

## SYNTHESIS, DECOMPOSITION AND CHARACTERIZATION OF FE AND NI SULFIDES AND FE AND CO NANOPARTICLES FOR AEROSPACE APPLICATIONS

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**Abstract:** We describe several related studies where simple iron, nickel, and cobalt complexes were prepared, decomposed, and characterized for aeronautics (Fischer-Tropsch catalysts) and space (high-fidelity lunar regolith simulant additives) applications. We describe the synthesis and decomposition of several new nickel dithiocarbamate complexes. Decomposition resulted in a somewhat complicated product mix with NiS predominating. The thermogravimetric analysis of fifteen tris(diorganodithiocarbamato)iron(III) has been investigated. Each undergoes substantial mass loss upon pyrolysis in a nitrogen atmosphere between 195° and 370°C, with major mass losses occurring between 279° and 324°C. Steric repulsion between organic substituents generally decreased the decomposition temperature. The product of the pyrolysis was not well defined, but usually consistent with being either FeS or Fe<sub>2</sub>S<sub>3</sub> or a combination of these. Iron nanoparticles were grown in a silica matrix with a long-term goal of introducing native iron into a commercial lunar dust simulant in order to more closely simulate actual lunar regolith. This was also one goal of the iron and nickel sulfide studies. Finally, cobalt nanoparticle synthesis is being studied in order to develop alternatives to crude processing of cobalt salts with ceramic supports for Fischer-Tropsch synthesis.

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# Synthesis and Characterization of Fe and Ni Sulfides & Fe and Co Nano-Particles for Aerospace Applications

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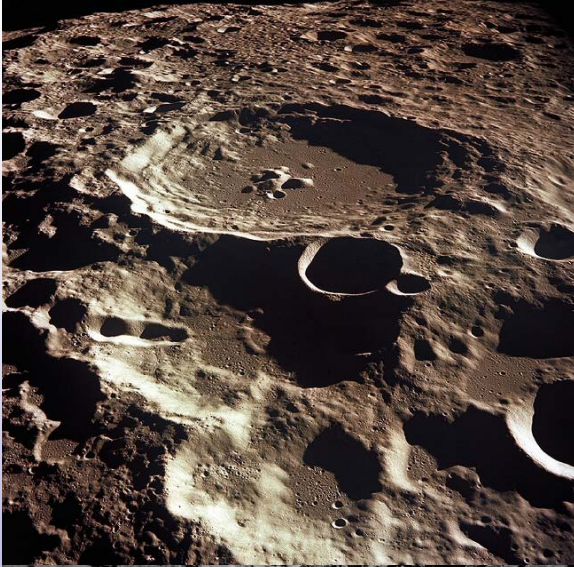


# Outline

- Lunar Regolith
  - Background
- Fischer-Tropsch Catalysis
  - Background
  - NASA Facilities
  - Co nanoparticles
    - Synthesis
    - Characterization



# Lunar Regolith



Regolith-is a layer of loose, heterogeneous material covering solid rock.

Rhegos-Greek-which means blanket

Lithos-Greek- which means rock

Literally translated-blanket of rocks



# Lunar Minerals in High Fidelity Simulants

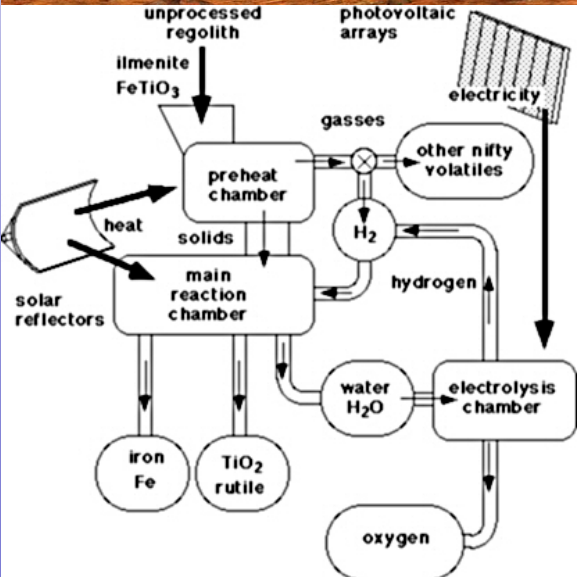
- **Silicate** minerals make up to **90%** volume of lunar rocks
  - Pyroxene -  $(\text{CaFeMg})_2\text{Si}_{12}\text{O}_6$
  - Plagioclase feldspar –  $(\text{CaNa})(\text{AlSi})_4\text{O}_8$
  - Olivine -  $(\text{MgFe})_2\text{SiO}_4$
- **Oxide** minerals make up to **20%** volume of lunar rocks
  - Ilmenite –  $(\text{MgFe})\text{TiO}_3$
  - Spinel –  $\text{FeCr}_2\text{O}_4$ ,  $\text{Fe}_2\text{TiO}_4$ ,  $\text{FeAl}_2\text{O}_4$ ,  $\text{MgTiO}_4$
  - Armalcolite –  $(\text{MgFe})\text{Ti}_2\text{O}_5$
- Low abundance of native metals
  - Fe, Ni, Co
- Most sulfur contained in single mineral
  - Troilite –  $\text{FeS}$
- Traces of many other minerals



# The Importance for High Fidelity Lunar Regolith Simulants

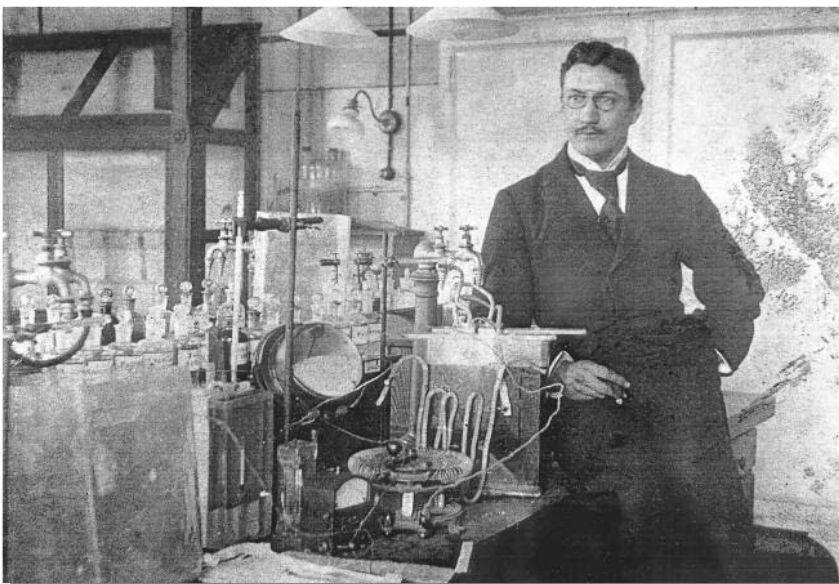


- Abrasion studies
- Thermal conductivity
- Solar attenuation
- Inherent chemistry



