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/H_2) 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

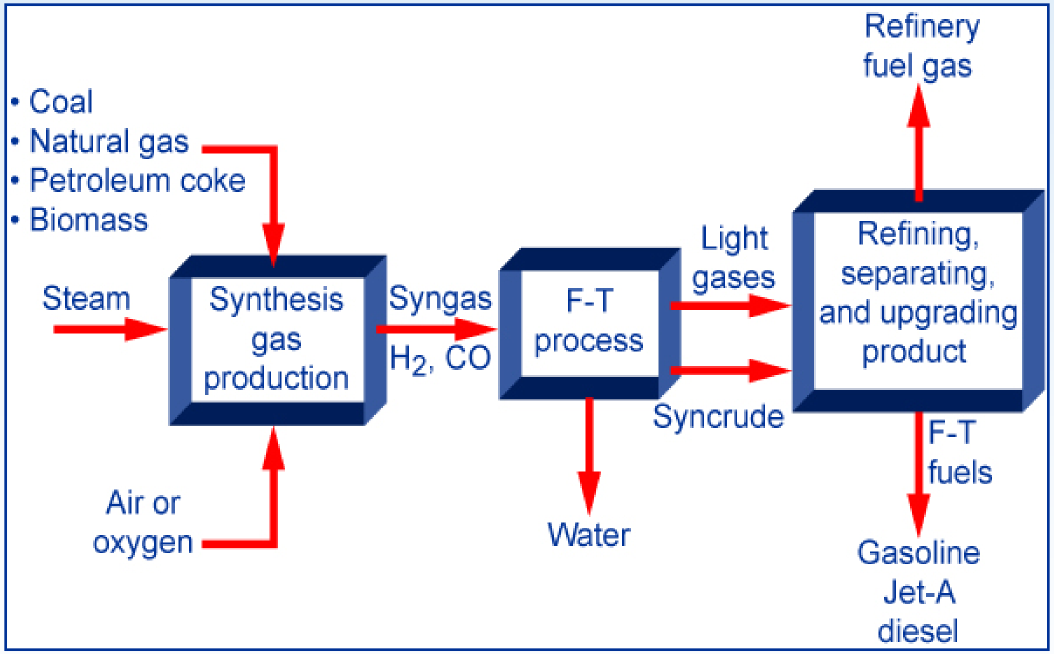
- Produced From Natural Gas, Coal, and Biomass
- Synthetic Petroleum and Chemical Feedstock
- Products can be used in Existing Infrastructure
- Reduced Emissions

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**

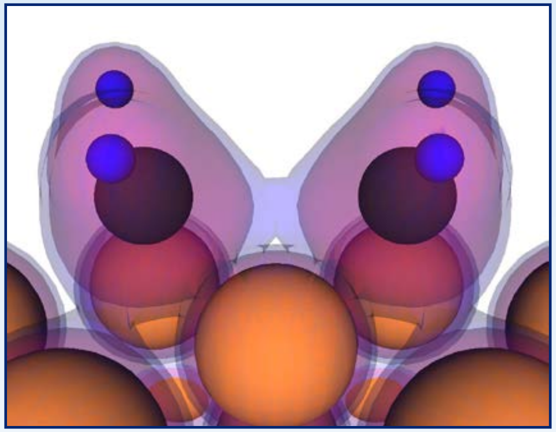
Significant Alternative Fuel Source **– Products can be converted to useful aviation fuel (C_8 – C_{18} hydrocarbon chains)**

Fischer-Tropsch Catalysts

Metallic catalyst is needed to facilitate reaction between CO and H_2

NASA cobalt catalyst

- ✓ **Most active metals: Co, Fe, Ru, Ni**
- ✓ **Catalyst is vital to performance of FT reaction**



FT surface-catalyzed polymerization reaction

Image credit: Univ. of Wisconsin

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

- ✓ **Co highly active – used for high H_2:CO ratio (natural gas)**
- ✓ **Fe used for low quality feedstocks (due to water-gas-shift activity)**

