Vanadium Nanoparticle Catalysis

UCSB MRL RESEARCH EXCHANGE TEACHER: ADAM GAMBOA

Visiting Scholar: Daniel Hirche
Principal Investigator: Mike Gordon, PhD

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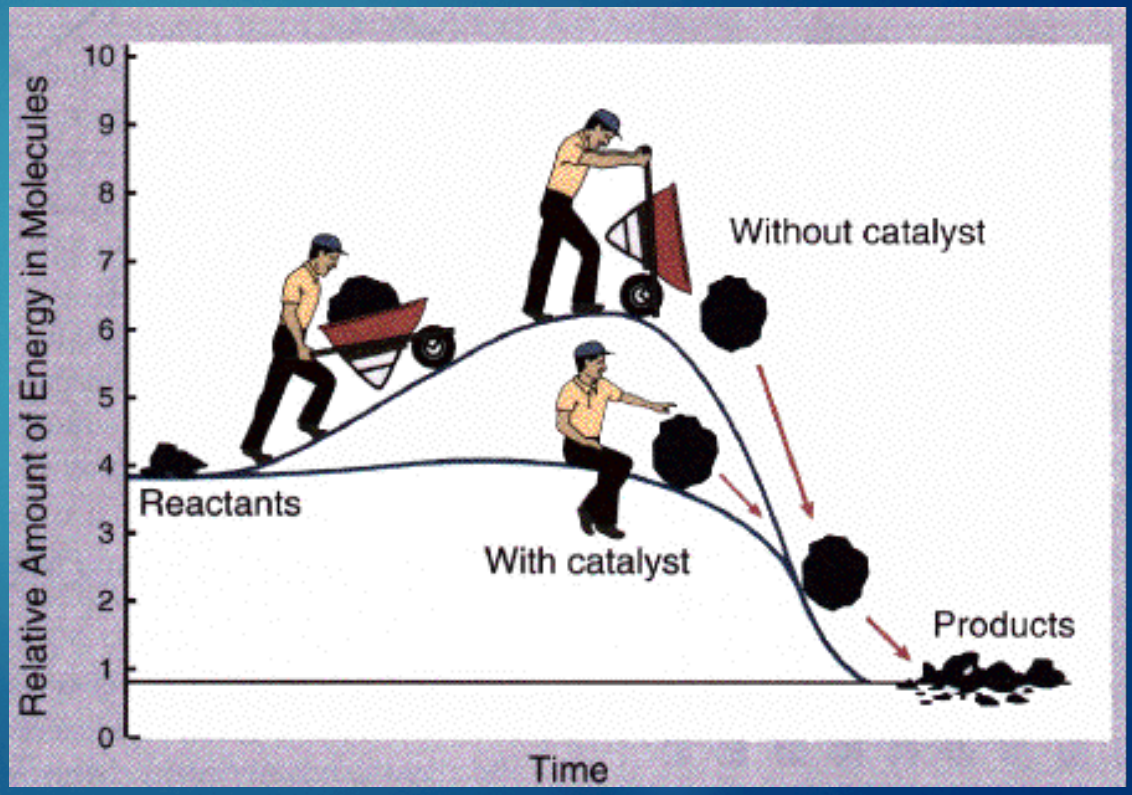
U.S. DEPARTMENT OF ENERGY

