

# Catalyst Synthesis

Modern Techniques in Heterogeneous Catalysis Research

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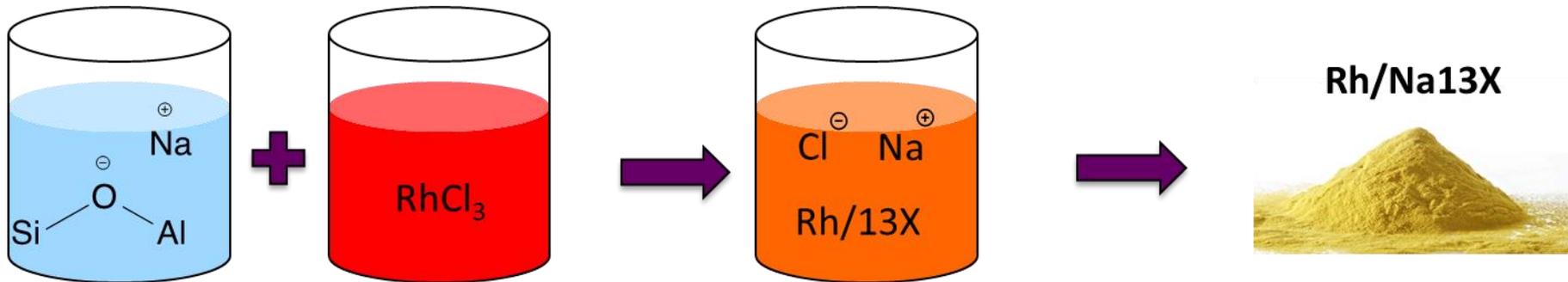
*Updated 2-4-16*



# Modern Techniques in Heterogeneous Catalysis

- Why “Catalyst Synthesis”?

- Many different catalyst preps are used
- Many more scientists develop materials than do catalysis
- Difficulty: Understanding what is different / novel, and when synthesis can become significant



- Goal: To find the best catalyst preparation for your research goals and to be critical of the existing literature

# Synthesis Overview

**Synthesis suffers from many specialized names of both processes and materials.**

- **Materials and syntheses clustered into broad categories.**
- **No recipes**
- **Some general guidelines**

# What matters in catalyst synthesis?

## ATTENTION TO DETAIL!

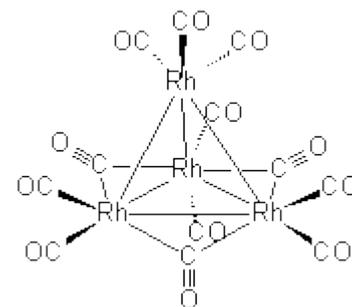
- Reagent purity and source
- Reaction 'cleanliness'
  - Nucleating crystals
  - Contaminants
  - Air/water/light/T sensitive reactions and precursors
- Rate and order of reagent addition
- Concentration, stoichiometry, and size of synthesis

**NOTE: Published syntheses may not be optimized, but they do (presumably) work. Do you really NEED to change the method?**