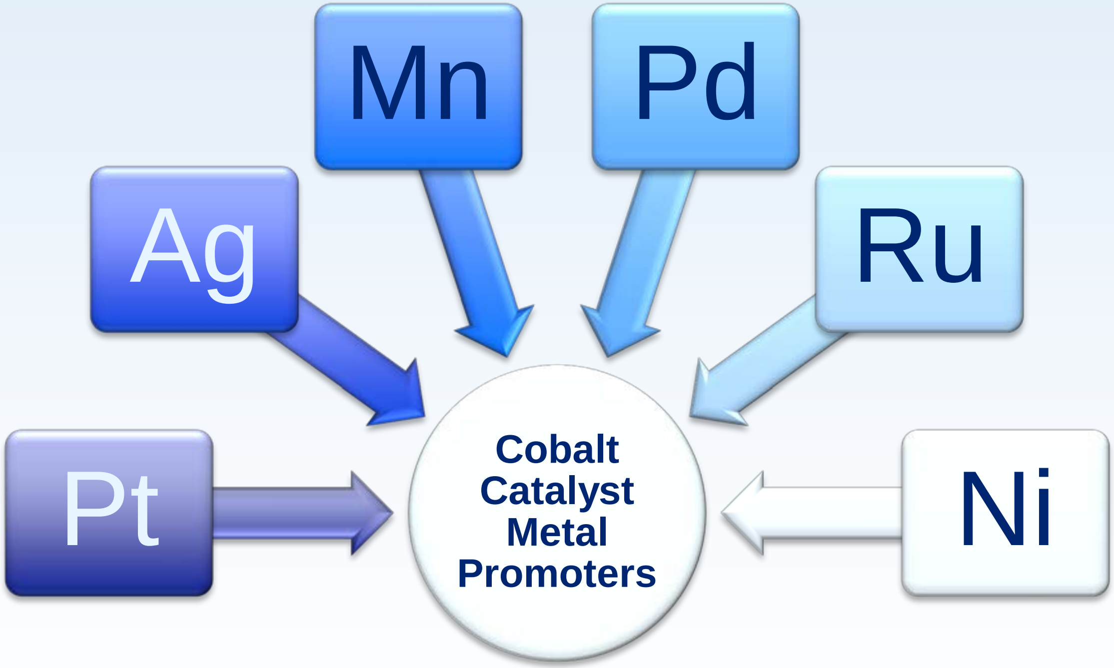
NASA GRC Catalysis Team – Cobalt Catalyst Research

Cobalt FT Catalysts and Promoters

Cobalt catalysts supported on *high surface area* binders (such as alumnia - Al_2O_3 or silica - SiO_2)

✓ 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!


Aviation-Grade Products
End-Product Improvement
Promoter Effects on Catalytic Activity
Catalyst Synthesis Optimization
Catalyst Characterization
NASA Glenn FT Research

NASA GRC Alternative Fuels Laboratory

GC Work Area

Control Room

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

CSTR Reactors

Catalyst Synthesis

Cobalt Nitrate ($Co(NO_3)_2 \cdot 6H_2O$) solution added dropwise to Alumnia (Al_2O_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_2O_3

Characterization

Cobalt Nitrate

($Co(NO_3)_2 \cdot 6H_2O$) soln. added dropwise

Catalyst drying before calcination on Rotavapor® 210

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

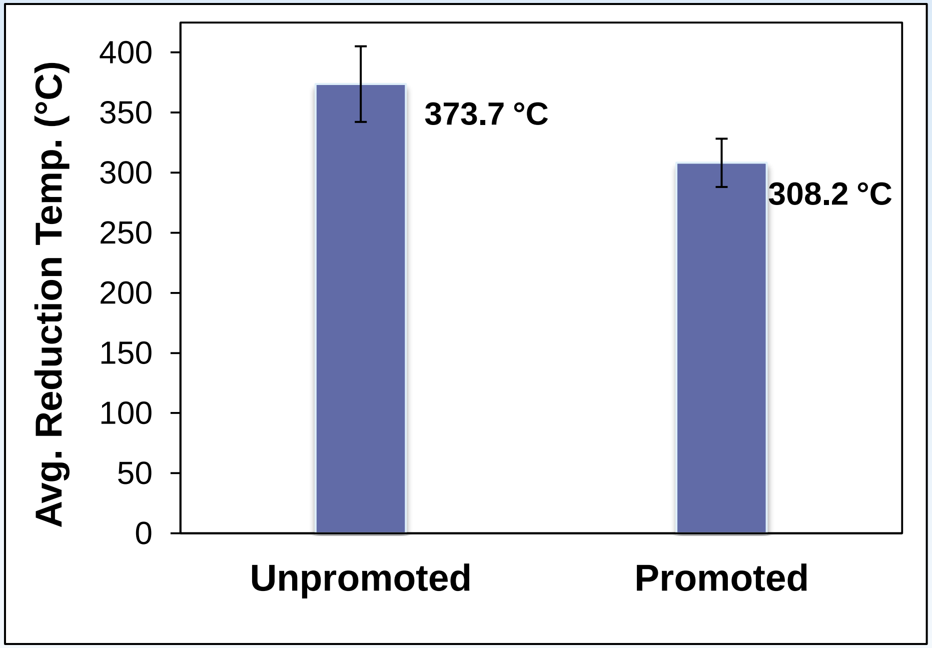
✓ **In this study, unpromoted and promoted (Pt and Ag) catalysts will be compared**

