Characterization of Catalyst Materials for Production of Aerospace Fuels

Due to environmental, economic, and security issues, there is a greater need for cleaner alternative fuels. There will undoubtedly be a shift from crude oil to non-petroleum sources as a feedstock for aviation (and other transportation) fuels. Additionally, efforts are concentrated on reducing costs coupled with fuel production from non-conventional sources. One solution to this issue is Fischer-Tropsch gas-to-liquid technology. Fischer-Tropsch processing of synthesis gas (CO/H₂) produces a complex product stream of paraffins, olefins, and oxygenated compounds such as alcohols and aldehydes. The Fisher-Tropsch process can produce a cleaner diesel oil fraction with a high cetane number (typically above 70) without any sulfur or aromatic compounds. This process is most commonly catalyzed by heterogeneous (in this case, silver and platinum) catalysts composed of cobalt supported on alumina or unsupported alloyed iron powders. Physisorption, chemisorptions, scanning electron microscopy (SEM), and energy dispersive spectroscopy (EDS) are described to better understand the potential performance of Fischer-Tropsch cobalt on alumina catalysts promoted with silver and platinum. The overall goal is to preferentially produce C8 to C18 paraffin compounds for use as aerospace fuels. Progress towards this goal will eventually be updated and achieved by a more thorough understanding of the characterization of catalyst materials. This work was supported by NASA’s Subsonic Fixed Wing and In-situ Resource Utilization projects.
Characterization of Catalyst Materials for Production of Aerospace Fuels

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Overview

Introduction

- Motivation
- Fischer-Tropsch Background

Alternative Fuels Laboratory

Catalyst Synthesis Methodology

Characterization

- Brunauer, Emmett, Teller (BET) Surface Area
- Temperature-Programmed Reduction (TPR)
- Scanning Electron Microscopy (SEM)/Energy Dispersive Spectroscopy (EDS)

Results & Conclusion
Motivation

Aeronautics and other transportation controlled by availability of non-renewable fossil fuels

New/Affordable renewable energies key to continuation of aeronautics future technologies

- Gas-to-Liquid (GTL) Technology
- Fischer-Tropsch Process

Image(s) credit: www.nasa.gov/topics/aeronautics
Why Gas-to-Liquid Technology (GTL)?

Fischer-Tropsch Synthesis

Produced From Natural Gas, Coal, and Biomass

Synthetic Petroleum and Chemical Feedstock

Products can be used in Existing Infrastructure

Reduced Emissions

Image credit: Sasol Chevron
Fischer-Tropsch Synthesis

\[(2n+1)H_2 + nCO \xrightarrow{\text{Catalyst}} C_nH_{2n+2} + nH_2O\]
\[\Delta H = -49 \text{ kcal/mol (n=1)}\]

FTS upgrades syn-gas to a wide array of products:
- Hydrocarbons
- Oxygenated compounds
- Alcohols

Significant Alternative Fuel Source – Products can be converted to useful aviation fuel (C_8 – C_{18} hydrocarbon chains)
Metallic catalyst is needed to facilitate reaction between CO and H₂

✓ Most active metals: Co, Fe, Ru, Ni

✓ Catalyst is vital to performance of FT reaction

Commercial Applications – FT synthesis utilizes Co and Fe due to lower costs

✓ Co highly active – used for high H₂:CO ratio (natural gas)
✓ Fe used for low quality feedstocks (due to water-gas-shift activity)

NASA GRC Catalysis Team – Cobalt Catalyst Research
Cobalt FT Catalysts and Promoters

Cobalt catalysts supported on high surface area binders (such as alumina - Al₂O₃ or silica - SiO₂)
✓ NASA GRC Research – Cobalt/Alumnia Catalysts

✓ Promoters – Transition Metals
✓ Promoters Benefits:
  o Enhance catalytic properties
  o Increase cobalt oxide reducibility
  o Stabilize catalyst

Mn and Ag considered due to low cost vs. Pt-group metals!
NASA GRC Alternative Fuels Laboratory

- $3 Million facility, opened in 2010
- 3 CSTR FT Reactors
- Automated product analysis capabilities (GC)
Catalyst Synthesis

Cobalt Nitrate (Co(NO$_3$)$_2$·6H$_2$O) solution added dropwise to Alumnia (Al$_2$O$_3$)

Cobalt Nitrate/Alumnia soln. placed on Rotavapor® 210 for water extraction until dry

Promoter metal salt solutions added dropwise – rotavap until dry

Catalyst calcinated – left with Co/Promoter/Al$_2$O$_3$

Characterization
Catalyst Characterization

Characterization Goal: Understand surface of catalyst at reaction specific conditions

- Heterogeneous catalyst that can generate specific range of hydrocarbons needed

- Brunauer, Emmett, and Teller surface area analysis (BET) – surface adsorption and catalytic activity/unit area
- Temperature-Programmed Reduction (TPR) – catalyst behavior based on material composition
- Scanning Electron Microscopy (SEM)/Energy Dispersive Spectroscopy (EDS) – material composition and surface properties
Characterization Instruments