# Reagent Purity

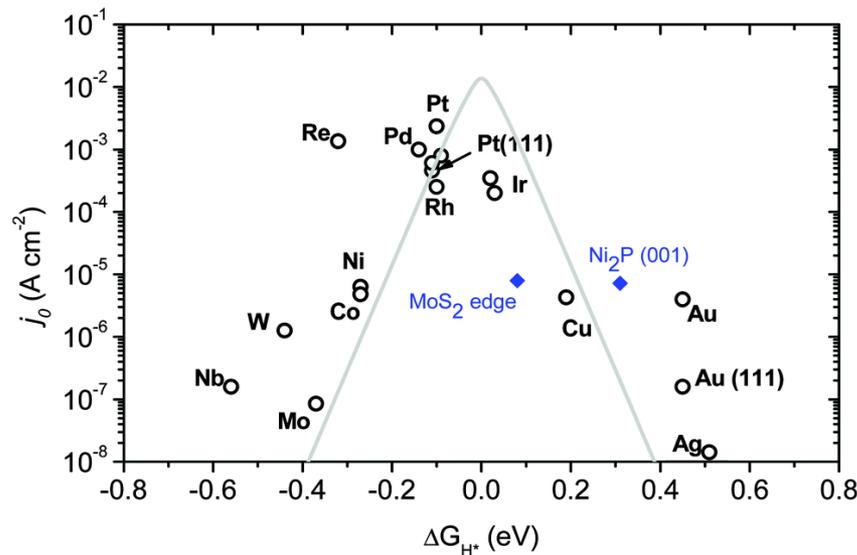
- **One reason why manuscripts require identification of suppliers and purity**
  - Some suppliers are more trust-worthy than others.
  - Different manufactures will use different sources, and leave different trace contaminants
  - Purchased materials will have different physiochemical properties.

**This Rh carbonyl (Strem) is listed as “min. 98%”.  
What does that mean?  
Metal? M:ligand ratio? Exact structure?**



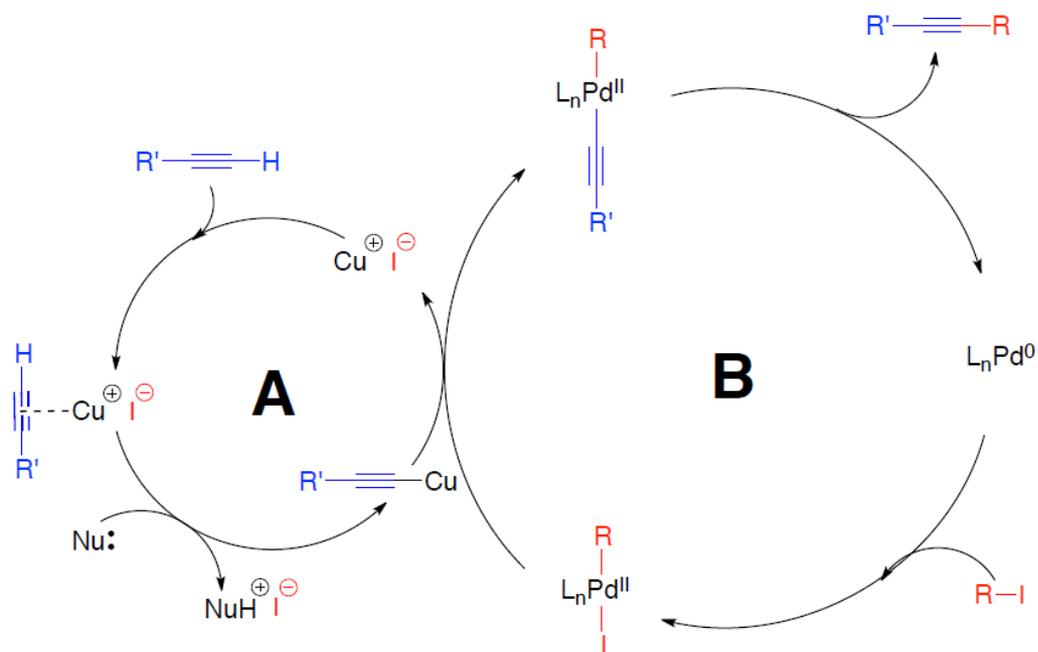
# Metal Purity Critical

- You are making **CATALYSTS**. One molecule can have a large effect.
- Different metals can have orders of magnitude different impacts. (Morales-Guio, Stern, Hu, Chem Soc Rev, 2014; H<sub>2</sub> evolution)



# Metal Purity Critical

- Different metals can have orders of magnitude different impacts.
- Reports of coupling using 'only' Cu turned out to be **ppb level contamination by Pd**. (Gonda, Tolnai, Novak, Chem. Eur. J. 2010)