# Fischer-Tropsch Catalysis

Franz Fischer at Work in 1918



Financial Mail 2000

## The Fischer-Tropsch Process

### 1) Synthesis Gas Formation



### 2) Fischer-Tropsch Reaction



### 3) Refining



Symtreum



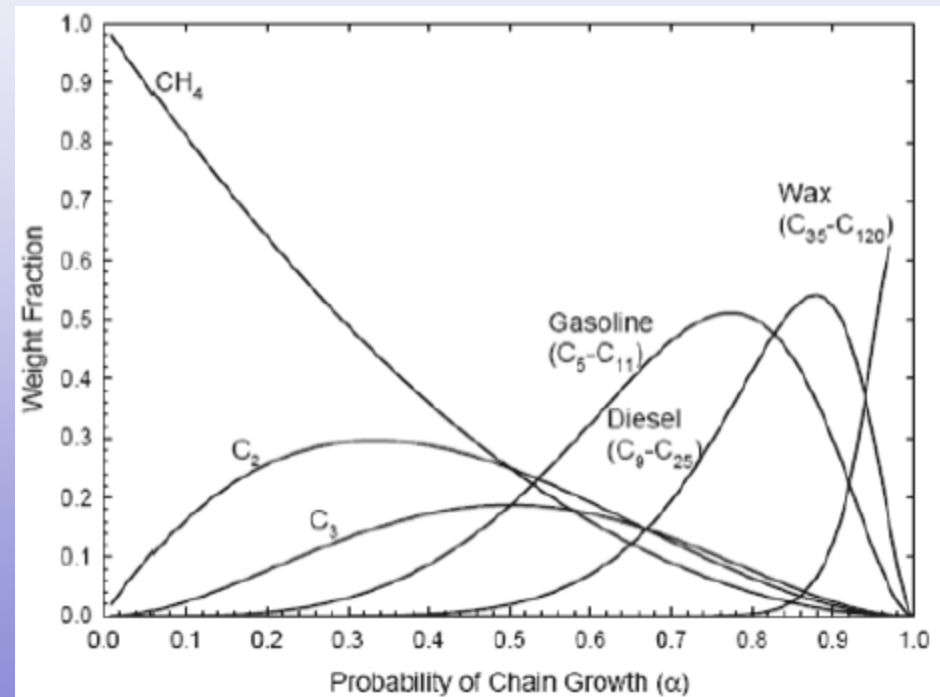
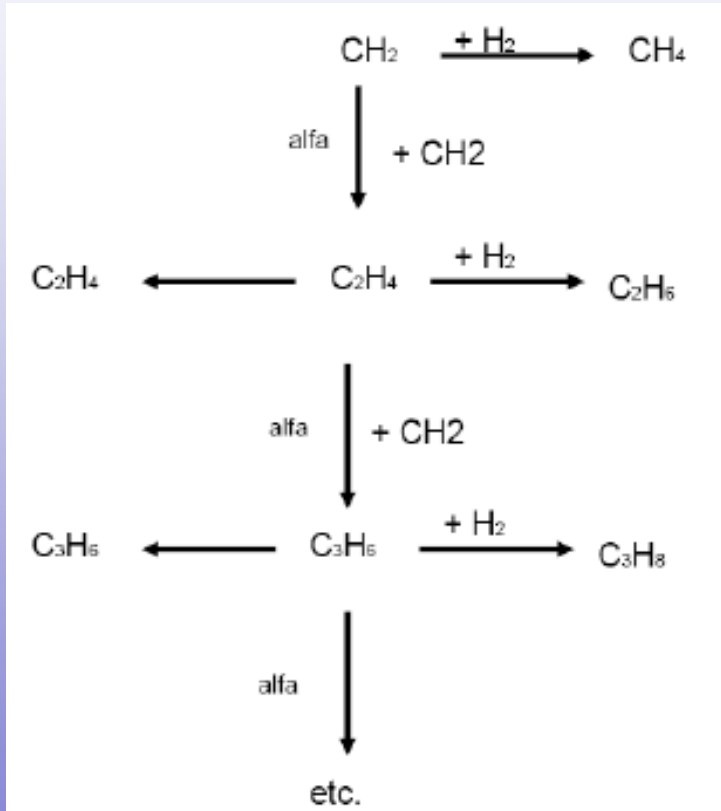
# History of FT Catalysis

- **1897 - Losanitsch and Jovitschitsch**
  - **Converted CO and hydrogen to liquid products using an electrical discharge**
  - **Primary product was formaldehyde**
- **1902 – Sabatier and Senderens**
  - **Converted CO and hydrogen to methane over nickel catalyst**
- **1923 – Fischer and Tropsch**
  - **Converted CO and hydrogen to liquid hydrocarbons using Catalysts used included CO, Fe, and Ru based catalysts**
- **1925 – German patent issued on process**
- **1936 – First commercial plant operates in Germany**
- **1944 – Wartime FT-process production peak**
  - **Germany 16,000 barrels per day**
  - **Japan 1,500 barrels per day**
- **1947 - 1952 US Synthetic Fuels Production**
  - **German plant moved to Louisiana, MO by Bureau of Mines**
  - **Texaco builds 120 bpd plant at Montebello, CA using NG feed**
- **1950 – 1953 Hydrocarbon Res. Inc. builds 5,000 bpd Hydrocol Plant in Brownsville, TX – operates briefly**
- **1953 - Koebel/Ackerman operate full commercial scale FT slurry process plant in Germany using Fe catalyst**
- **1955 – Sasol operates 8,000 bpd SASOL 1 plant in Sasolburg, SA using Fe catalyst and Fixed bed and CFB reactors**