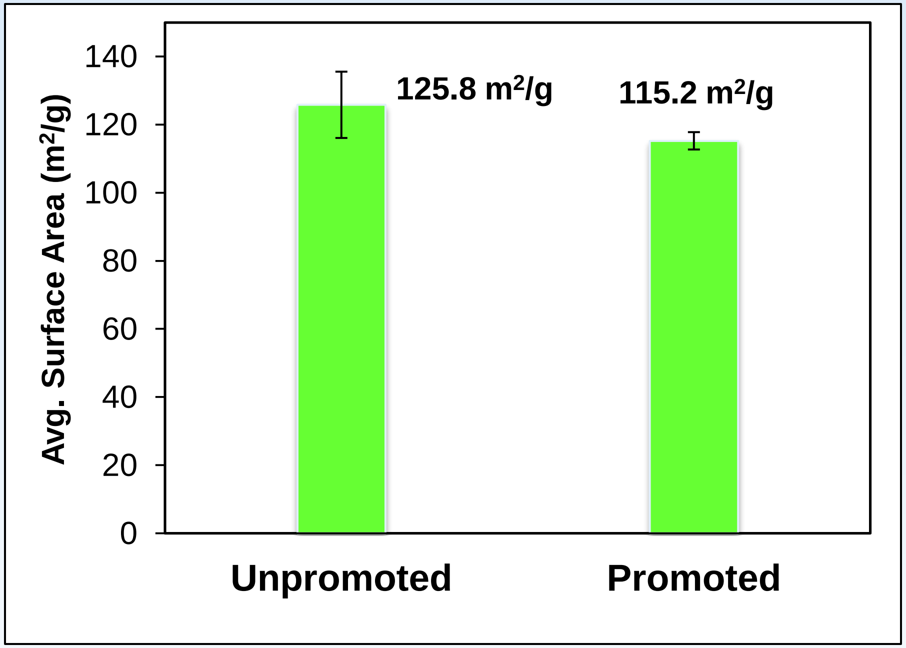
✓ ***Pt and Ag will be also be compared to evaluate economical promoter options***

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

Sample #	Promoter	ICP-AES Element Analysis (*Galbraith Laboratories, Inc.*)	Energy Dispersive Spectroscopy (EDS)	Surface Area (m^2/g)	Reduction Temperature (°C)
1	None	21.6% Co/Al_2O_3	30.3% Co/Al_2O_3	126.3	350
2	None	9.31% Co/Al_2O_3	9.45% Co/Al_2O_3	142.4	335
3	None	31.7% Co/Al_2O_3	47.2% Co/Al_2O_3	108.7	436
4	Pt	21.5% Co/0.845% Pt/Al_2O_3	25.4% Co/2.57% Pt/Al_2O_3	123.7	254
5	Pt	20.9% Co/0.397% Pt/Al_2O_3	24.1% Co/1.49% Pt/Al_2O_3	106.6	349
6	Pt	24.8% Co/0.459% Pt/Al_2O_3	34.8% Co/2.30% Pt/Al_2O_3	115.9	265
7	Ag	21.0% Co/0.806% Ag/Al_2O_3	25.9% Co/1.31% Ag/Al_2O_3	118.2	275
8	Ag	23.6% Co/0.278% Ag/Al_2O_3	33.3% Co/2.19% Ag/Al_2O_3	109.4	369
9	Ag	22.9% Co/0.510% Ag/Al_2O_3	26.7% Co/1.63% Ag/Al_2O_3	117.6	337

