Design of bifunctional structured Fischer-Tropsch catalysts with improved heat conductivity for modular small-scale reactor applications

Michael Nigra, Bobby Mohanty, Eric Eddings, and Kevin Whitty

Wednesday, October 6, 2021
University of Utah Team Overview

Dr. Michael Nigra  
PI

Dr. Bobby Mohanty  
Co-PI

Dr. Eric Eddings  
Co-PI

Dr. Kevin Whitty  
Co-PI

1 post-doc (part-time) + 2 Ph.D. students
• Motivation
• Materials design and synthesis
• Reactor testing
• Kinetics and CFD Modeling
Overall goal

• This project develops new structured Fischer-Tropsch catalysts which have **improved heat conductivity** and **higher selectivity** for the formation of long chain hydrocarbon products.
Fischer-Tropsch Synthesis (FTS)

- Reaction: $\text{CO} + \text{H}_2 \rightarrow \text{C}_1 + \text{C}_2 + \ldots + \text{C}_{30}$
- Typical catalysts are supported Co and Fe.
- Operates at 10-60 bar and temperatures between 200-350°C
- Highly exothermic reaction: $\Delta H = -165 \text{ kJ/mol CO}$.
- **Need strategies to manage heat from reaction!**
- Product distribution and catalyst deactivation rate are highly sensitive to temperature.
Critical need and hypothesis

• **Critical need:** Rapid removal of heat generated by reaction.

• **Hypothesis:** By designing a support with better heat transfer properties, hotspots can be minimized and deactivation can be slowed.

• **Novelty:** First structured TiO$_2$ nanotube supported FTS catalyst with controlled acidity.
Expected outcomes

• New FT catalysts that exhibit enhanced thermal conductivity, activity, and selectivity.
• Environmentally-responsible utilization of coal with positive economic impact.
Outline

• Motivation
• **Materials design and synthesis**
• Reactor testing
• Kinetics and CFD Modeling
• **Solution:** 3-dimensional structured catalyst with conductive materials (Ti or graphite support) with FeCo nanoparticles.
• FeCo was chosen because it performs better than Fe in H₂ lean feedstocks from coal or biomass.
• Support will be functionalized with acid groups to perform both hydrocarbon grown and hydrocracking/isomerization processes simultaneously.
• Two types of supports: **Ti-based** and C-based.
Materials summary

- New materials will consist of structured, bifunctional catalysts for FTS.
- 3-D printing techniques will allow for flexibility in design of catalyst.
- Improved **heat transfer** by:
  - Using a structured catalyst
  - Using a conductive support material.
Preparation of Ti-based materials

CAD Modeling → CFD Simulation → Two Step Anodization → Annealing → Impregnation → Annealing → Impregnation and Annealing
Proposed structure for Ti-based support materials

- Structure is designed to enable heat transfer away from active sites.
• Test printing with PLA polymer before using Ti.
3D-printing with optimized printing parameters

- Example of Ti 3D-printed structured material.

Before annealing

After annealing
Annealing yields surprise appearance of TiN

• After annealing in Ar, we found that there was titanium nitride in the sample.
• Nitrogen does not appear to be coming from PLA polymer.
Outline

• Motivation
• Materials design and synthesis
• Reactor testing
• Kinetics and CFD Modeling
Reactor set-up

Reactor diameters: 1.77 in. and 0.37 in.
Baseline catalytic testing

- Prepared unstructured catalytic materials supported on P25 TiO₂ and activated carbon.
- Fe and FeCo (1:1 ratio) nanoparticles supported on TiO₂ or C.
- Full characterization of these materials was completed.
**Baseline catalytic testing—Transient temperature profiles**

**Reaction conditions:** pressure: 18 barg, gas flow: 175 SCCM (50 SCCM H2, 25 SCCM CO, 100 SCCM He), temperature set point: 250°C.
• Measurements taken over the reaction time of 8 hours.
• Alpha value is measured from C$_3$ and greater.
Outline

- Motivation
- Materials design and synthesis
- Reactor testing
- **Kinetics and CFD Modeling**
CO-insertion mechanism based kinetic model of the Fischer–Tropsch synthesis reaction over Re-promoted Co catalyst

Branislav Todic\textsuperscript{a}, Wenping Ma\textsuperscript{b}, Gary Jacobs\textsuperscript{b}, Burtron H. Davis\textsuperscript{b}, Dragomir B. Bukur\textsuperscript{a,c,}\textsuperscript{*}

\textsuperscript{a} Chemical Engineering Program, Texas A\&M University at Qatar, PO Box 23874, Doha, Qatar

\textsuperscript{b} Center for Applied Energy Research, 2540 Research Park Drive, Lexington, KY 40511, United States

\textsuperscript{c} Artie McFerrin Department of Chemical Engineering, Texas A\&M University, 3122 TAMU, College Station, TX 77843, United States
Kinetic modeling—Product formation rate

T = 503 K, P = 1.5 MPa, 
\( \text{H}_2/\text{CO} = 2.1, \text{WHSV} = 11.3 \text{ NL/g}_{\text{cat}}/\text{h.} \)

**Calculations from paper**

![Graph showing product formation rate vs. carbon number](image)

**Our calculations based on the paper**

![Graph showing product formation rate vs. carbon number](image)
Kinetic modeling—Total hydrocarbon formation rate

\[ T = 503 \text{ K}, \ P = 1.5 \text{ MPa}, \ 
\text{H}_2/\text{CO} = 2.1, \ \text{WHSV} = 11.3 \text{ NL/g}_{\text{cat}}/\text{h}. \]

Calculations from paper

Our calculations based on the paper
Kinetic modeling—1-olefin to paraffin ratio

T = 503 K, P = 1.5 MPa,
$H_2/CO = 2.1$, WHSV = 11.3 NL/g$_{cat}$/h.

Calculations from paper

Our calculations based on the paper
Comsol modeling—Temperature profiles

TiO$_2$

Line Graph: Temperature (degC)

**Ti**

Line Graph: Temperature (degC)
Future work

- Add FeCo and Fe nanoparticles to acid-functionalized TiO$_2$ nanotube structure and TiN support materials.
- Reaction testing of Ti 3D-printed materials.
- 3D-printing of carbon-based structures.
- Additional kinetic and CFD modeling.
Thank you to DOE/NETL/UCFER for funding this project!
Group website: https://nanointerfaces.che.utah.edu