# Don't Forget Everything Else

1. You suspend 1.0 g alumina in 50 mL toluene.
2. You graft 1 mmol  $\text{TiCl}_4$  (typical)
3. The toluene has 0.6 mmol  $\text{H}_2\text{O}$

1. You suspend 1.0 g silica in anhydrous toluene.
2. You graft 1 mmol  $\text{TiCl}_4$ .
3. You didn't dry your silica!
4. You easily added 2 wt%  $\text{H}_2\text{O}$  or 1.1 mmol

**This could kill your catalyst, change it, or make it irreproducible.**

**Know how to cleanup solvents and catalyst precursors / supports!**

- Drying
- Sublimation
- Recrystallization
- Distillation
- Degassing

TABLE 1. Water Content in THF after Drying<sup>a</sup>

desiccant	time (h)	residual water content (ppm)
none, "wet" solvent		107.8 ± 0.7
sodium/benzophenone <sup>b</sup>	48	43.4 ± 0.7
3 Å molecular sieves (10% m/v)	24	27.7 ± 1.0
3 Å molecular sieves (20% m/v)	24	14.7 ± 0.3
3 Å molecular sieves (20% m/v)	48	6.1 ± 0.2
3 Å molecular sieves (20% m/v)	72	4.1 ± 0.1
silica (28–200 mesh) <sup>c,d</sup>	c	56.2 ± 2.5
silica (35–60 mesh) <sup>c,e</sup>	c	105.7 ± 3.5
silica (60–100 mesh) <sup>c,e</sup>	c	89.4 ± 2.8
silica (70–230 mesh) <sup>c,e</sup>	c	82.5 ± 1.2
silica (100–200 mesh) <sup>c,e</sup>	c	74.6 ± 2.9
silica (200–425 mesh) <sup>c,e</sup>	c	59.5 ± 3.7
silica (100–200 mesh) <sup>c,f</sup>	c	69.0 ± 3.3
silica (200–425 mesh) <sup>c,f</sup>	c	60.8 ± 1.9
neutral alumina <sup>c</sup>	c	5.9 ± 0.4

<sup>a</sup>Drying was performed in triplicate;  $n = 6$  for each dried solvent analyzed, providing  $n = 18$  for each desiccant. <sup>b</sup>THF was distilled from the desiccant once the indicator had turned a persistent blue color. <sup>c</sup>Solvent was passed over a column of the desiccant, 10% m/v, inside the glovebox. The system was not assessed for "breakthrough" of water, i.e., to establish the capacity of the desiccant. <sup>d</sup>Silica (pore size 22 Å). <sup>e</sup>Silica (pore size 60 Å). <sup>f</sup>Silica (pore size 100 Å).

**Williams and Lawton, JOC 2010**

# Don't Trust Anything

**Batch-to-batch variability is a real thing.**

- surface area, dispersion, reducibility, etc.
- synthesized and purchased materials

**You must either:**

- Plan synthesis batches to last for ALL planned experiments (catalysis, characterization, etc)**
- Explicitly test for reproducibility**

You know that really awesome catalyst run you just had?

**MAKE THE CATALYST AGAIN!**

# Classes of Solid Catalysts

- Bulk materials
- Supported catalysts
- Immobilized catalysts or pre-catalysts

# Bulk Materials

- Supports or active catalysts
- Porous materials
  - Meso- or un-structured oxides or chalcogenides (non-Xstal, inorganic)
  - Zeolites (Xstal, inorganic)
  - Hybrid organic / inorganics (non-Xstal, hybrid)
  - MOFs and their kin (Xstal, hybrid)
  - Carbons (mixed, hybrid)
  - (permanently porous) polymer beads (non-Xstal, organic)
- Non-porous materials
  - Nanocrystalline materials (e.g.  $\text{CeO}_2$  or Pt nanoshapes)
  - Colloidal materials (metals)
  - Complex oxides: (e.g. perovskites,  $\text{MoVTaNbO}$ )
  - Sulfides, other layered materials
- Reactivity heavily influenced by defects, added active sites (e.g. oxygen vacancies,  $\text{Ti-SiO}_2$ )

