

Catalyst Synthesis

Modern Techniques in Heterogeneous Catalysis Research

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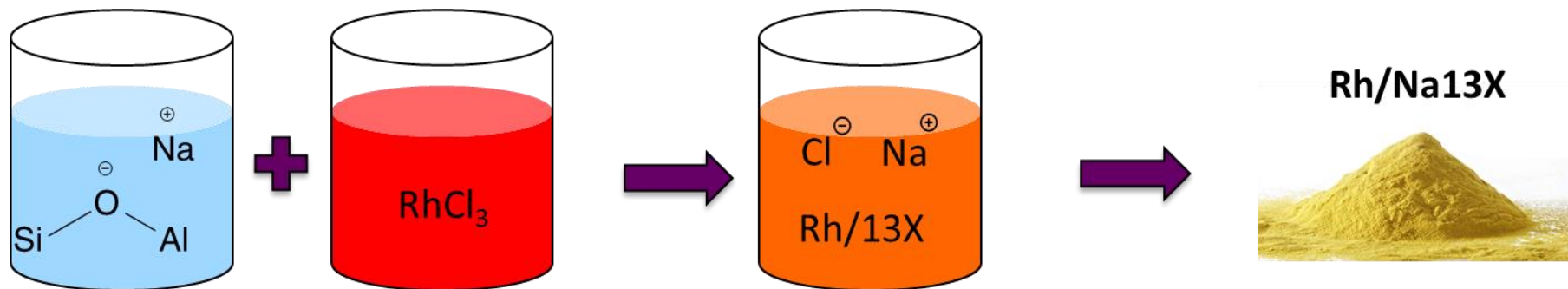
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Modern Techniques in Heterogeneous Catalysis

- 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!

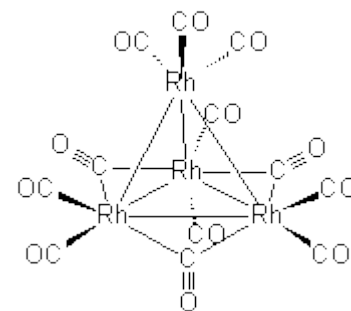
- Reagent purity and source
- Reaction 'cleanliness'
 - Nucleating crystals
 - Contaminants
 - Air/water/light/T sensitive reactions and precursors
- Rate and order of reagent addition
- Concentration, stoichiometry, and size of synthesis

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

Reagent Purity

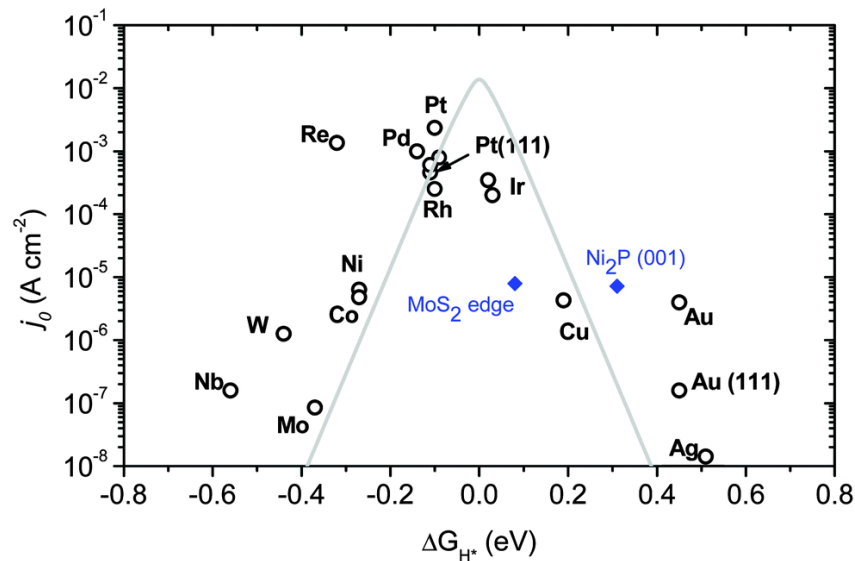
- **One reason why manuscripts require identification of suppliers and purity**
 - Some suppliers are more trust-worthy than others.
 - Different manufactures will use different sources, and leave different trace contaminants
 - Purchased materials will have different physiochemical properties.