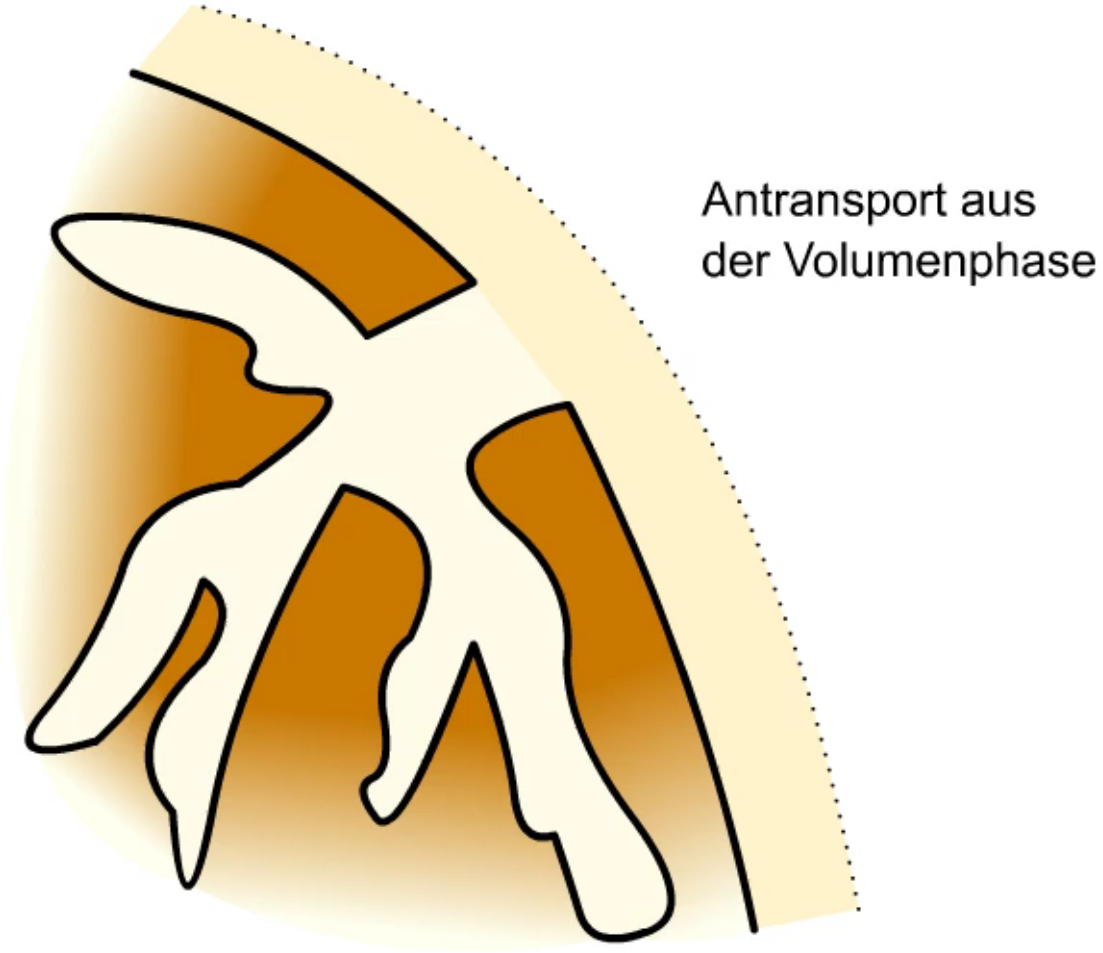
Catalyst: (n) anything that speeds up a chemical rxn but isn't consumed in the process

Examples of Catalysis

1. **Biochemistry**: enzymes speed up important rxns in the body
2. **Refineries**: metallic oxides are used crack long chain hydrocarbons into gasoline
3. **Automotive**: Catalytic converters aid in complete combustion of criteria pollutants (CO, unburned HC's, NO_x etc.)