Promoted vs. Unpromoted Catalysts

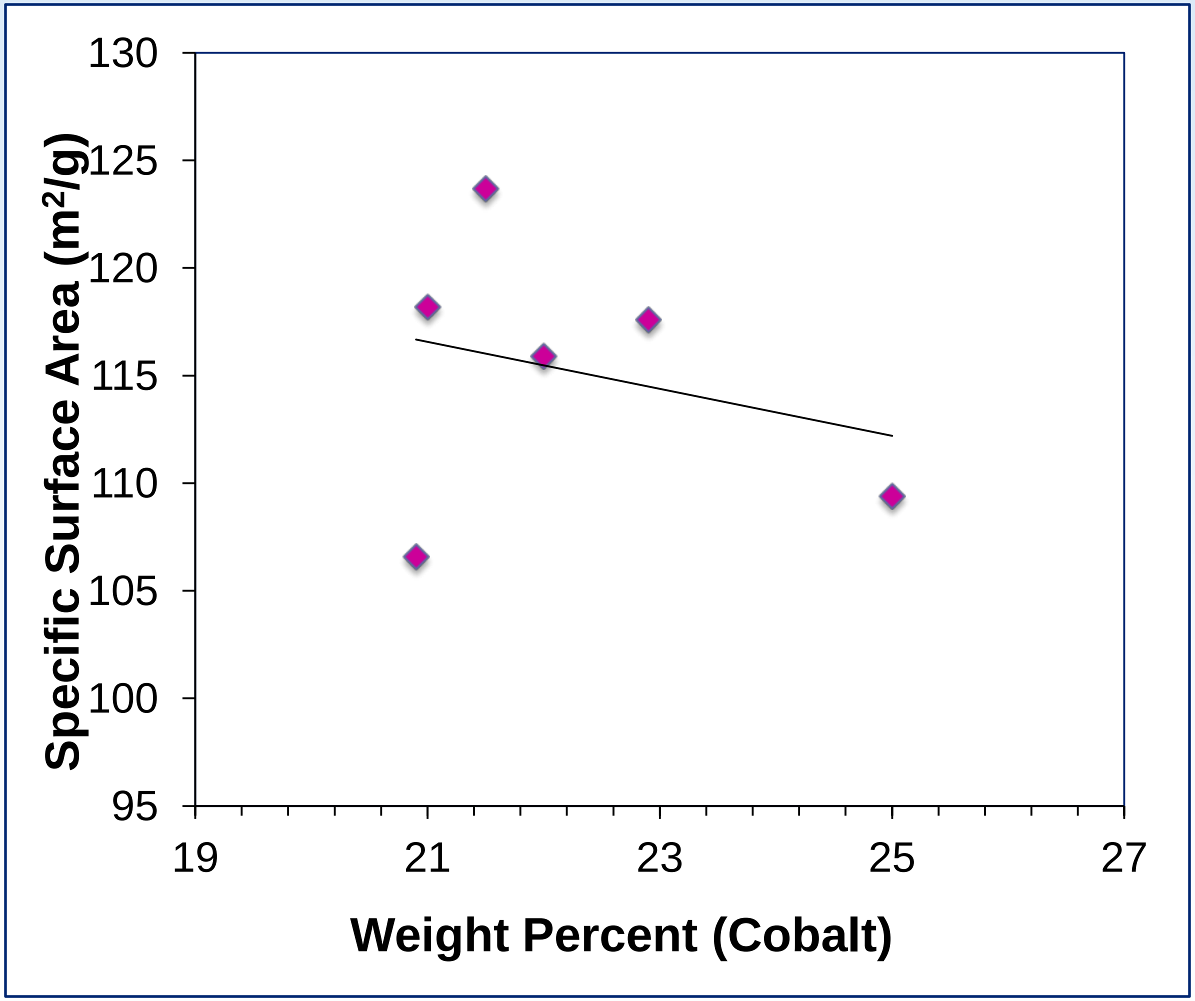




- ✓ **Addition of promoter decreases the necessary activation temperature of catalyst**
- ✓ **Since cobalt fills porous space of catalyst, promoter does not reduce surface area by significant amount**