# Alpha-probability of chain growth





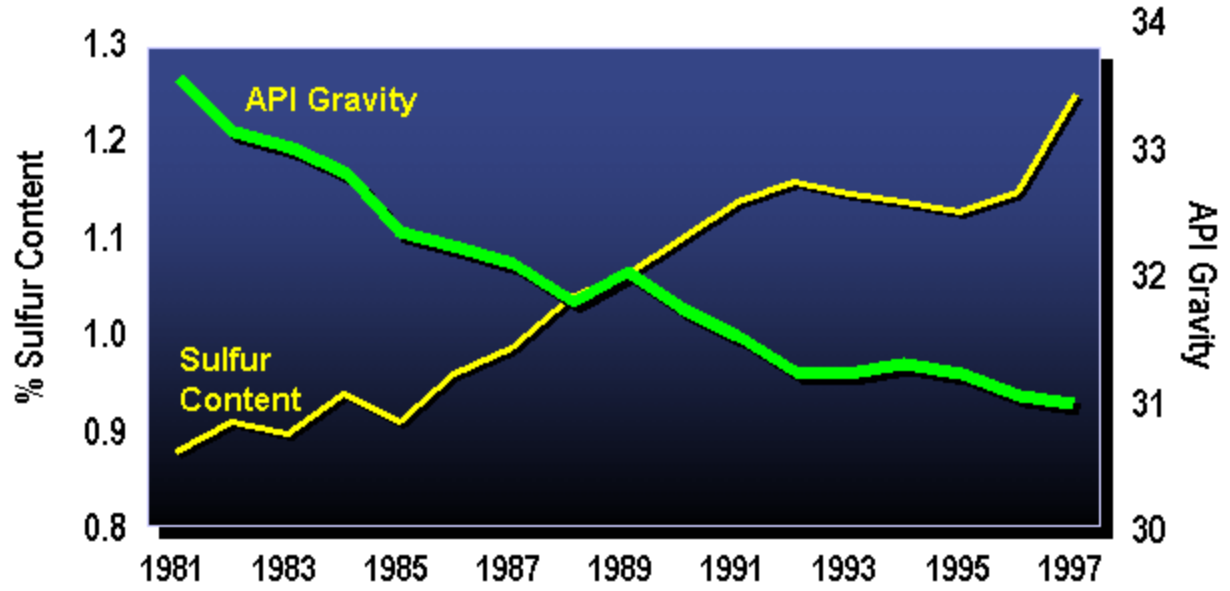
# Pros & Cons of Alternative Fuels

- **FT fuel advantages:**
  - No sulfur
  - Reduced CO emission
  - *Reduced particulate matter (PM) emissions*
  - Less toxic, no aromatics
- **FT fuel Issues**
  - *Low lubricity: new additives or blending (bio-fuel?)*
  - Smaller particle size distribution in particulates emissions
- **Bio-fuel Advantages**
  - Clean burning as F-T fuel
- **Bio-fuel Issues**
  - High freezing point, gel problem
  - Heavier than Jet-A (C16-C18, vs. C12 avg.)



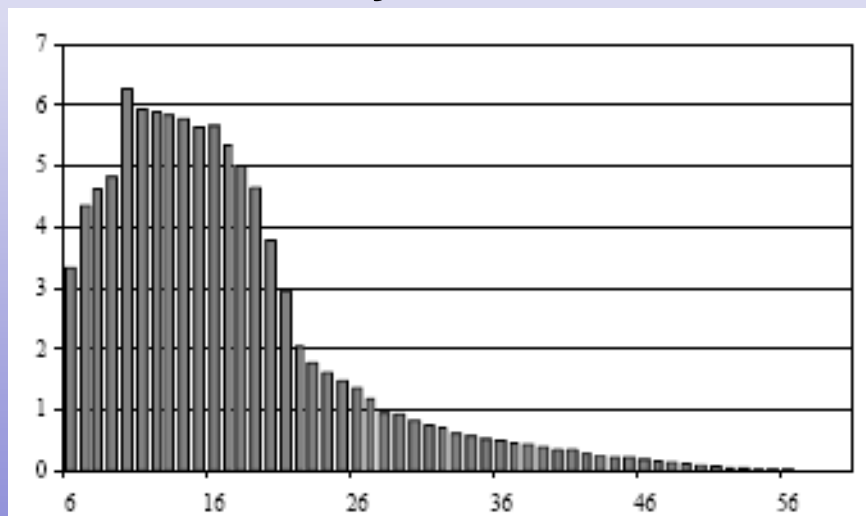
# Clean Fuel Regs Run Counter to Oil Quality Trends

## U.S. Average Crude Quality of Refinery Runs



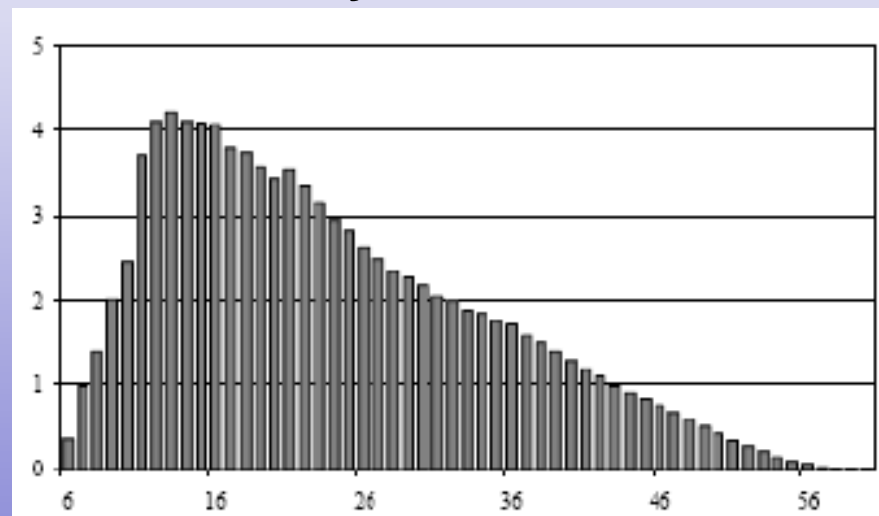
# Product Selectivity Dependent on Catalysts Material