Pathways for a Catalytic Reaction



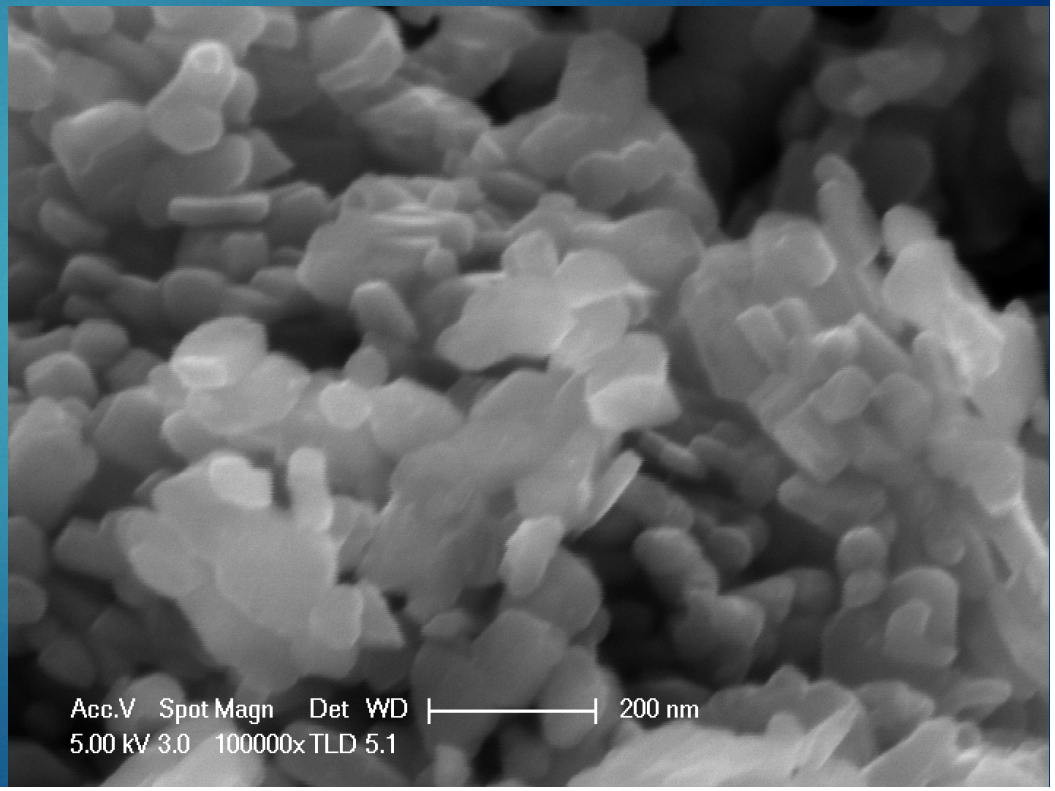
http://www.chemgapedia.de/vsengine/vlu/vsc/de/ch/10/makrokinetik/einfuehrung_makrokinetik/einfuehrung_makrokinetik.vlu.html

Background: Bulk Catalysts vs. 2-D Catalysts

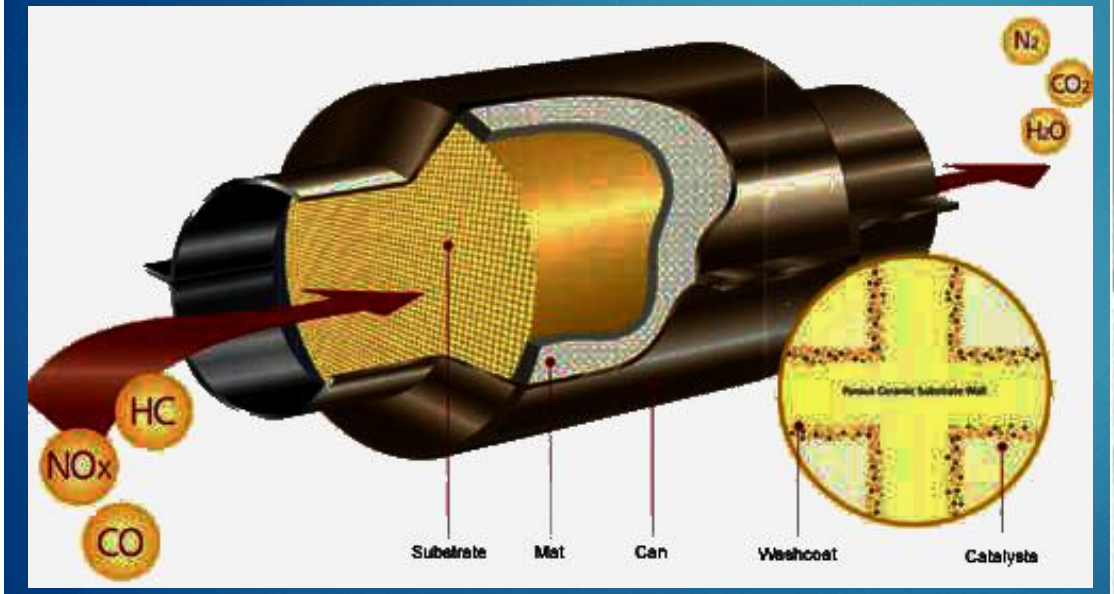
- Traditionally larger **"bulk"** catalysts are used
- **Bulk** catalysts require more material than nanoparticles
- More importantly **bulk** particles have different chemical properties than **2-D** catalysts
- **2-D** catalysts behave chemically according to quantum mechanics