# Needed Information

Once you have a solid, you need to quantify properties

- After synthesis of a bulk catalyst or support
- Before creating a supported catalyst
  - Particle size
  - Surface area
  - Crystallite size
  - Bulk and surface elemental composition
  - Surface charge
  - Density of defects
    - O vacancies
    - OH groups
    - Functional tethers
    - Exchange sites
- For verification of synthesis and further use

# Needed Information – ‘Physical’

- Particle size
  - Sieve sets (micron to mm)
  - Dynamic light scattering (nm to micron)
- Surface area and pore volume
  - N<sub>2</sub> (CO<sub>2</sub> or Ar) physisorption (additional lecture)
- Crystallite size
- Surface charge
  - Depends on solution pH; from zeta potential, titration
- Density of defects
  - O vacancies, OH groups, Functional tethers, Exchange sites
  - A number of specialized techniques covered in other lectures

# Needed Information – ‘Composition’

- Bulk and surface composition
  - ICP-AES (-OES), ICP-MS
    - requires sample digestion by (acid/peroxide) dissolution or (borate) salt fusion
  - XPS, XRF
    - no sample digestion, variable surface penetration
  - Combustion analysis
    - e.g. TGA
    - may be –MS or calibrated specifically for H<sub>2</sub>O/CO<sub>2</sub>, etc.
  - NMR
    - Element specific
    - Calculates (relative) numbers of functional groups
    - (e.g. linkers vs. nodes, COO<sup>-</sup> sites, tetrahedral vs. octahedral Al)
    - May require sample digestion
- Do not assume that the final elemental composition matches the synthesis composition.
- Covered in other lectures: Microscopy, XAS, Chemisorption, Physisorption, Spectroscopy

# Syntheses of Bulk Materials

- 'Kinetic' Processes

- Carbons

- Sol-gel

- Co-precipitation

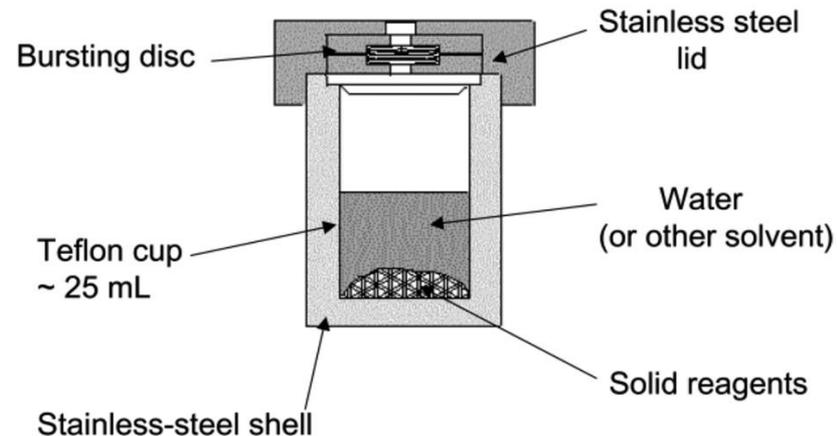
- With and without a template (to constrain pores, external S.A.)
- precursor 1 + precursor 2 + ... + solvent
- Trigger (typically pH switch) to induce reaction. Acid or base catalyzed.
- Strongly dependent on pH, solvent, reactant concentrations, T, time
- Typically there will be subsequent second aging and size commutation steps
- Things matter: isopropoxide  $\neq$  ethoxide (rates of hydrolysis)