***For higher accuracy purposes, ICP-AES data was used**

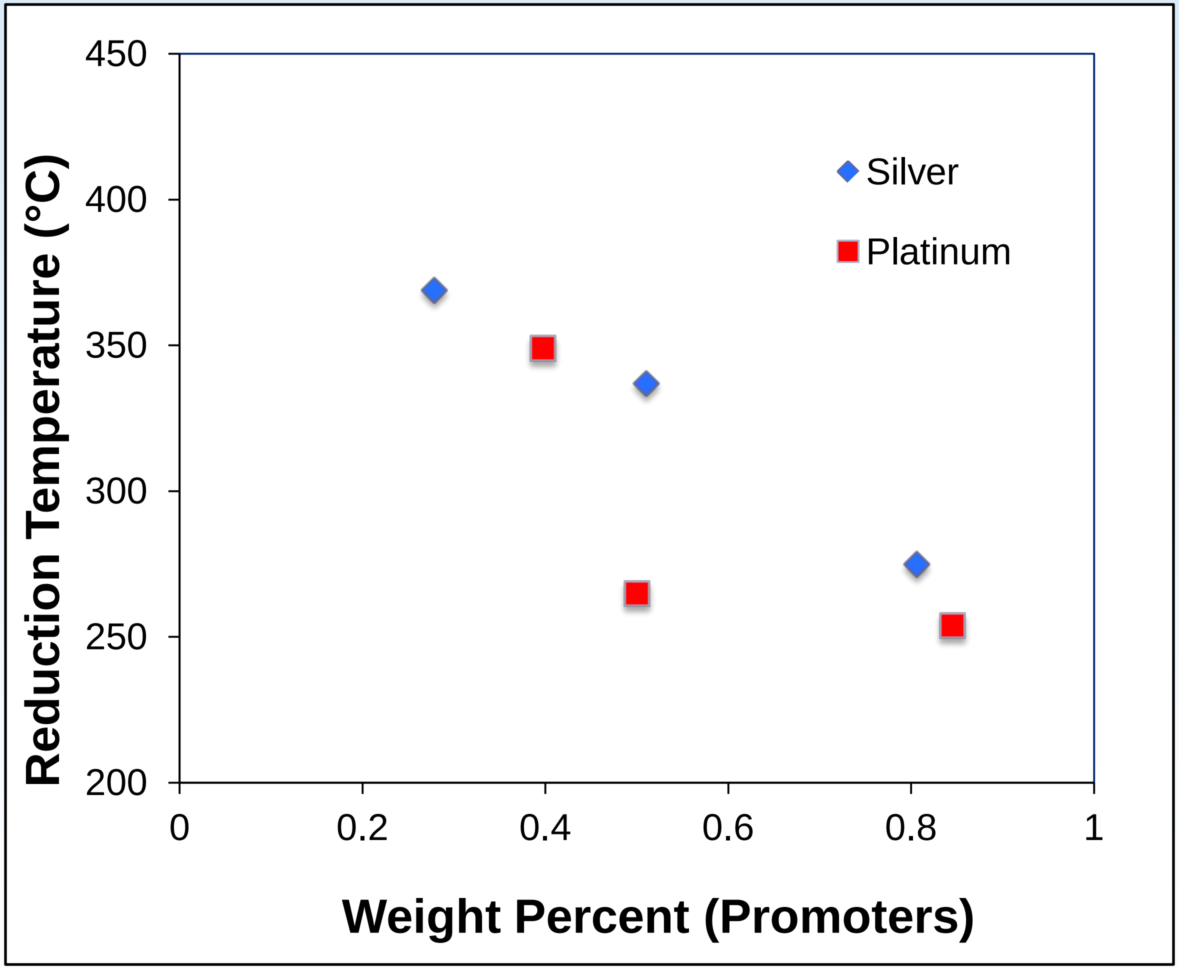
Cobalt Loading and Catalyst Surface Area



- ✓ Weight percent of cobalt loading analyzed
- ✓ Downward trend with regards to Co% and surface area
  - ✓ Additional Co fills porous space of Al_2O_3

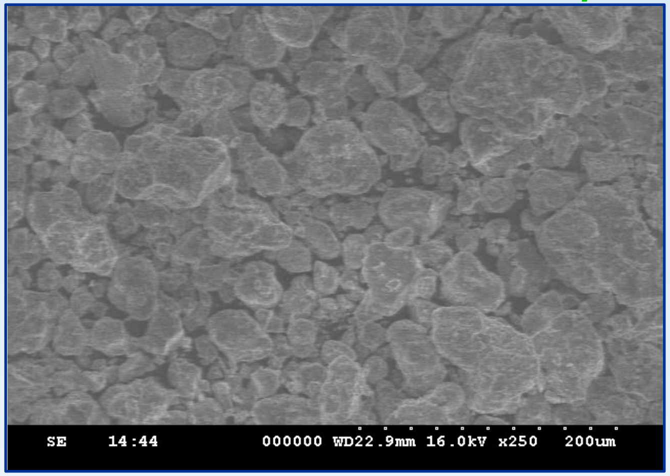
Platinum & Silver and Reduction Temperature