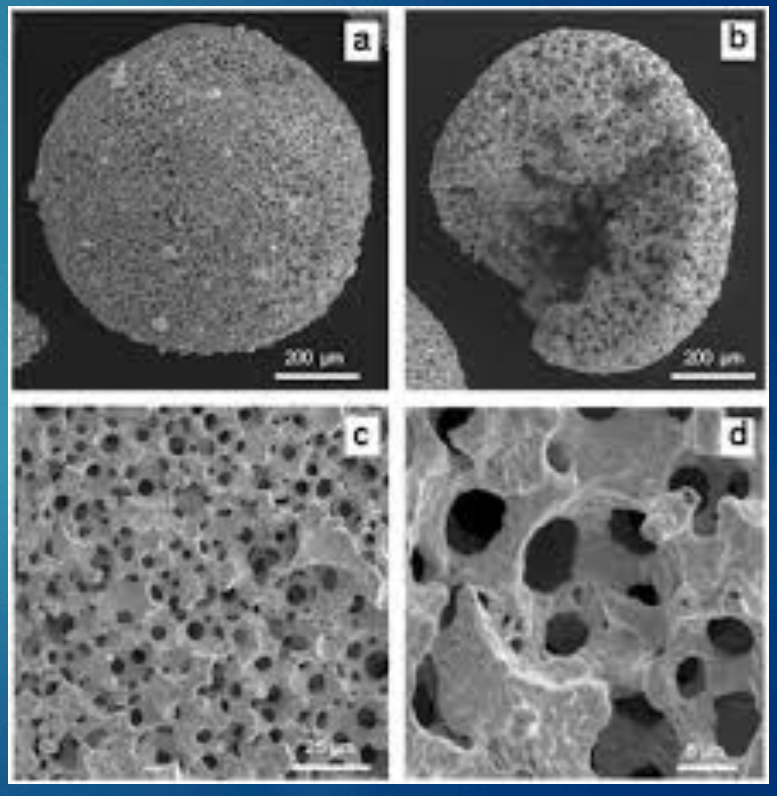
Motivation: Maybe nanoparticles are better catalysts?

- Enhanced catalytic properties
  - **Higher Conversion/ Selectivity**
- Less costly
  - Less material costs
- Increased Value as conversion increases while costs of production decrease



Increased surface area per unit weight for nanoparticle substrates





Methods Overview

BET Measurements

- Brunauer-Emmett-Teller
- Aims to explain the adsorption of gas molecules on surfaces
- Determines the total surface area of a porous substrate (Outer area + pore area)
- Determines the pore volume