Temperature-Programmed Reduction (TPR)
- Micromeritics AutoChem II 2920

Brunauer, Emmett, and Teller Surface Area Analysis (BET)
- Micromeritics FlowSorb II 2300

Scanning Electron Microscopy (SEM)/Energy Dispersive Spectroscopy (EDS) – Hitachi S-3000N
Catalyst Study

 ✓ In this study, unpromoted and promoted (Pt and Ag) catalysts will be compared

 ✓ Pt and Ag will be also be compared to evaluate economical promoter options

Table 1. Samples of Promoted/Unpromoted Co/Alumina Catalysts Prepared at NASA GRC

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Promoter</th>
<th>ICP-AES Element Analysis (Galbraith Laboratories, Inc.)</th>
<th>Energy Dispersive Spectroscopy (EDS)</th>
<th>Surface Area (m²/g)</th>
<th>Reduction Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>None</td>
<td>21.6% Co/Al₂O₃</td>
<td>30.3% Co/Al₂O₃</td>
<td>126.3</td>
<td>350</td>
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<tr>
<td>2</td>
<td>None</td>
<td>9.31% Co/Al₂O₃</td>
<td>9.45% Co/Al₂O₃</td>
<td>142.4</td>
<td>335</td>
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<tr>
<td>3</td>
<td>None</td>
<td>31.7% Co/Al₂O₃</td>
<td>47.2% Co/Al₂O₃</td>
<td>108.7</td>
<td>436</td>
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<tr>
<td>4</td>
<td>Pt</td>
<td>21.5% Co/0.845% Pt/Al₂O₃</td>
<td>25.4% Co/2.57% Pt/Al₂O₃</td>
<td>123.7</td>
<td>254</td>
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<tr>
<td>5</td>
<td>Pt</td>
<td>20.9% Co/0.397% Pt/Al₂O₃</td>
<td>24.1% Co/1.49% Pt/Al₂O₃</td>
<td>106.6</td>
<td>349</td>
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<tr>
<td>6</td>
<td>Pt</td>
<td>24.8% Co/0.459% Pt/Al₂O₃</td>
<td>34.8% Co/2.30% Pt/Al₂O₃</td>
<td>115.9</td>
<td>265</td>
</tr>
<tr>
<td>7</td>
<td>Ag</td>
<td>21.0% Co/0.806% Ag/Al₂O₃</td>
<td>25.9% Co/1.31% Ag/Al₂O₃</td>
<td>118.2</td>
<td>275</td>
</tr>
<tr>
<td>8</td>
<td>Ag</td>
<td>23.6% Co/0.278% Ag/Al₂O₃</td>
<td>33.3% Co/2.19% Ag/Al₂O₃</td>
<td>109.4</td>
<td>369</td>
</tr>
<tr>
<td>9</td>
<td>Ag</td>
<td>22.9% Co/0.510% Ag/Al₂O₃</td>
<td>26.7% Co/1.63% Ag/Al₂O₃</td>
<td>117.6</td>
<td>337</td>
</tr>
</tbody>
</table>
Promoted vs. Unpromoted Catalysts

- Addition of promoter decreases the necessary activation temperature of catalyst
- Since cobalt fills porous space of catalyst, promoter does not reduce surface area by significant amount

*For higher accuracy purposes, ICP-AES data was used*
Cobalt Loading and Catalyst Surface Area

- Weight percent of cobalt loading analyzed
- Downward trend with regards to Co% and surface area
- Additional Co fills porous space of Al₂O₃
**Platinum & Silver and Reduction Temperature**

- Addition of promoters reduces reduction temperature.
- As wt.% of promoter increases, temperature decreases.
- Platinum has a greater effect on T than silver.
- Temp. reduction is still significant with Ag.

![Graph showing the relationship between reduction temperature and weight percent of promoters for Silver and Platinum.](image)
Surfaces look smooth and spherical – Particles look evenly dispersed!

21.6% Co/Al₂O₃ catalyst at 250X

9.31% Co/Al₂O₃ catalyst at 600X

21.5% Co/0.845% Pt/ Al₂O₃ catalyst at 200X

21.0% Co/0.806% Ag/ Al₂O₃ catalyst at 600X
Conclusions and Future Work

✓ Increase in Co loaded → surface area decreases
  ✓ Smoother Surface
  ✓ Promoter attaches to surface – no increase/decrease in SA

✓ Promoting Co/Al₂O₃ decreases reduction temp.
  ✓ Platinum-group metals great choice (reduces extent!)
  ✓ Silver may be a good economical option

Future Work:
- Investigate other promoters in platinum and coinage metals
- Additional supports (TiO₂, SiO₂)
- Pulse re-oxidation to investigate extent of reduction
- X-Ray Diffraction (XRD) to examine crystal structure
Acknowledgements

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Questions?