- Microphase segregation is an important issue

- 'Thermodynamic' Processes

- Hydro(solvo)thermal

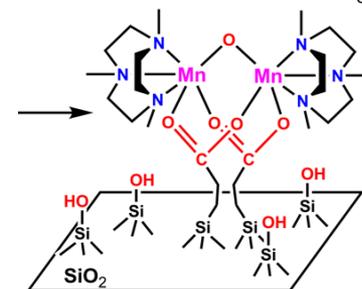
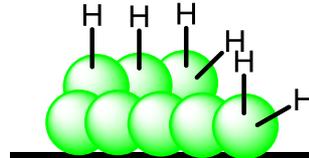
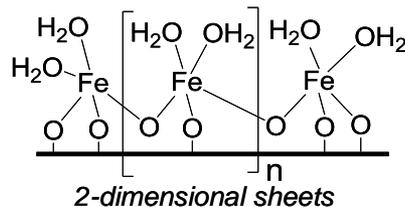
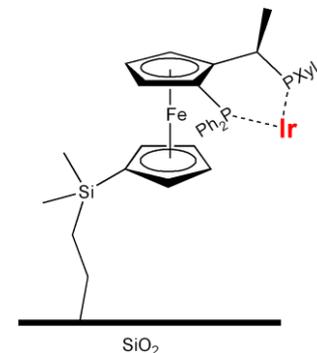
- At sufficient T and reversibility to allow thermodynamic (metastable) phase
- Often uses a pressure vessel for  $T > BP_n$



# Supported Catalysts

- Adding active sites to an existing catalyst

- Immobilizing pre-formed active sites (immobilized)
- Adding a pre-catalyst
- Synthesizing a new site on the surface



- Support may (or may not) be kinetically relevant

- Support may create transport effects
  - Alter local concentrations
  - Induce shape selectivity
- Control local 'solvent' sphere
- Reaction site may be the support-additive interface or strongly influenced by support

# Syntheses of Supported Catalysts

- Not much more than three basic categories:
  - Impregnation / Deposition
  - Grafting
  - Exchange
- All concern how a precursor is added to a support
- Subsequent oxidative, reductive, or thermal steps give the final catalyst (and thus matter at least as much)

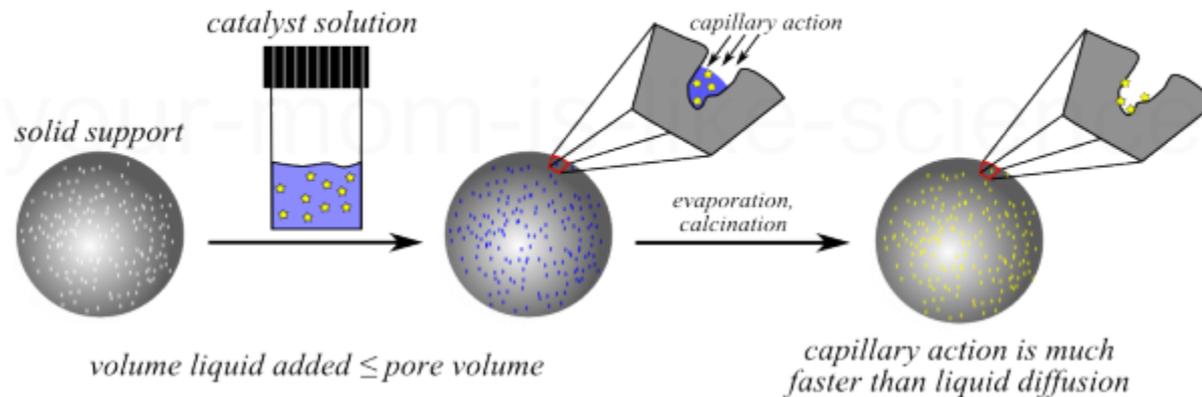
NOTE: a failed two-component bulk material recipe may effectively give you a 'supported' catalyst.