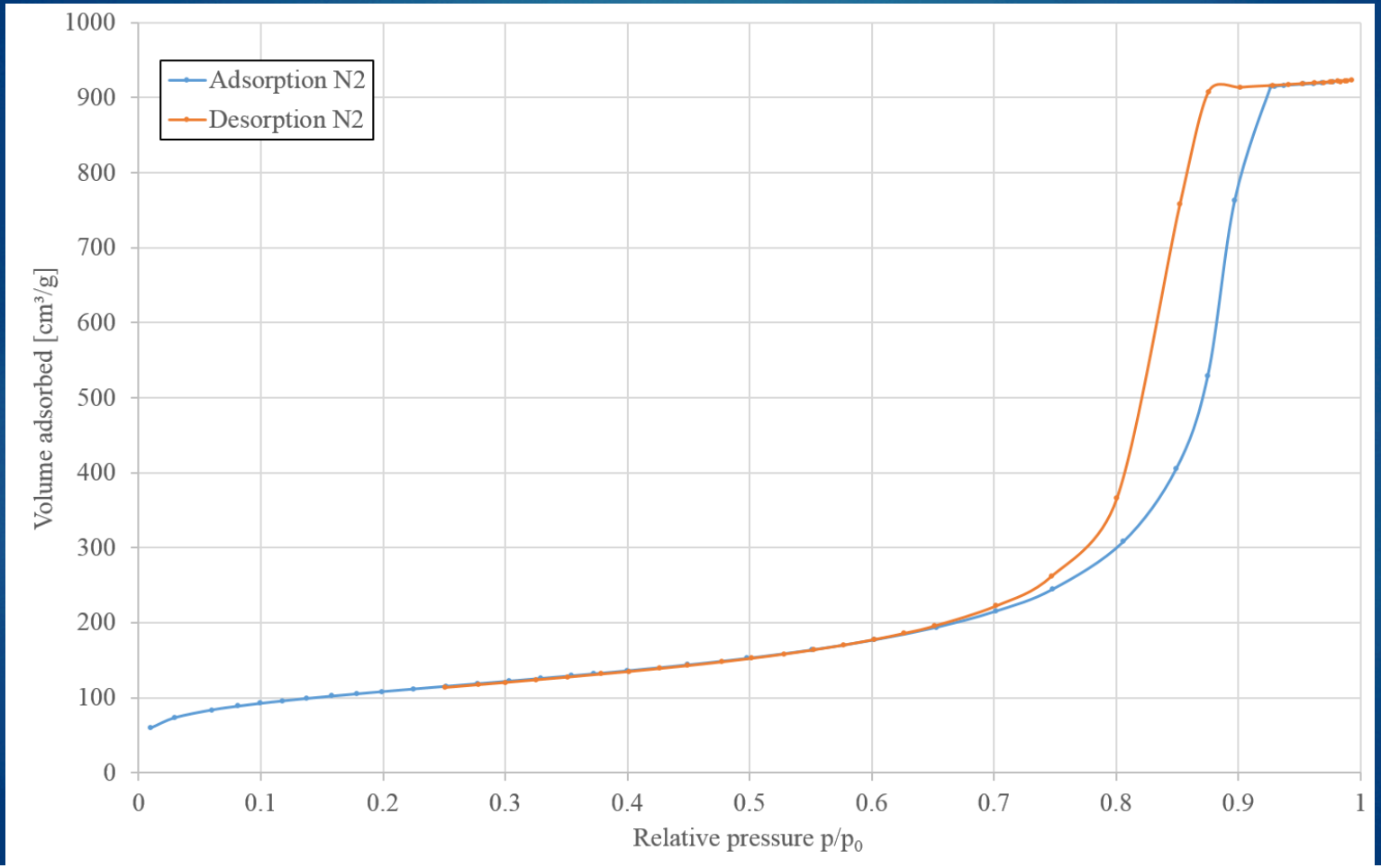
Catalyst Synthesis

- Precipitation, ultrasonication and polymerization methods
- Incipient wetness impregnation of V_2O_5 nanoparticles and bulk V_2O_5 on SiO_2 and TiO_2 substrates

