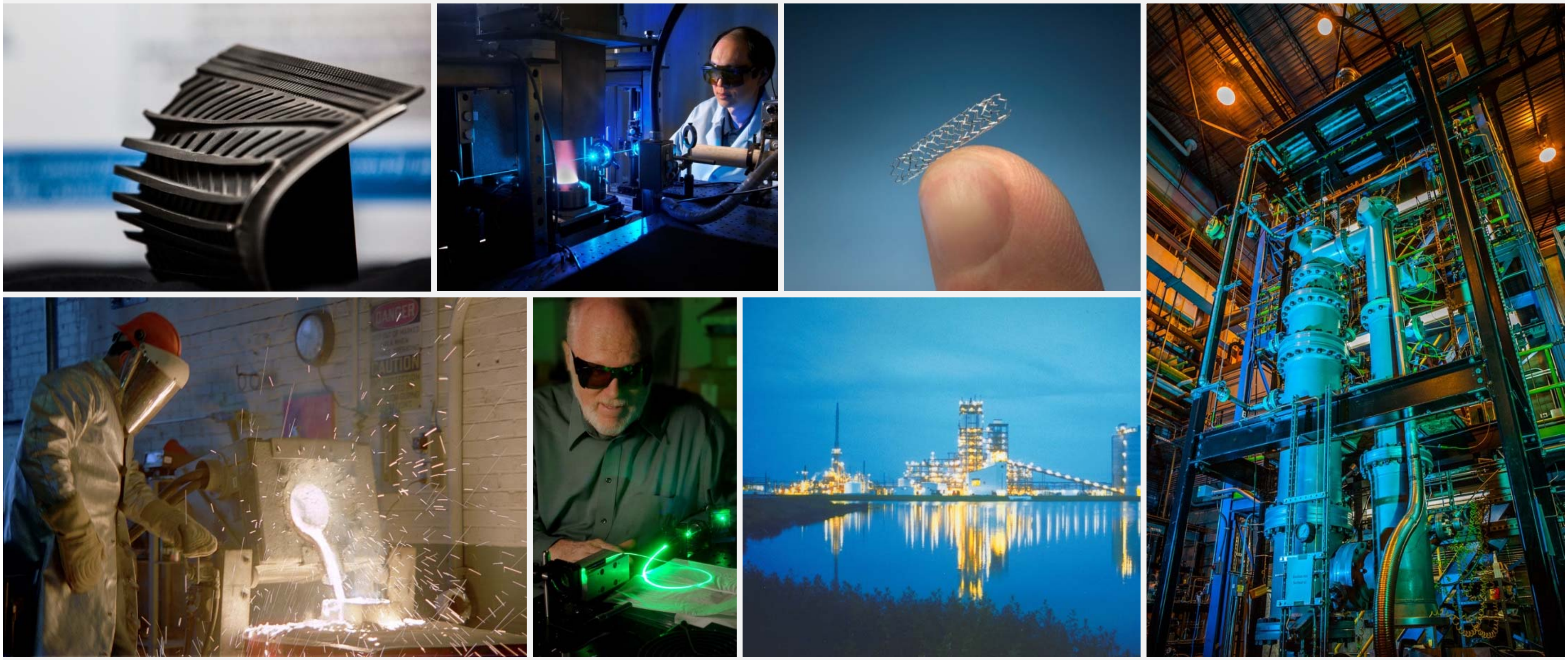
Driving Innovation ♦ Delivering Results



New Advances for Fischer-Tropsch Catalysis

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Office of Research and Development