- e.g. separate condensation of each component,
- then one deposits on the other

# Impregnation / Deposition

- Vapor, solution, or melt

*incipient wetness impregnation  
(or dry impregnation, capillary impregnation)*



- Goal is to ‘mechanically’ fill (intraparticle or interparticle) pores
  - Driven by capillary effects. Issues like solution viscosity.
  - Amount deposited  $\sim$  amount added
  - Subsequent heating to ‘lock in’ the added sites
  - Aim is to give uniform deposition throughout particle

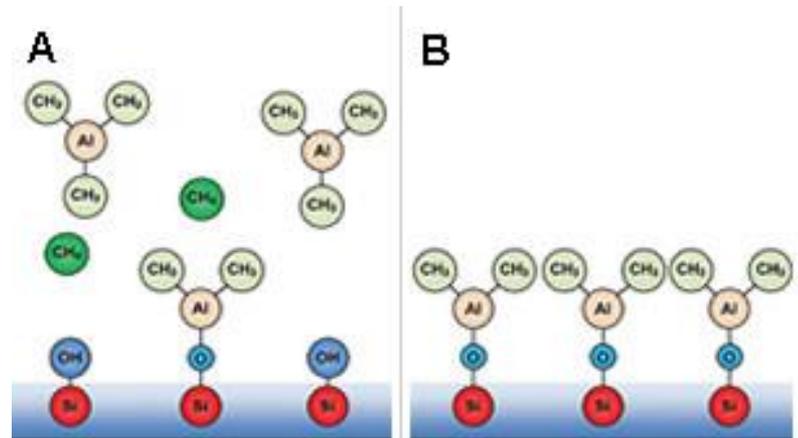
# Grafting

- Vapor or liquid

- Implies covalent bond formation between support and active species

- Often protonolytic

- e.g.  $\text{TiCl}_4 + \equiv\text{SiOH}$
- e.g.  $\text{RSi}(\text{OEt})_3 + \equiv\text{SiOH}$
- e.g.  $\text{Al}(\text{CH}_3)_3 + \equiv\text{SiOH}$



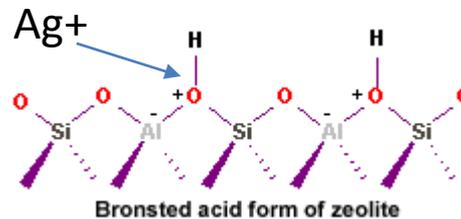
- Can be self-limiting

- If precursor can't react with itself or adsorbed version

- ALD is a gas-phase version, in some cases
- Presence of a contaminant, e.g.  $\text{H}_2\text{O}$ , can lead to self-reaction

# Exchange

- Exclusively in solution
  - Can be static (expose material to excess) or dynamic (flow)
  - Implies a salt exchange – ionic bonds
  - Intrinsically self limiting if well-defined exchange sites
    - zeolites, clays, exchange resins, functionalized surfaces



- Strong electrostatic adsorption (SEA) is a relative that exploits surface charge vs. pH on extended surfaces
- Exchange of di- (tri-) valent species is more tricky
  - need multiple exchange sites in proximity

# Subsequent Steps and Outcomes

## More steps after precursor deposition:

- Typically a heat treatment
- Oxidation (for oxides), Reduction (for supported metals)
- C source (for carbides), S source (for sulfides)
- Structures formed **VERY** sensitive to post-synthesis treatment
  - temperature, time, heating rate, reactive gases
  - max T often set by materials phase changes, NP sintering

## Even dispersion is a primary goal of the syntheses:

- **Impregnation:** good distribution throughout the carrier, but may have range of molecular structures
- **Grafting:** structural heterogeneity matches heterogeneity of the support
- **Exchange:** can be very selective in limiting cases

# Takeaways

- Catalyst synthesis is touchy and impacts everything else. Be careful!
- Few catalyst synthesis methods are generally 'novel', and there is not always a good reason for novelty
- Catalyst syntheses should be considered path independent: what matters most is what you get, not how you got there!