Catalyst Testing

- Benchmark testing of substrates (SiO_2 and TiO_2)
- 0.5 wt % V_2O_5, 1.5 wt % V_2O_5, 3.0 wt % V_2O_5 samples
- Oxidative dehydration of methanol to formaldehyde
- Temperatures ranging from: 180 ^{o}C to 320 ^{o}C

BET: SiO_2 Adsorption/Desorption Isotherms



Template-free Hydrothermal Approach

Yellow Slurry Mix

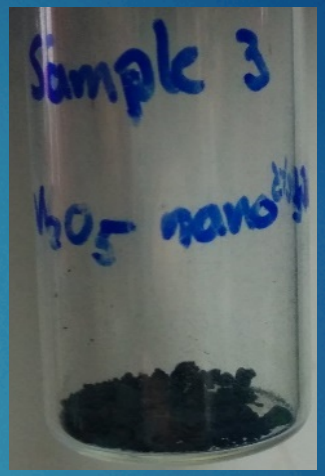
0.5 g V_2O_5 powder is magnetically stirred into 20 mL of DI water. Then 10 mL of ethylene glycol is added.

Autoclave

14 hours at 180 °C

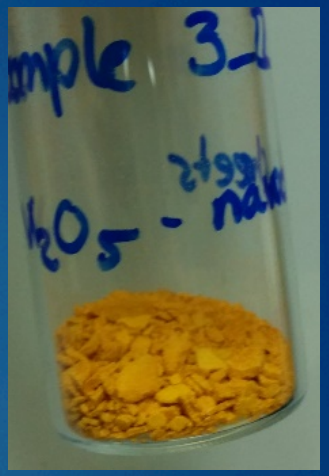
Black Precipitate

Filtered. Washed with water and EtOH.