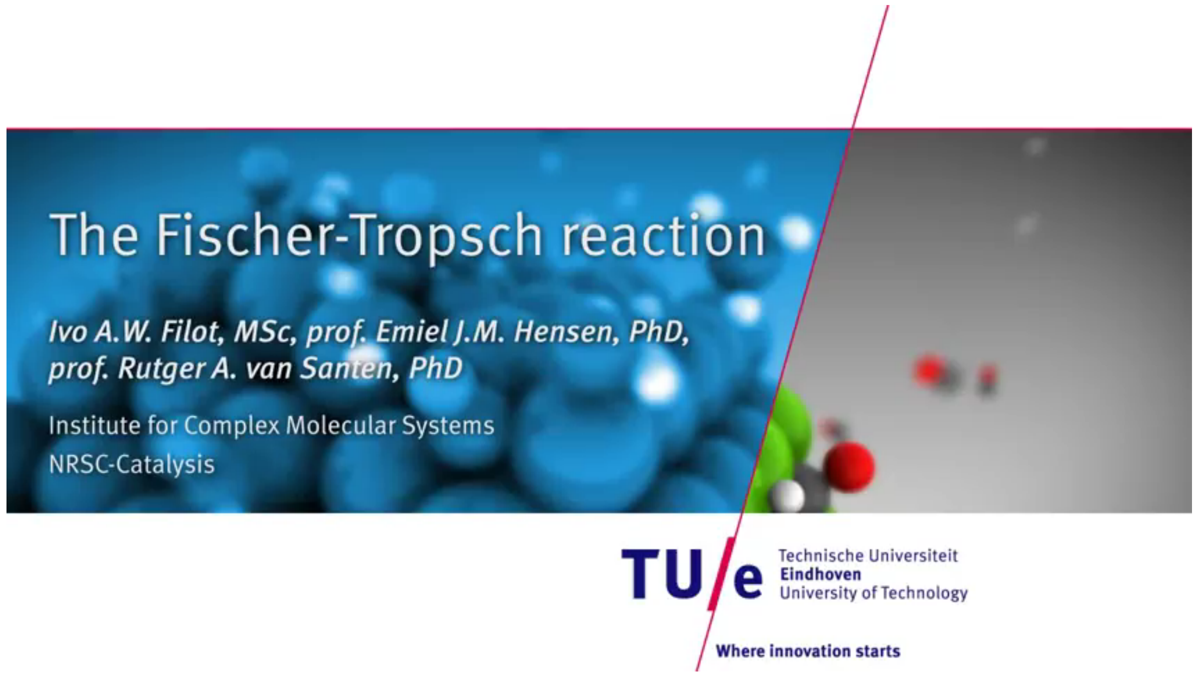
August 2015

U.S. DEPARTMENT OF ENERGY | National Energy Technology Laboratory

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
- Readsorption/further rxn



3 widely considered mechanisms on Fe:

- Surface carbide (shown)
- Surface enol
- CO insertion

https://youtu.be/44OU4JxEK4k

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

Figure from Weckhuysen Chem. Soc. Rev., 2008, 37, pgs 2758–2781

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Surface Carbide Mechanism

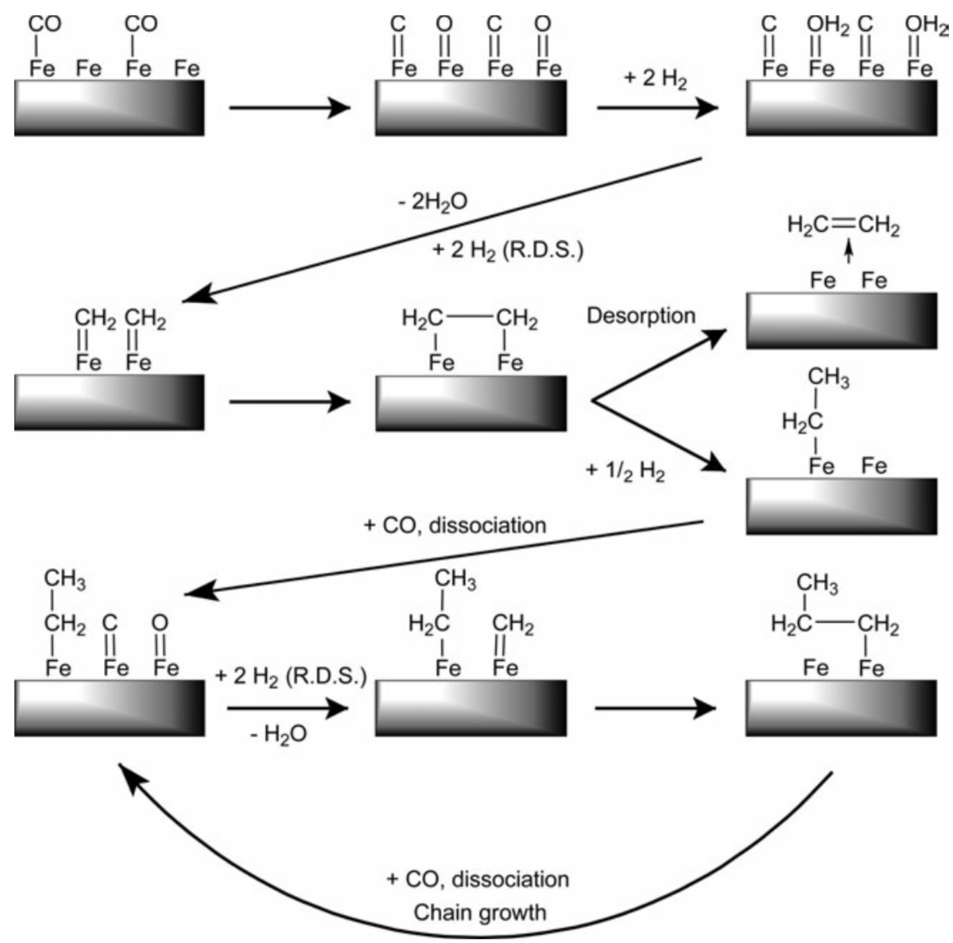
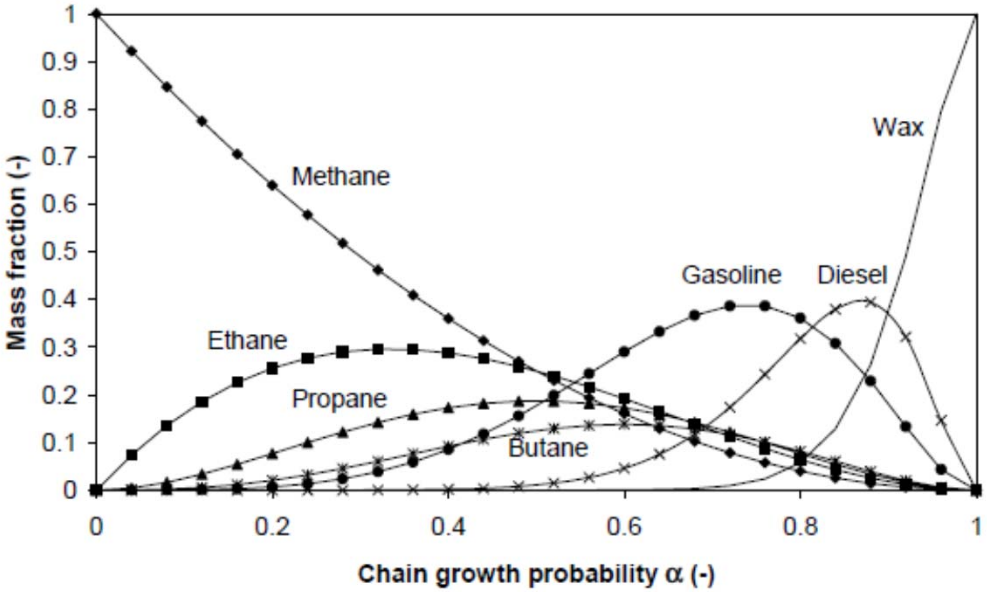


Figure from Weckhuysen Chem. Soc. Rev., 2008, 37, pgs 2758–2781

Anderson-Shulz-Flory (ASF) Product Distributions



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

	Chain growth probability	Olefin/paraffin ratio	Carbon deposition	Methane selectivity
Temperature ↑	↓	↓	↑	↑
Pressure ↑	↑	*	*	↓
H_2/CO ratio ↑	↓	↓	↓	↑
Conversion ↑	*	↓	↑	↑
Space velocity ↑	*	↑	*	↓

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

$$\alpha = \frac{R_p}{R_p + R_t}$$

Are Controlled Deviations from ASF Possible?