## Fe catalyst distribution



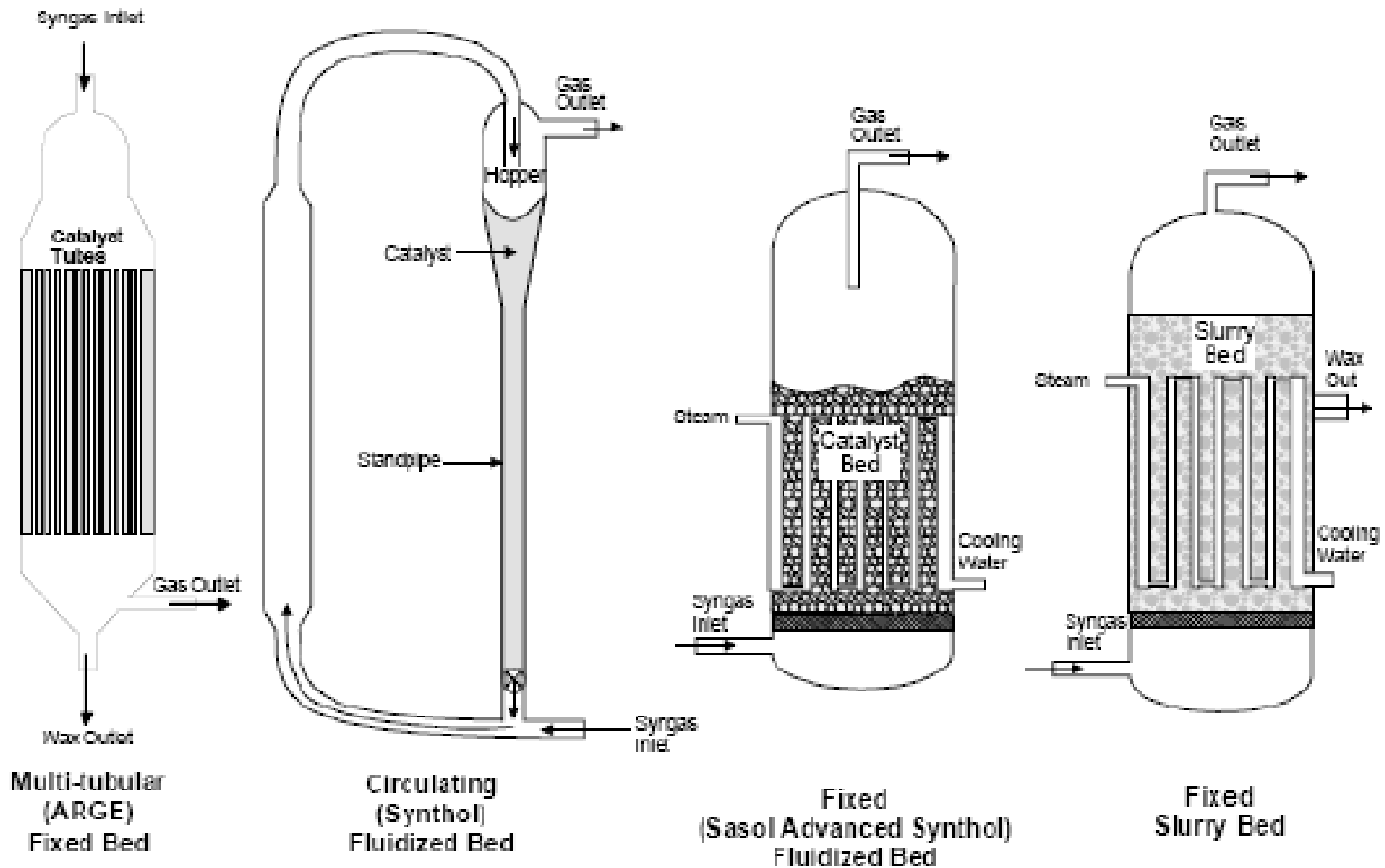
# of Carbon atoms

## Co catalyst distribution



# of Carbon atoms

# Main types of FT Reactors





# Bldg 109 Test Facility



Control Room



Test Facility



Gas Chromatograph work area

## Agilent 6890N Capillary GCs

### Oil + Wax Analysis

- Oils: C4 thru C44 Alkanes and Alkenes
  - Sample Prep – 0.2 ml Neat Injection (inj)
- Wax: C11 thru C80 Alkanes and Alkenes
  - Sample Prep – Dissolve w/O-Xylene (1 ml inj)
- FID – carrier gases H<sub>2</sub>, He & Zero-Air
- Data Acquisition – Cerity NDS Software



## RGA (Refinery Gas Analyzer)

### Agilent 3000A Micro GC

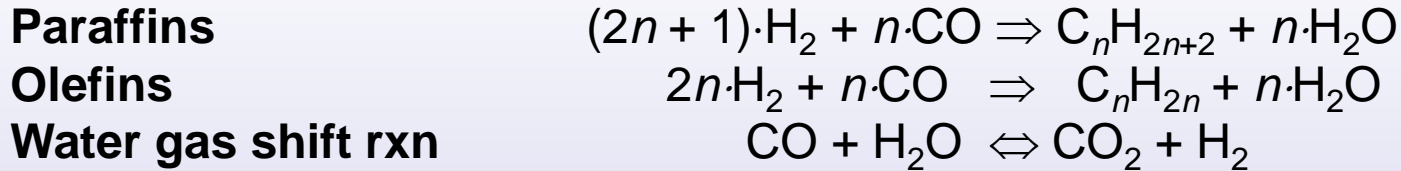
- CO, CO<sub>2</sub>, H<sub>2</sub>, N<sub>2</sub> & C1 thru C8 Hydrocarbons
- TCD detector w/4 columns – carrier gas He & Ar
  - Gas Samples – Continuous from reactors
- Data Acquisition – Cerity NDS Software







## Fischer-Tropsch Reaction – Over View Chemistry & Testing



### Catalysts

Cobalt

Iron

### Pressure

180 – 450 psig

180 – 450 psig

### Temperature

210 – 240 °C

240 – 270 °C

### Feed conditions / test variables (typical)

H<sub>2</sub>:CO ratio

0.6 – 2.5

H<sub>2</sub> / CO flow rates

20 – 100 SLPH

(Max design 120 SLPH – H<sub>2</sub>/CO/Ar)

Argon mol %

10 – 50 (inert carrier gas)

Space velocity

1,000 to 10,000 hr<sup>-1</sup> at STP (2 – 4 SLPH/gm-Cat)