Pre-Calcined

Dried in air for 12 hr @ 50 °C



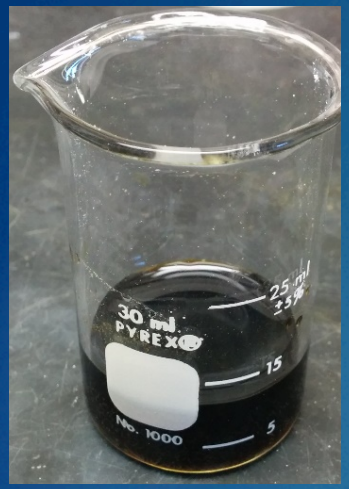
Post-Calcined

Calcined in air for 1 hr @ 400 °C

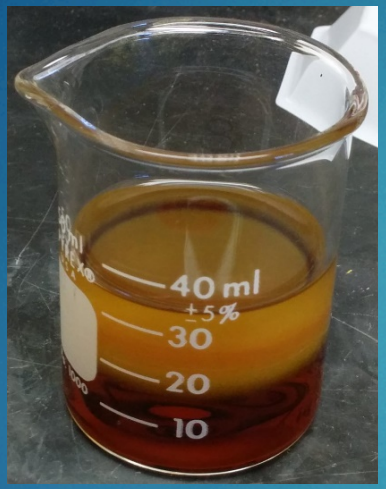
92.4% yield

Qin, M. et al., *Journal of Power Sources,* 2014, **268**, 700-705

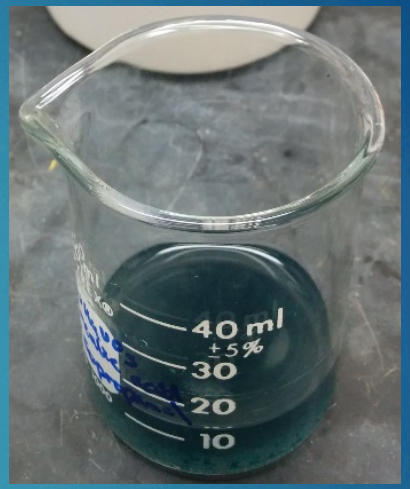
Solvothermal rxn w/ calcination



0.77 g NH_4VO_3
+
1.25 g oxalic acid +
10 ml deionized water



35 ml Isopropanol is added then sol'n is centrifuged



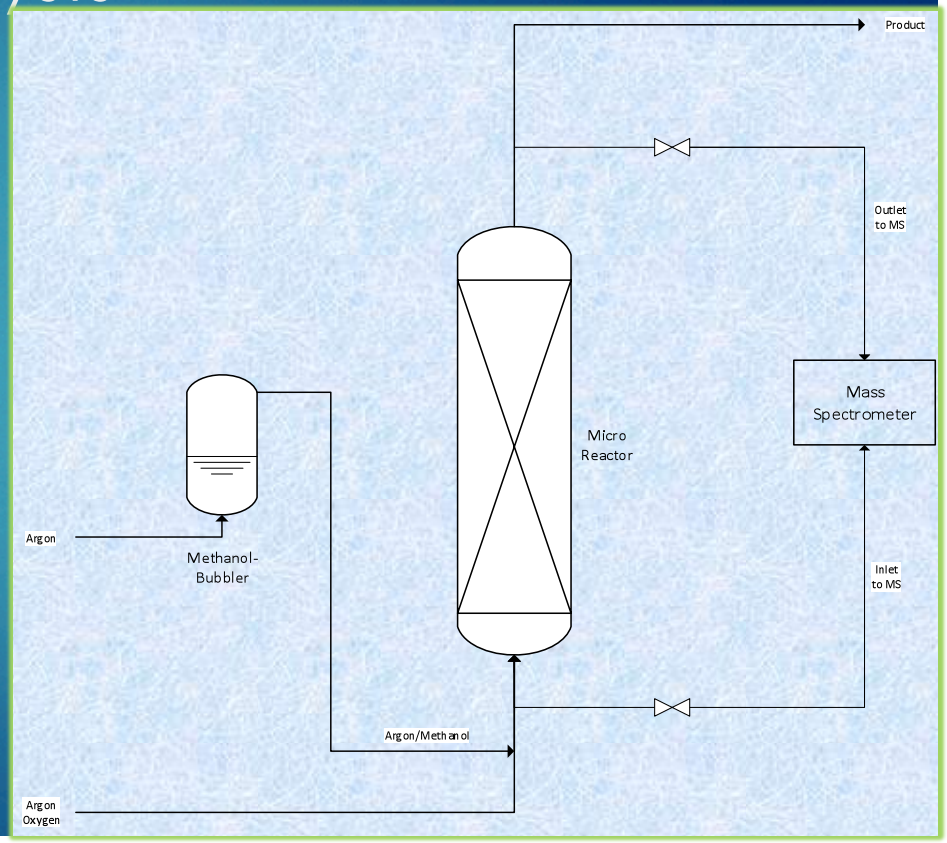
teflon lined stainless steel autoclave for 6 h @ 200 °C

washed with DI water and EtOH
Dried overnight then calcined for 2 hr @ 350 °C

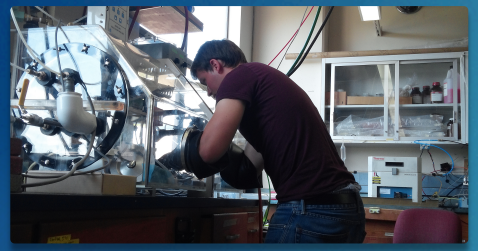
Liang, C. et al, *Journal of Power Sources*, 2014, **272**, 991-996

Catalyst Testing: Compare rxn conversion using nanoparticle catalysts

- Catalyst of interest:
  - V_2O_5 nanosheets
- Reaction of interest:
  - Oxidative dehydration of **methanol** to formaldehyde



Special thanks to the bros that made it all possible…



Daniel Hirche

Visiting scholar from Munchen. Instrumental in keeping me guided through 5 weeks of intense research.

Mike Gordon, PhD

Talented principal investigator. Clear and articulate explanations of key concepts. Always there for his students. In touch with the spirit of grad school.

Frank Kinnaman

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