Nano-structured Catalyst Materials

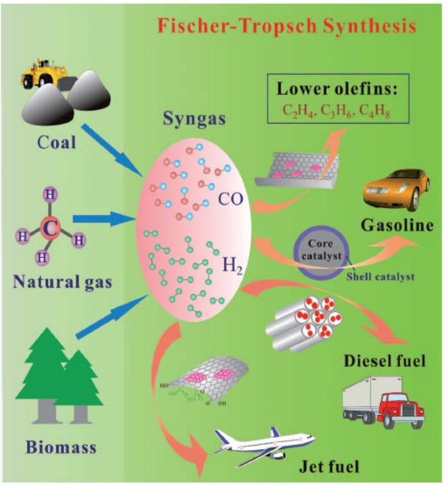
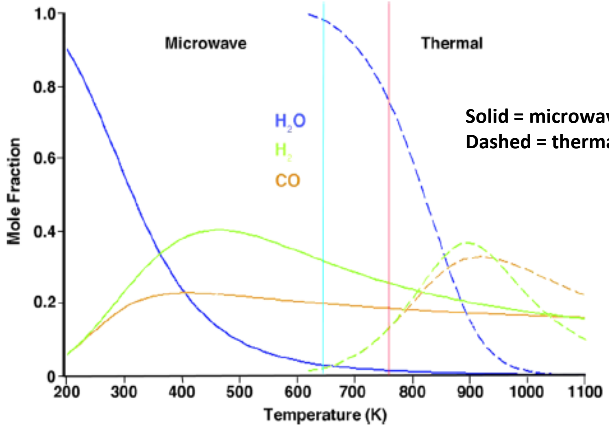


Image from Wang et. al. ChemCatChem Doi: 10.1002/cctc.201000071

Potential Benefits

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

Non-equilibrium Reactors (Microwave-MW)

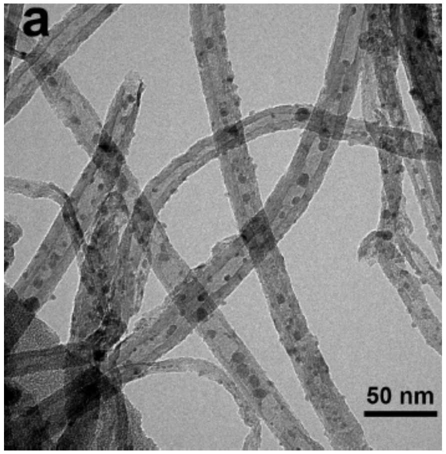


Potential Benefits

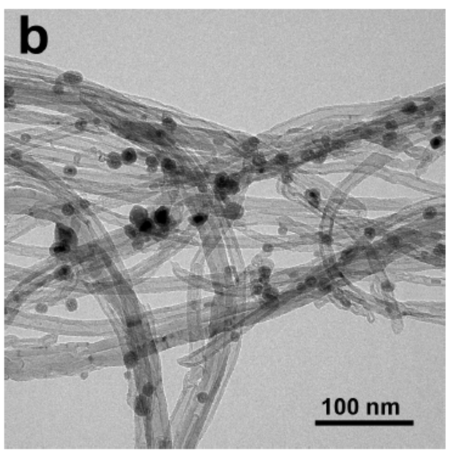
- Non-thermal & Non-ASF Product Distributions
- Lowered reactor temperatures
- Improved kinetics, reactivity & conversion