Catalyst Type

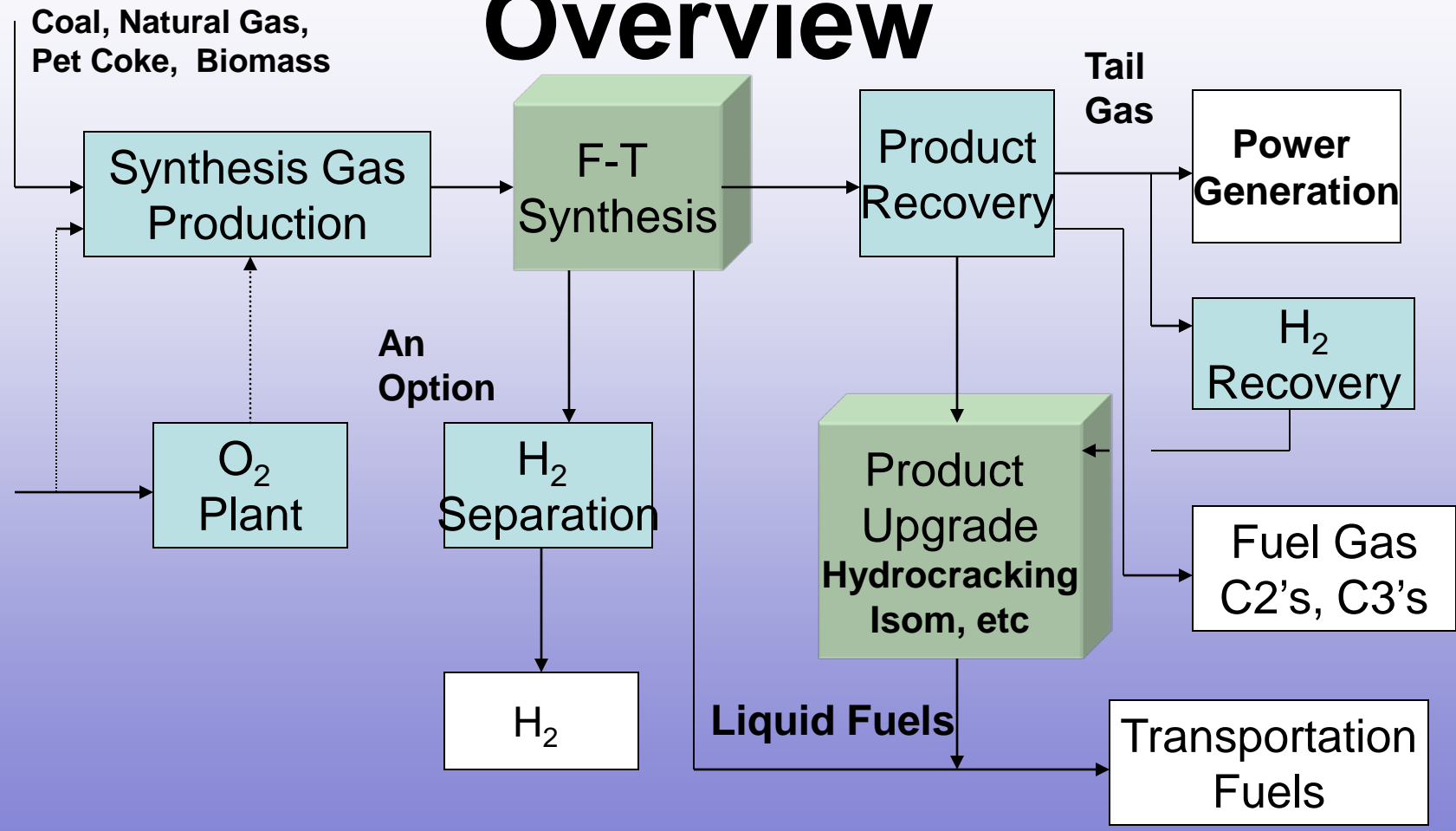
Co, Fe, Ru; promoted/unpromoted; supports

Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, TiO<sub>2</sub>



# Fischer-Tropsch Process

## Overview

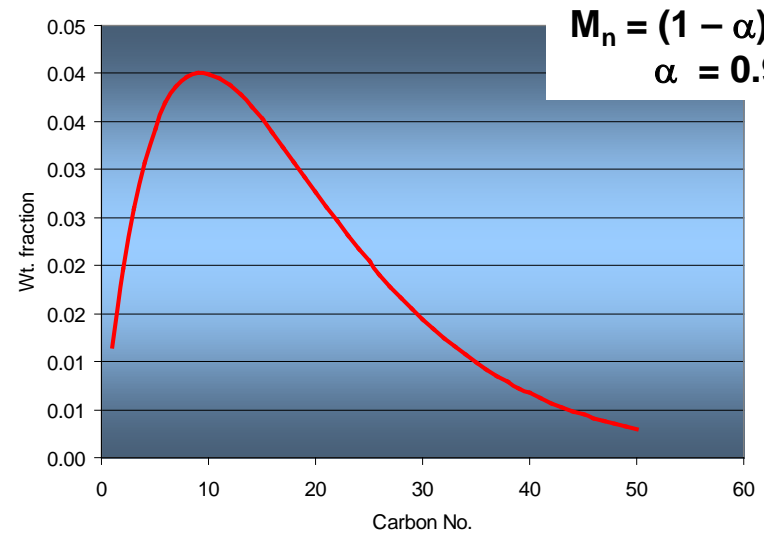


# Fischer-Tropsch - Products of Reaction

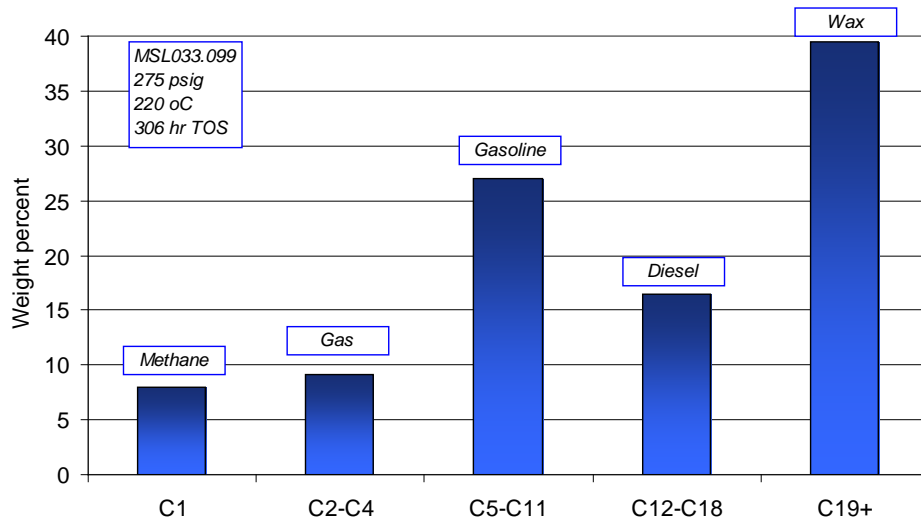
Cobalt Catalyst Wax    Iron Catalyst Wax



