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\degree and 370\degree C, with major mass losses occurring between 279\degree and 324\degree 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\textsubscript{2}S\textsubscript{3} 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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Mr. Jonathan C. Cowen is a graduate student presenter from CWRU.
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 – 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

The Fischer-Tropsch Process

1) Synthesis Gas Formation

\[ \text{Catalyst} \quad \text{CH}_n + \text{O}_2 \rightarrow \frac{1}{2} n \text{H}_2 + \text{CO} \]

2) Fischer-Tropsch Reaction

\[ \text{Catalyst} \quad 2n \text{H}_2 + \text{CO} \rightarrow - (\text{CH}_2^-)_n^- + \text{H}_2\text{O} \]

3) Refining

\[ \text{Catalyst} \quad - (\text{CH}_2^-)_n^- \rightarrow \text{Fuels, lubricants, etc.} \]
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 - Koelbel/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

- API Gravity
- Sulfur Content

American Petroleum Institute (API > 10 floats on water  API < 10 sinks in water)
Product Selectivity Dependent on Catalysts Material

Fe catalyst distribution

Co catalyst distribution

\# of Carbon atoms

\# of Carbon atoms
Main types of FT Reactors

- Multi-tubular (ARGE) Fixed Bed
- Circulating (Synthol) Fluidized Bed
- Fixed (Sasol Advanced Synthol) Fluidized Bed
- Fixed Slurry Bed
Bldg 109 Test Facility

Control Room

Gas Chromatograph work area

Test Facility
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 H2, He & Zero-Air
- Data Acquisition – Cerity NDS Software

RGA (Refinery Gas Analyzer)

Agilent 3000A Micro GC

- CO, CO2, H2, N2 & 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

\[ 2\text{H}_2 + \text{CO} \rightarrow \text{CH}_2\text{C} + \text{H}_2\text{O} \] (exothermic)

<table>
<thead>
<tr>
<th>Paraffins</th>
<th>((2n + 1)\cdot\text{H}<em>2 + n\cdot\text{CO} \Rightarrow \text{C}</em>{n\cdot\text{H}_{2n+2}} + n\cdot\text{H}_2\text{O})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Olefins</td>
<td>(2n\cdot\text{H}<em>2 + n\cdot\text{CO} \Rightarrow \text{C}</em>{n\cdot\text{H}_{2n}} + n\cdot\text{H}_2\text{O})</td>
</tr>
<tr>
<td>Water gas shift rxn</td>
<td>(\text{CO} + \text{H}_2\text{O} \Leftrightarrow \text{CO}_2 + \text{H}_2)</td>
</tr>
</tbody>
</table>

**Catalysts**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pressure</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cobalt</td>
<td>180 – 450 psig</td>
<td>210 – 240 °C</td>
</tr>
<tr>
<td>Iron</td>
<td>180 – 450 psig</td>
<td>240 – 270 °C</td>
</tr>
</tbody>
</table>

**Feed conditions / test variables** (typical)

<table>
<thead>
<tr>
<th>Condition</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{H}_2\cdot\text{CO} \text{ ratio})</td>
<td>0.6 – 2.5</td>
</tr>
<tr>
<td>(\text{H}_2 / \text{CO} \text{ flow rates})</td>
<td>20 – 100 SLPH (Max design 120 SLPH – (\text{H}_2/\text{CO}/\text{Ar}))</td>
</tr>
<tr>
<td>(\text{Argon} \text{ mol} %)</td>
<td>10 – 50 (inert carrier gas)</td>
</tr>
<tr>
<td>(\text{Space velocity})</td>
<td>1,000 to 10,000 hr(^{-1}) at STP (2 – 4 SLPH/gm-Cat)</td>
</tr>
<tr>
<td>(\text{Catalyst Type})</td>
<td>Co, Fe, Ru; promoted/unpromoted; supports Al(_2)O(_3), SiO(_2), TiO(_2)</td>
</tr>
</tbody>
</table>
Fischer-Tropsch Process Overview

Coal, Natural Gas, Pet Coke, Biomass

Synthesis Gas Production → F-T Synthesis → Product Recovery

An Option:

O₂ Plant → H₂ Separation → H₂ → Product Upgrade Hydrocracking Isom, etc

H₂ Recovery → Fuel Gas C2’s, C3’s

Power Generation

Tail Gas

Liquid Fuels → Transportation Fuels
Fischer-Tropsch - Products of Reaction

Cobalt Catalyst Wax  Iron Catalyst Wax

F-T Product Distribution - UofKy

Anderson-Schulz-Flory Distribution

\[ M_n = (1 - \alpha) \alpha^{(n-1)} \]
\[ \alpha = 0.9 \]

F-T Light Oil Product Sample

Methane  Gas  Gasoline  Diesel  Wax

F-T Product Distribution - UofKy

- MSL033.099
- 275 psig
- 220 oC
- 306 hr TOS
Synthesis of SiO₂ supports

\[
\text{Si(OR)}_4 + 4 \text{H}_2\text{O} \rightarrow \text{Si(OH)}_4 + 4 \text{ROH}
\]

TEOS - tetraethylorthosilicate
Typical synthesis of Co loaded SiO$_2$ supports

- Cobalt is typically loaded onto commercially available supports.
  - Cobalt precursors are typically CoCl$_2$·6H$_2$O or Co(NO$_3$)$_2$·6H$_2$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$_2$
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
  - PPh$_3$
- Adjustable parameters
  - Temp
  - Time
  - Concentration/surfactant ratio
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

Cursor = 5.705 keV  55 cnt  ID = Ce b5 Nd b1 Nd b4
Vert = 1403        Window 0.005 - 40.955 = 112,387 cnt
Co Particles