New Advances for Fischer-Tropsch Catalysis

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A Simplified View of Fischer-Tropsch Mechanistic Chemistry

6 general rxn steps:
(independent of model, catalysts, rxn conditions)
- Adsorption/activation
- Chain initiation
- Chain growth
- Product desorption
- Chain termination
- Readsoption/further rxn

3 widely considered mechanisms on Fe:
- Surface carbide (shown)
- Surface enol
- CO insertion

Youtube Movie Credit: I. Filot, E. Hensen, R. van Santen
Institute for Complex Molecular Systems, Eindhoven University of Technology

https://youtu.be/44OU4JxEK4k

Figure from Weckhuysen Chem. Soc. Rev., 2008, 37, pgs 2758–2781
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**Anderson-Shulz-Flory (ASF) Product Distributions**

- Radical polymerization type distro
- Chain termination/proagation are critical/rate-determining steps
- Occur for fully thermalized, “equilibrium” or “steady state” conditions

### Equilibrium Molar Mass Distribution

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

\[ \alpha = \frac{R_p}{R_p + R_t} \]
Are Controlled Deviations from ASF Possible?

Nano-structured Catalyst Materials

- Non Anderson-Shulz-Flory Product Distributions
- Stabilization of active catalyst phase
- Controlled production of oxygenates/aromatics
- Improved reactivity & conversion

Image from Wang et. al. ChemCatChem Doi: 10.1002/cctc.201000071

Non-equilibrium Reactors (Microwave-MW)

- Non-thermal & Non-ASF Product Distributions
- Lowered reactor temperatures
- Improved kinetics, reactivity & conversion

Potential Benefits

- Non-thermal & Non-ASF Product Distributions
- Lowered reactor temperatures
- Improved kinetics, reactivity & conversion
Motivation from Previous Literature: Process Intensification w/Nano-Catalysis

Fe$_2$O$_3$ *in* Carbon Nanotubes

Fe & Fe-carbide form at lower T For Fe$_2$O$_3$ inside CNTs

Fe$_2$O$_3$ *outside* Carbon Nanotubes

Altered Product Distros

Legend:
- **Black** = Fe inside CNTs
- **Red** = Fe outside CNTs
- **Blue** = Fe on act. carbon

Data & Images from Bao et. al. JACS, doi: 10.1021/ja8008192
Recent Nano-catalyst results from ORD
Layered Graphene Catalyst Supports for Breaking ASF Distributions

Can this be exploited for FT?

Layered graphene controls **surface mobility** of FT-type species (Li et. al., Science, 2013)

**Adsorption Isotherms in Graphene Oxides**

- Surface mobility disrupted (kinetic effect)
- More H₂ adsorbed than N₂ (size exclusion)
Nanostructured Fe$_5$C$_2$ “Häggs Phase”

- Fe$_5$C$_2$ Häggs phase one of most active phases for FT
- ORD synthesis produces high yield, gram, batches of nearly pure Fe$_5$C$_2$
- Nanoparticle shell is a mixed amorphous Fe-carbide/oxide
- Future work will incorporate into layered graphene and/or carbon nanotube supports
Synchrotron X-ray characterization of nano- Fe$_5$C$_2$

**O K edge X-ray absorbance**

- 20 nm Fe-carbide
- 10 nm Fe-carbide
- Fe$_3$C
- Fe$_3$O$_4$
- Fe$_2$O$_3$
- FeO

**Fe L edge X-ray absorbance**

- 20 nm Fe-carbide
- 10 nm Fe-carbide
- Fe$_3$C
- Fe$_3$O$_4$
- Fe$_2$O$_3$
- FeO
- Fe
Summary

• ASF arises from a radical chain polymerization process at thermal equilibrium

• Deviations from ASF require disrupting molecular processes on catalyst/support surface (adsorption, diffusion, etc)

• Microwave reactors offer additional opportunities to deviate from ASF

• Nano-structured Graphene and Fe₅C₂ have been synthesized and initial characterization started.