Motivation from Previous Literature: Process Intensification w/Nano-Catalysis

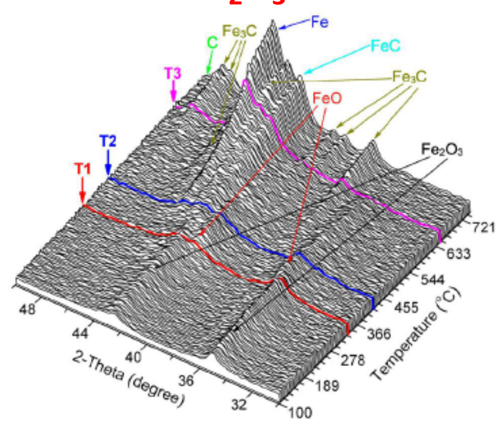
Fe_2O_3 *in* Carbon Nanotubes

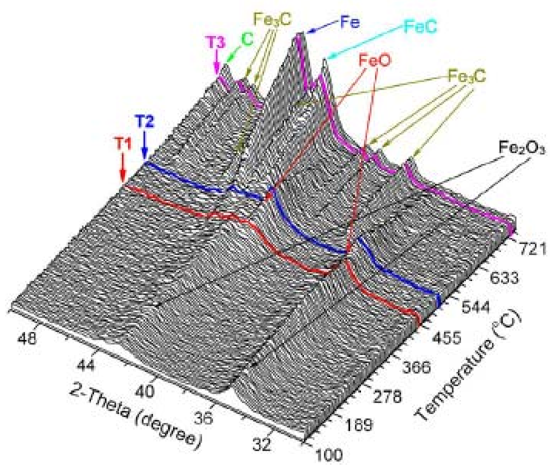


Fe_2O_3 *outside* Carbon Nanotubes



Fe & Fe-carbide form at lower T For Fe_2O_3 inside CNTs

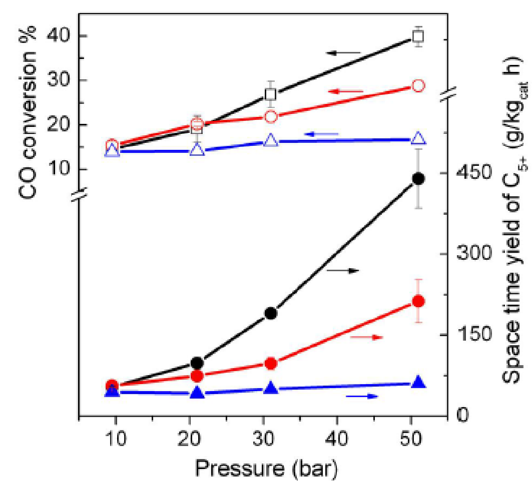




Altered Product Distros

Table 2 Comparison of the FTS Activity and Product Selectivities at 51 bar

catalyst	CO conversion (%)	yield (g C_{5+}/kg_{cat}·h)	CO_2 selectivity (%)	hydrocarbon selectivities (%) CH_4	C_2–C_4	C_{5+}
Fe-*in*-CNT	40	440	18	12	41	29
Fe-*out*-CNT	29	210	12	15	54	19
Fe/AC	17	61	5	15	71	9



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

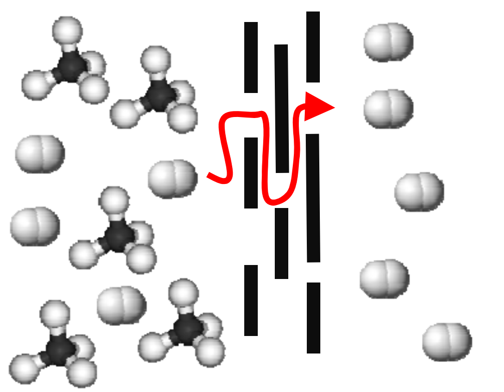
Data & Images from Bao et. al. JACS, doi: 10.1021/ja8008192