Anderson-Schulz-Flory Distribution



F-T Product Distribution - UofKy



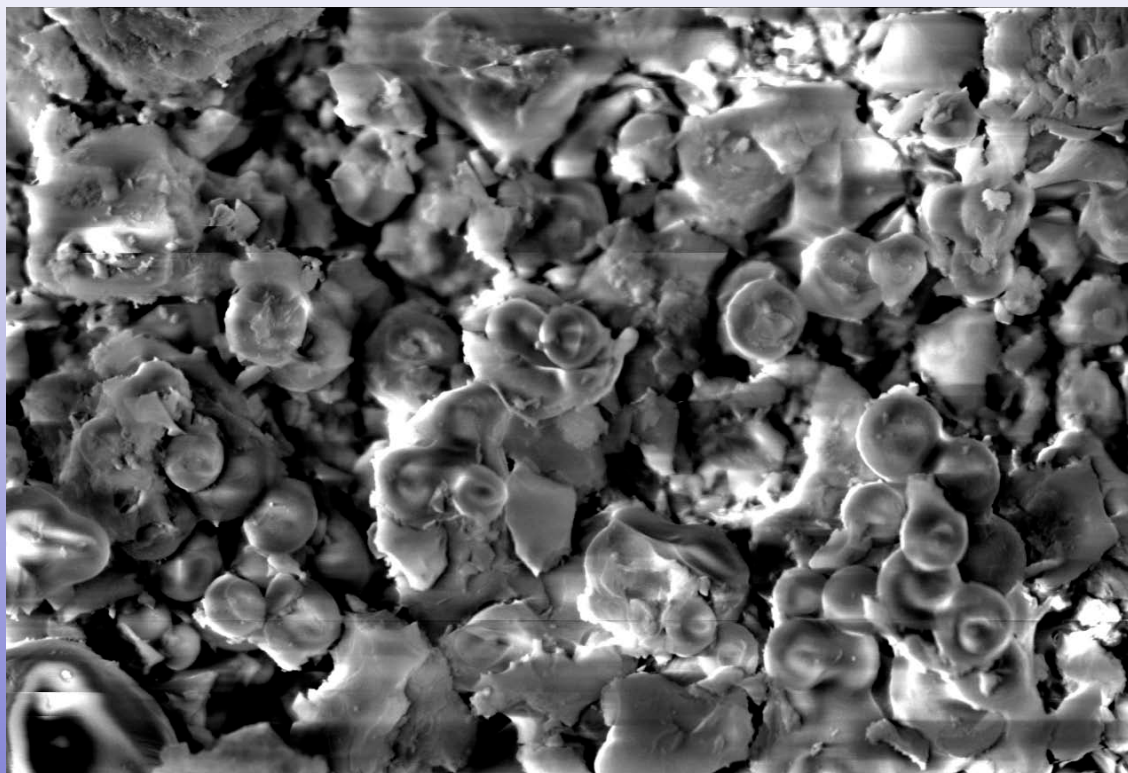
F-T Light Oil Product Sample



# Synthesis of SiO<sub>2</sub> supports



TEOS - tetraethylorthosilicate

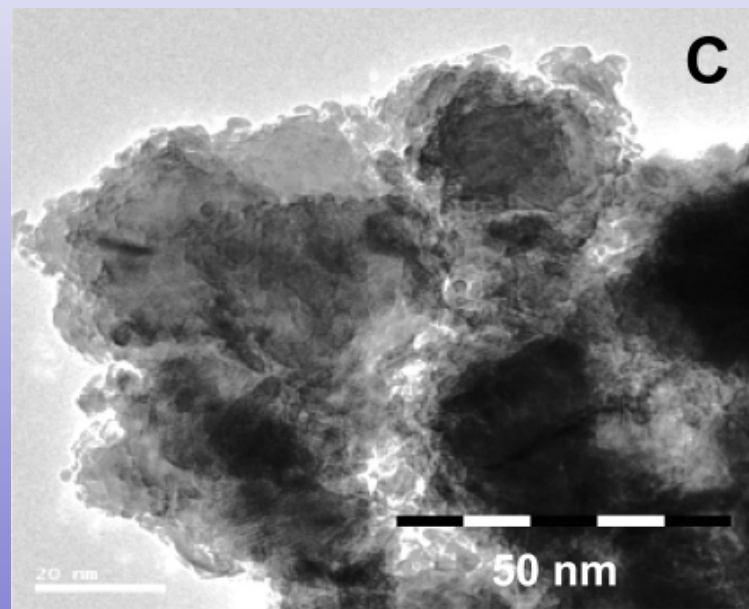


SE 15:10 000000 WD 6.6mm 10.0kV x1.5k 20um

# Typical synthesis of Co loaded SiO<sub>2</sub> supports

- Cobalt is typically loaded onto commercially available supports.
- Cobalt precursors are typically CoCl<sub>2</sub>·6H<sub>2</sub>O or Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O
- Loading is typically ~ 10-20% by weight.
- Loading is usually achieved through **chemical infiltration** or **Incipient wetness impregnation**.
- Often promoters are added to enhance the activation of the catalysts.
  - Common promoters include Pt, Re, Ru, Pd.
  - Loading of the promoters is typically ~ 0.5-3.0% by weight.

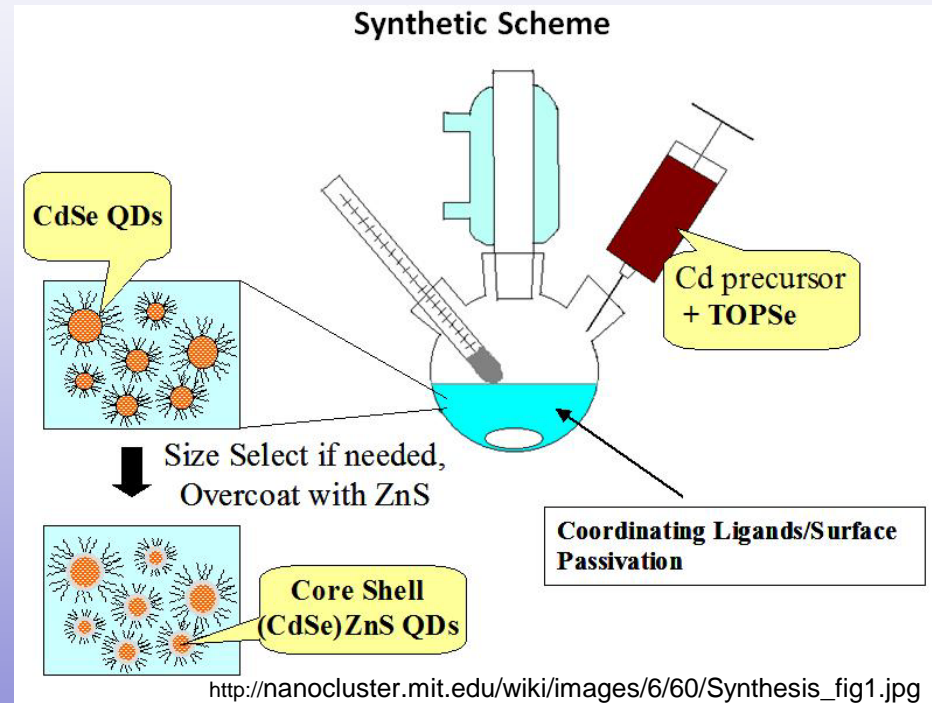
This type of deposition yields catalysts with much non-uniformity with regards to shape and size



