Vanadium Nanoparticle Catalysis

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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, 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 $\text{V}_2\text{O}_5$ nanoparticles and bulk $\text{V}_2\text{O}_5$ on $\text{SiO}_2$ and $\text{TiO}_2$ substrates

### Catalyst Testing
- Benchmark testing of substrates ($\text{SiO}_2$ and $\text{TiO}_2$)
- 0.5 wt % $\text{V}_2\text{O}_5$, 1.5 wt % $\text{V}_2\text{O}_5$, 3.0 wt % $\text{V}_2\text{O}_5$ samples
- Oxidative dehydration of methanol to formaldehyde
- Temperatures ranging from: 180 °C to 320 °C
BET: SiO$_2$ Adsorption/Desorption Isotherms

![Graph showing adsorption and desorption isotherms for SiO$_2$](image)

- **Adsorption N2**
- **Desorption N2**

The graph illustrates the volume adsorbed [cm$^3$/g] as a function of the relative pressure $p/p_0$. The data shows the typical behavior of adsorption and desorption processes for silica dioxide ($SiO_2$).
0.5 g $\text{V}_2\text{O}_5$ powder is magnetically stirred into 20 mL of DI water. Then 10 mL of ethylene glycol is added. The mixture is autoclaved for 14 hours at 180 °C. The black precipitate is filtered and washed with water and EtOH. The pre-calcined sample is dried in air for 12 hr at 50 °C. The post-calcined sample is calcined in air for 1 hr at 400 °C. The yield is 92.4%.

Solvothermal rxn w/ calcination

0.77 g NH$_4$VO$_3$ + 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

Catalyst Testing: Compare rxn conversion using nanoparticle catalysts

- Catalyst of interest:
  - $V_2O_5$ nanosheets

- Reaction of interest:
  - Oxidative dehydration of methanol to formaldehyde
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