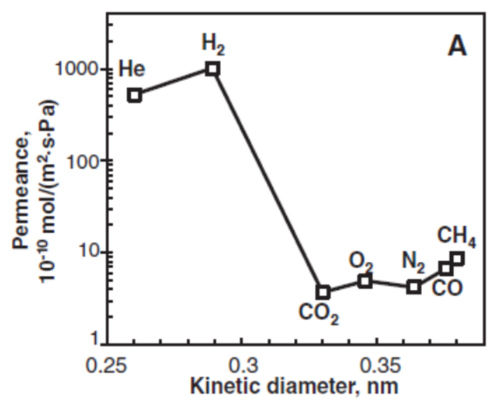
Recent Nano-catalyst results from ORD

Layered Graphene Catalyst Supports for Breaking ASF Distributions

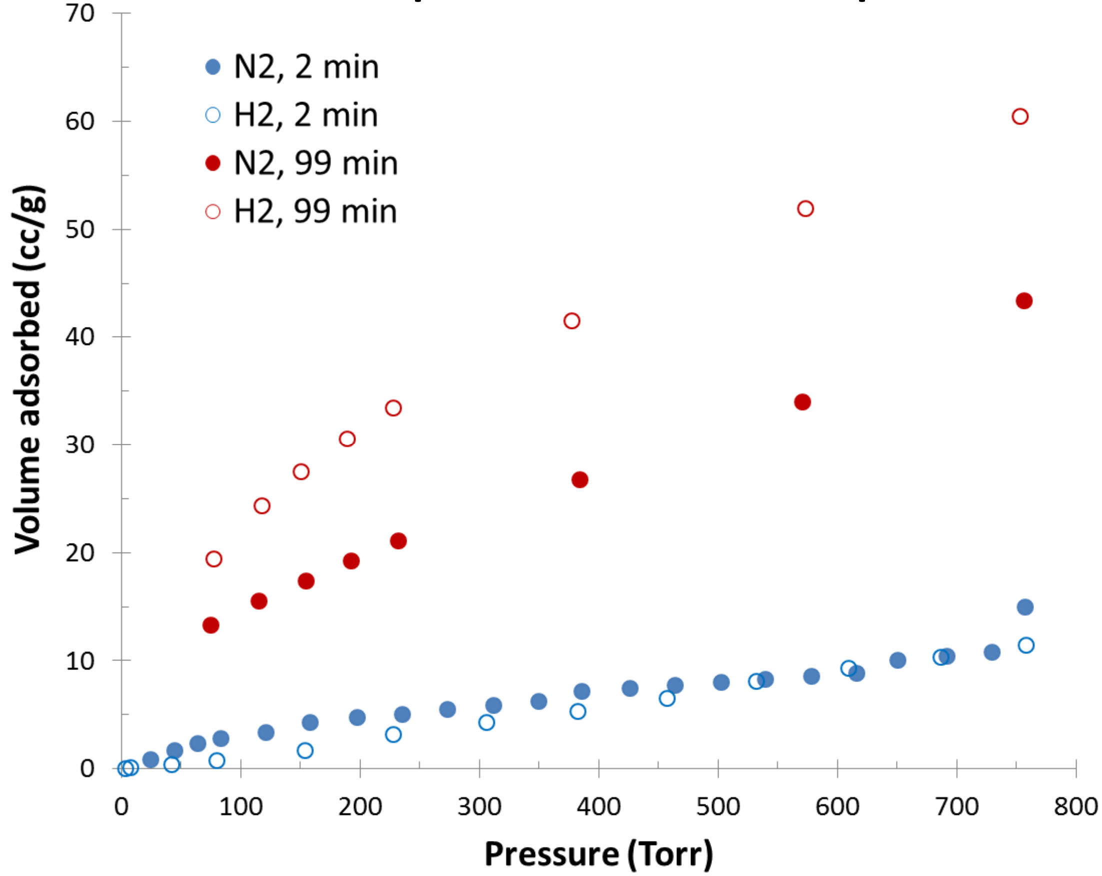
Can this be exploited for FT ?