**X-ray absorption spectroscopy of Mn/Co/TiO<sub>2</sub>**  
 Morales, Fernando; Grandjean, Didier; Mens, Ad; de Groot, Frank M. F.; Weckhuysen, Bert M. Journal of Physical Chemistry B (2006), 110(17), 8626-8639.

# Synthesis of Co particles

- Co source is  $\text{Co}_2(\text{CO})_8$
- Capping group/Surfactant
  - TOPO
  - TOP
  - Oleic Acid
  - $\text{PPh}_3$
- Adjustable parameters
  - Temp
  - Time
  - Concentration/surfactant ratio



# Synthesis Lab at NASA GRC

Reactions are carried out under inert atmosphere conditions

Glove box to store air sensitive materials



Schlenk line

Reaction temperature controlled via programmable temperature controller



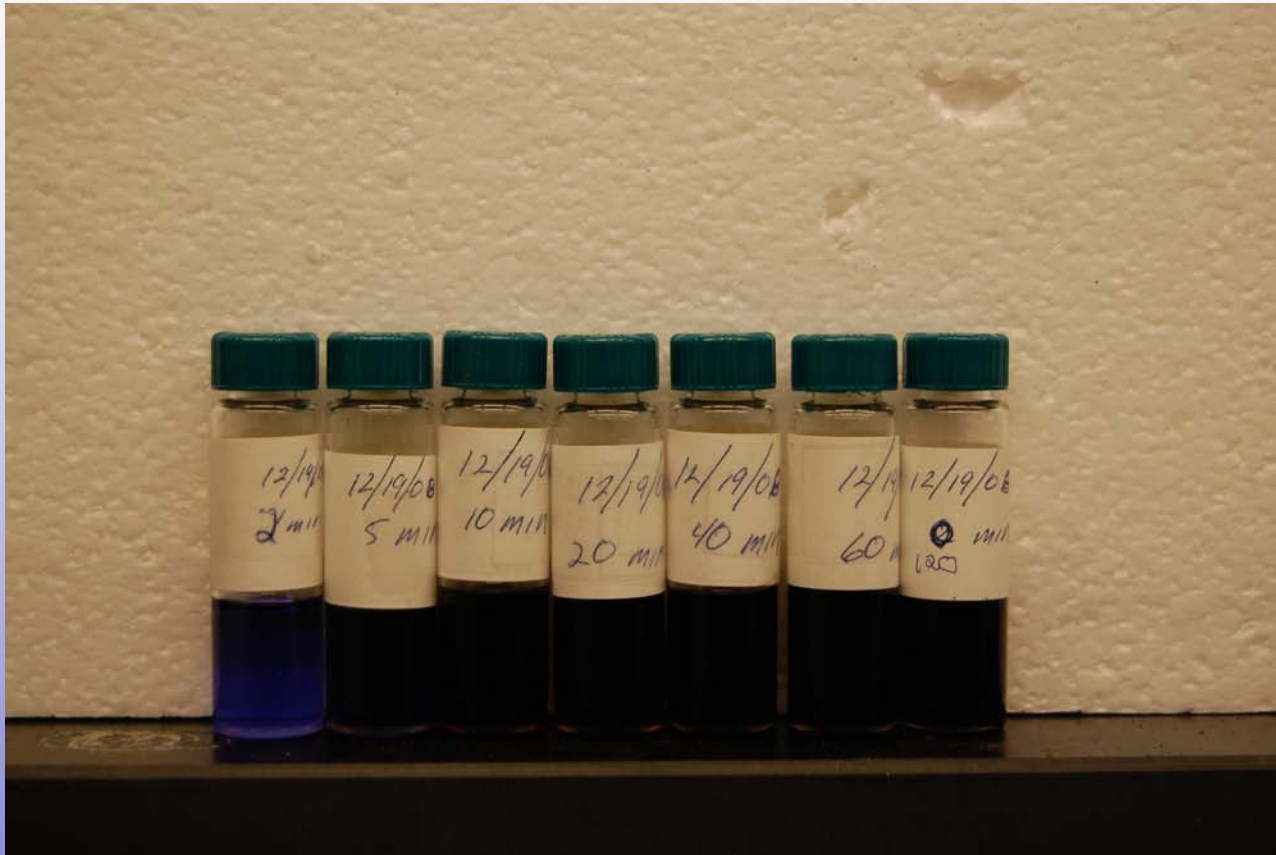
# Synthesis Lab at NASA GRC



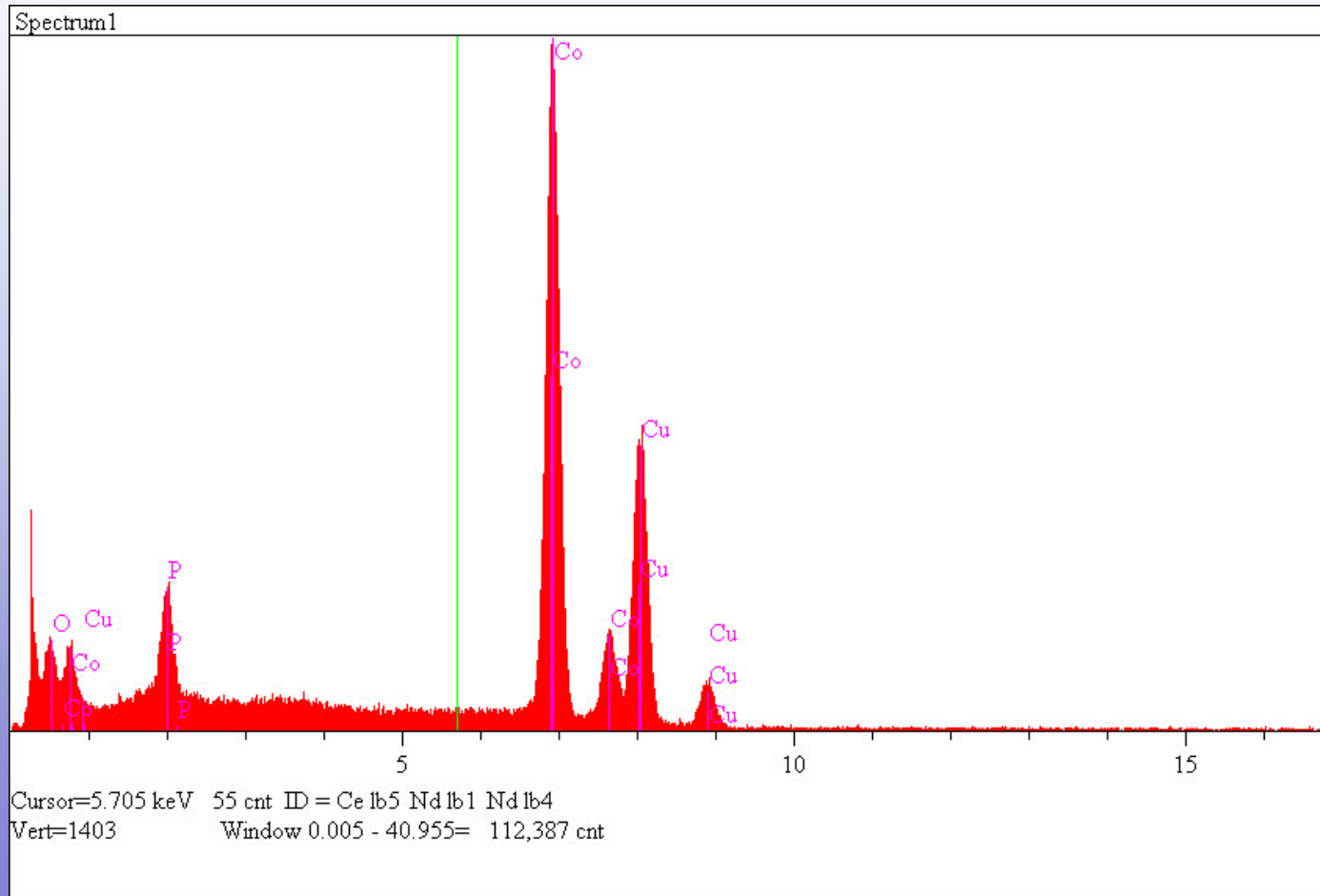




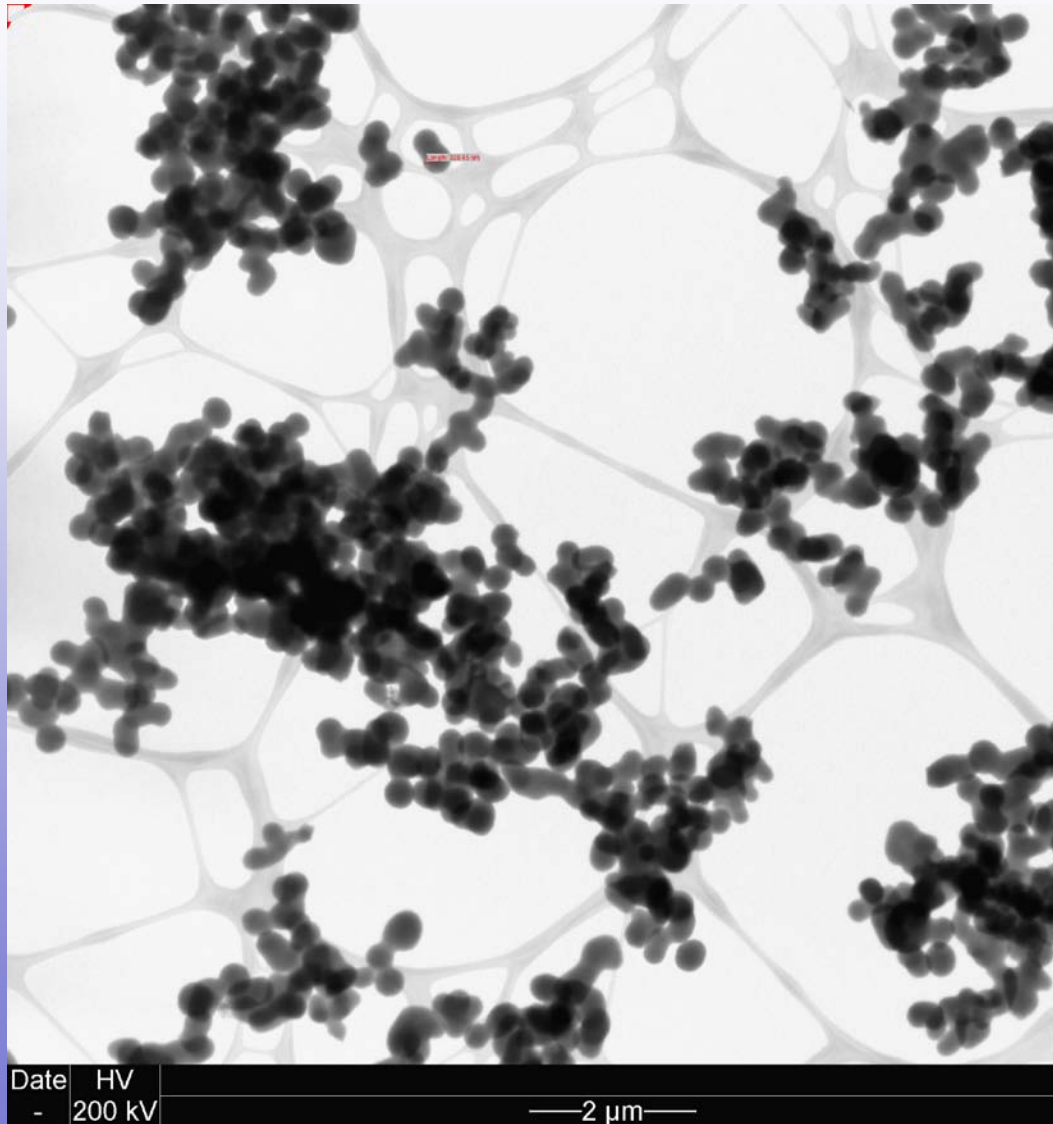
# Co particles



# EDS Spectrum of Co Particles



# Co Particles





XRD Pattern of Co Particles

