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

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University of Utah Team Overview

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Outline

- 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.
• Motivation
• **Materials design and synthesis**
• Reactor testing
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• **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 H$_2$ 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.
• 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
Proposed structure for Ti-based support materials

• Structure is designed to enable heat transfer away from active sites.
Materials synthesis—3D printing model structures

- Test printing with PLA polymer before using Ti.
3D-printing with optimized printing parameters

- Example of Ti 3D-printed structured material.
3D-printing with optimized printing parameters

• Example of Ti 3D-printed structured materials.
• Left sample printed at 260°C, right at 265°C
3D-printing with optimized printing parameters

- Example of Ti 3D-printed structured materials.
- Left sample printed at 260°C, right at 265°C
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.
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Reactor set-up

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

• Prepared unstructured catalytic materials supported on P25 TiO$_2$ and activated carbon.
• Fe and FeCo (1:1 ratio) nanoparticles supported on TiO$_2$ 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.
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CO-insertion mechanism based kinetic model of the Fischer–Tropsch synthesis reaction over Re-promoted Co catalyst

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Kinetic modeling—Product formation rate

\[ T = 503 \text{ K}, \quad P = 1.5 \text{ MPa}, \]
\[ \frac{H_2}{CO} = 2.1, \quad \text{WHSV} = 11.3 \text{ NL/g}_{\text{cat}}/\text{h}. \]

Calculations from paper

Our calculations based on the paper
Kinetic modeling—Total hydrocarbon formation rate

\[ T = 503 \text{ K}, \quad P = 1.5 \text{ MPa}, \quad H_2/CO = 2.1, \quad \text{WHSV} = 11.3 \text{ NL/g}_{\text{cat}}/\text{h}. \]

**Calculations from paper**

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

\[ T = 503 \text{ K}, \quad P = 1.5 \text{ MPa}, \]
\[ \frac{H_2}{CO} = 2.1, \quad \text{WHSV} = 11.3 \text{ NL/g}_{\text{cat}}/\text{h}. \]

Our calculations based on the paper
Comsol modeling—Temperature profiles

TiO₂

Ti

Line Graph: Temperature (degC)

Distance=0
Distance=0.0127
Distance=0.0254
Distance=0.0381
Distance=0.0508
Distance=0.0635
Distance=0.0762
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.
Questions?

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Group website: https://nanointerfaces.che.utah.edu