Layered graphene controls <u>surface mobility</u> of FT-type species (Li et. al., Science, 2013)





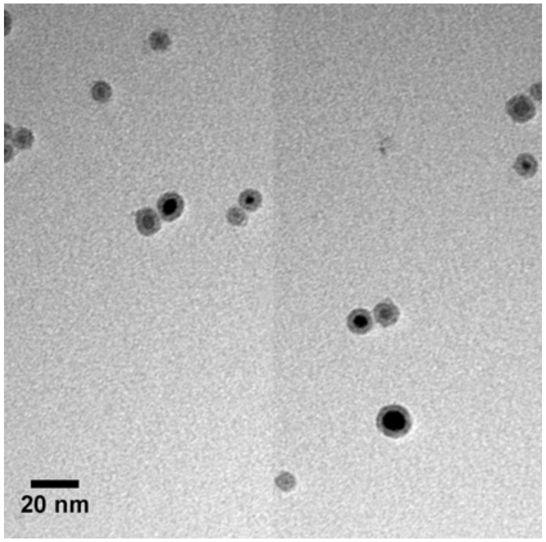
Adsorption Isotherms in Graphene Oxides



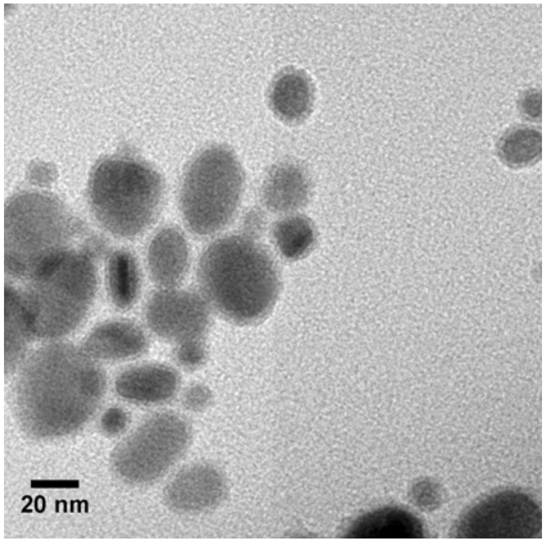
- Surface mobility disrupted (kinetic effect)
- More H_2 adsorbed than N_2 (size exclusion)

Nanostructured Fe_5C_2 "Häggs Phase"