- ✓ Addition of promoters reduces reduction temperature
- ✓ As wt.% of promoter ↑ temperature ↓
- ✓ Platinum has greater effect on T than silver
- ✓ Temp. reduction still significant with Ag

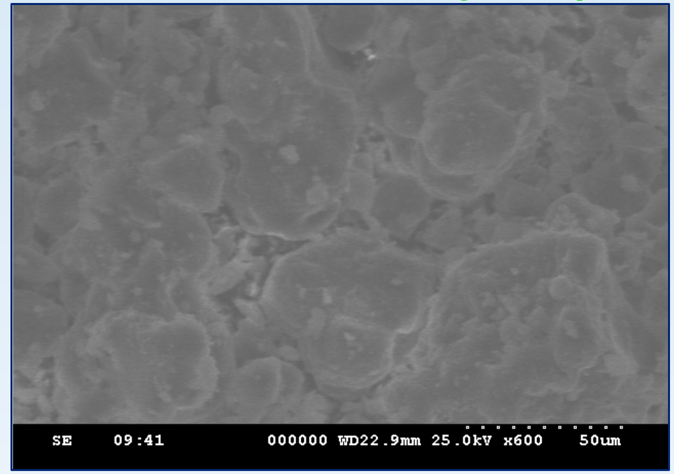


SEM Images

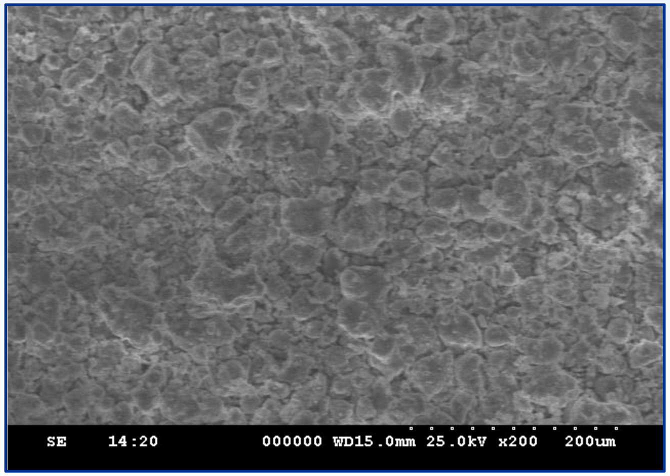
Surfaces look smooth and spherical – Particles look evenly dispersed!



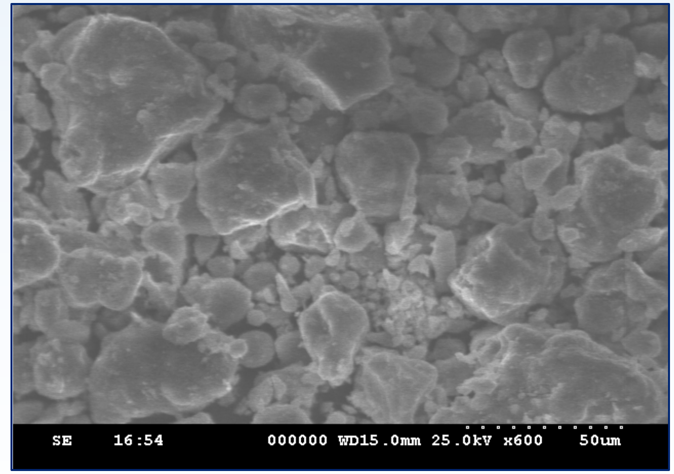
21.6%Co/Al_2O_3 catalyst at 250X



9.31%Co/Al_2O_3 catalyst at 600X



21.5% Co/0.845% Pt/ Al_2O_3 catalyst at 200X



21.0% Co/0.806% Ag/ Al_2O_3 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/Al_2O_3 *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 (TiO_2, SiO_2)***
- ***Pulse re-oxidation to investigate extent of reduction***
- ***X-Ray Diffraction (XRD) to examine crystal structure***

Acknowledgements

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Questions?