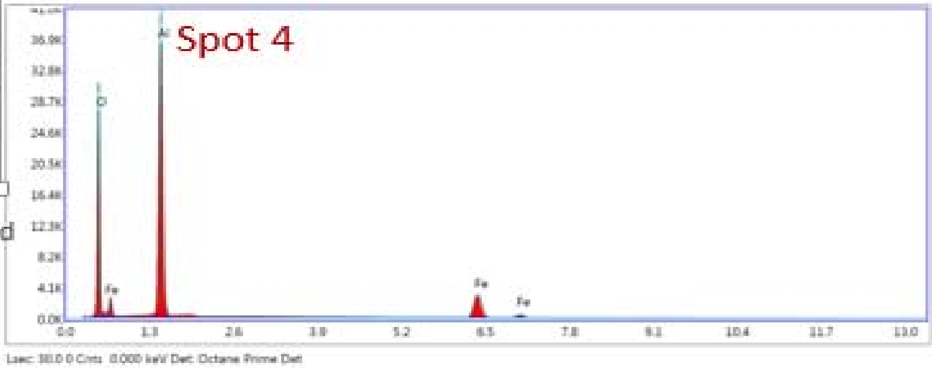
- Increasing nitrogen flushing time
  - Allowing more time for iron to diffuse per redox cycle before being oxidized

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

Acknowledgements

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