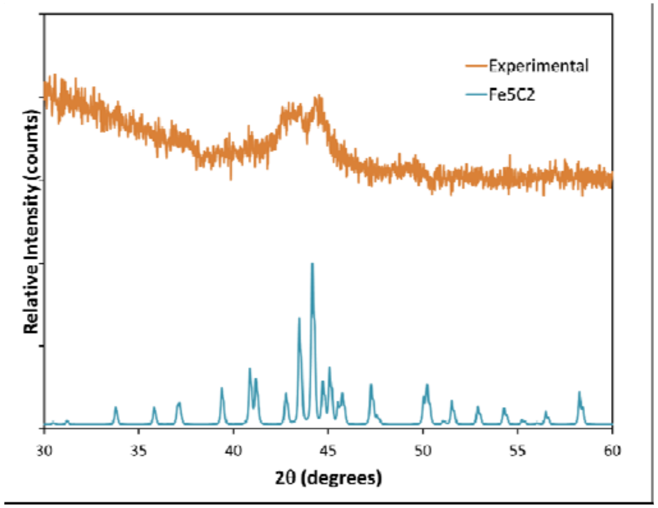
10 nm Fe_5C_2



20 nm Fe_5C_2



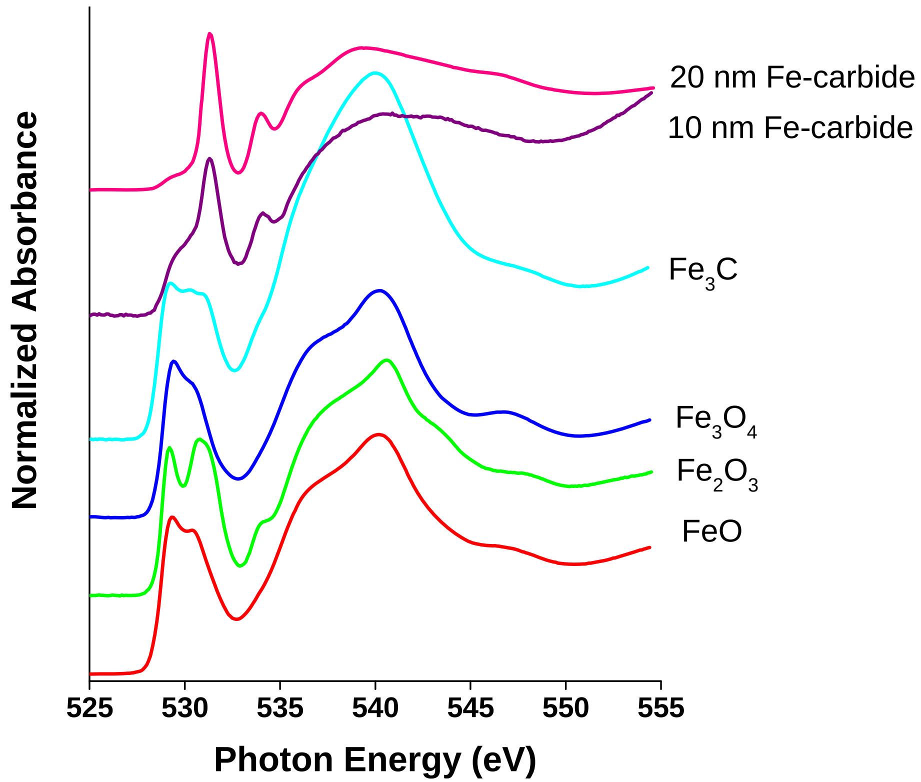
X-ray diffraction confirms nano-Fe_5C_2 structure



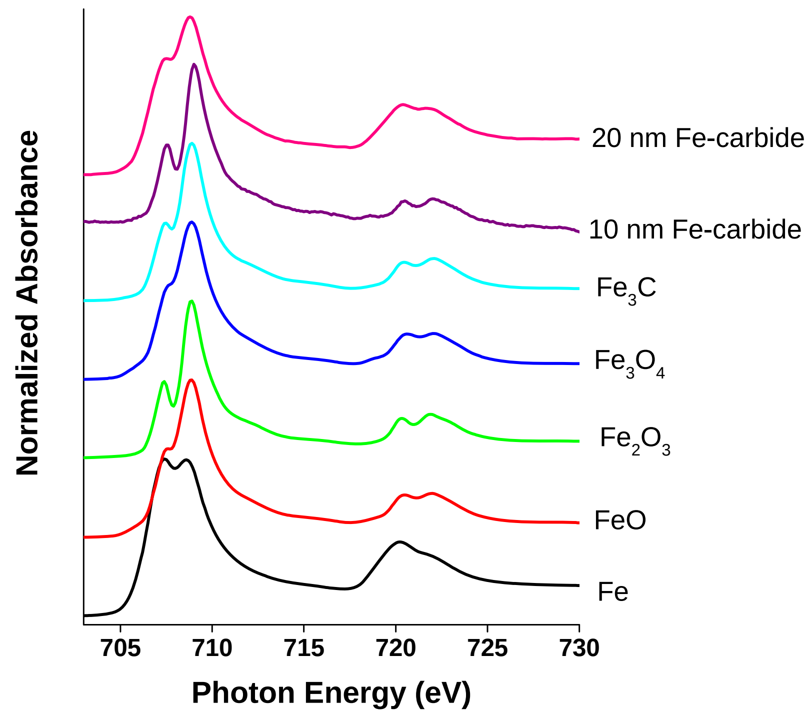
- Fe_5C_2 Häggs phase one of most active phases for FT
- ORD synthesis produces high yield, gram, batches of nearly pure Fe_5C_2
- Nanoparticle shell is a mixed amorphous Fe-carbide/oxide
- Future work will incorporate into layered graphene and/or carbon nanotube supports

Synchrotron X-ray characterization of nano- Fe_5C_2

O *K* edge X-ray absorbance



Fe *L* edge X-ray absorbance



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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 Fe_5C_2 have been synthesized and initial characterization started.**