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



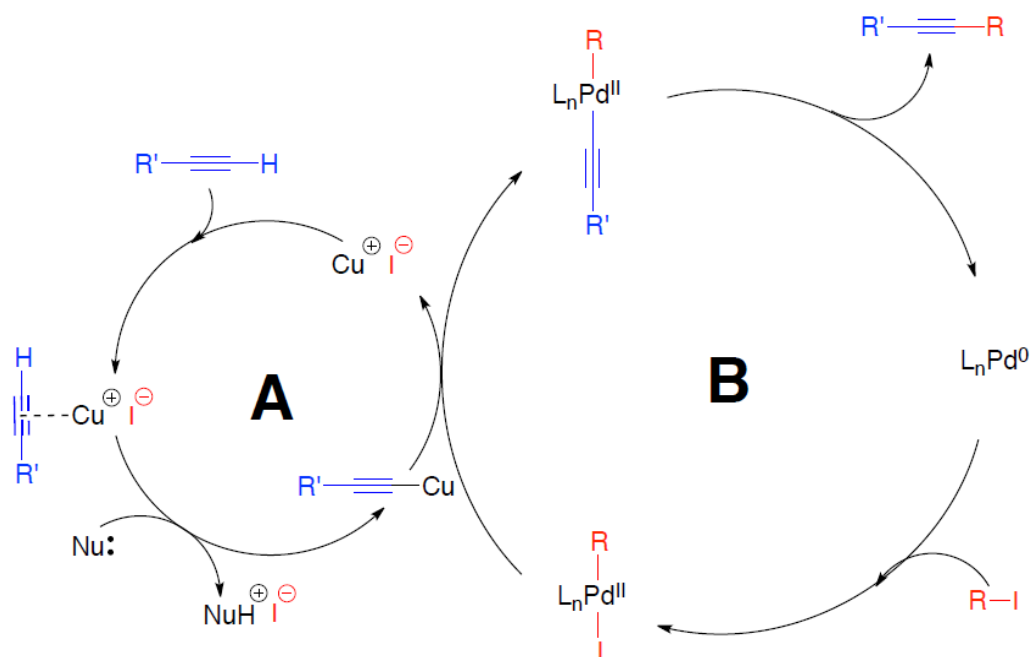
Metal Purity Critical

- 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; H₂ 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 TiCl_4 (typical)
3. The toluene has 0.6 mmol H_2O

1. You suspend 1.0 g silica in anhydrous toluene.
2. You graft 1 mmol TiCl_4 .
3. You didn't dry your silica!
4. You easily added 2 wt% H_2O 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^a

desiccant	time (h)	residual water content (ppm)
none, "wet" solvent		107.8 ± 0.7
sodium/benzophenone ^b	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) ^{c,d}	c	56.2 ± 2.5
silica (35–60 mesh) ^{c,e}	c	105.7 ± 3.5
silica (60–100 mesh) ^{c,e}	c	89.4 ± 2.8
silica (70–230 mesh) ^{c,e}	c	82.5 ± 1.2
silica (100–200 mesh) ^{c,e}	c	74.6 ± 2.9
silica (200–425 mesh) ^{c,e}	c	59.5 ± 3.7
silica (100–200 mesh) ^{c,f}	c	69.0 ± 3.3
silica (200–425 mesh) ^{c,f}	c	60.8 ± 1.9
neutral alumina ^c	c	5.9 ± 0.4

^aDrying was performed in triplicate; $n = 6$ for each dried solvent analyzed, providing $n = 18$ for each desiccant. ^bTHF was distilled from the desiccant once the indicator had turned a persistent blue color. ^cSolvent 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. ^dSilica (pore size 22 Å). ^eSilica (pore size 60 Å). ^fSilica (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. CeO_2 or Pt nanoshapes)
 - Colloidal materials (metals)
 - Complex oxides: (e.g. perovskites, MoVTaNbO)
 - Sulfides, other layered materials
- Reactivity heavily influenced by defects, added active sites (e.g. oxygen vacancies, 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
 - N₂ (CO₂ 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 H₂O/CO₂, etc.
 - NMR
 - Element specific
 - Calculates (relative) numbers of functional groups
 - (e.g. linkers vs. nodes, COO⁻ 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

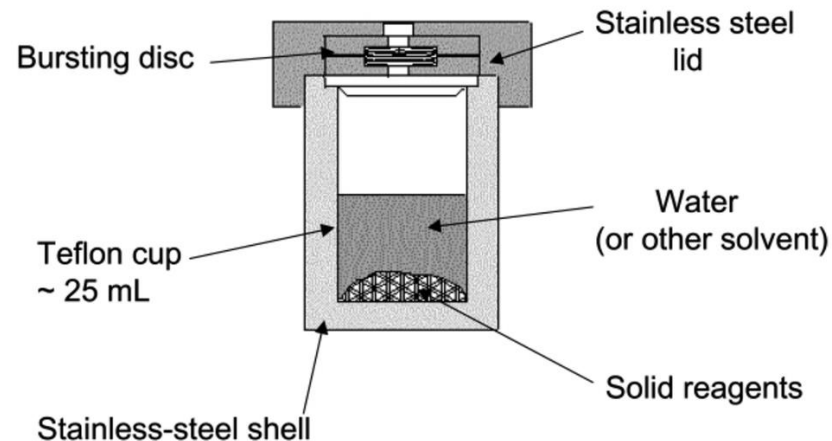
- With and without a template (to constrain pores, external S.A.)
- precursor 1 + precursor 2 + ... + solvent
- Trigger (typically pH switch) to induce reaction. Acid or base catalyzed.
- Strongly dependent on pH, solvent, reactant concentrations, T, time
- Typically there will be subsequent second aging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

- Microphase segregation is an important issue

- 'Thermodynamic' Processes

- Hydro(solvo)thermal

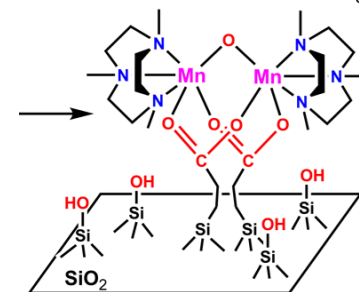
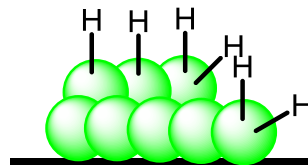
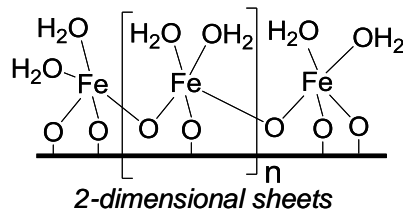
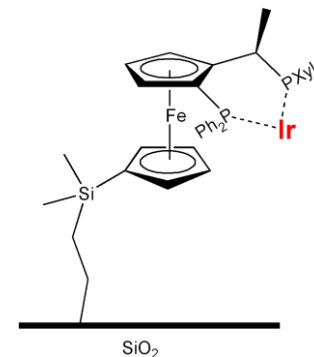
- At sufficient T and reversibility to allow thermodynamic (metastable) phase
- Often uses a pressure vessel for $T > BP_n$



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)

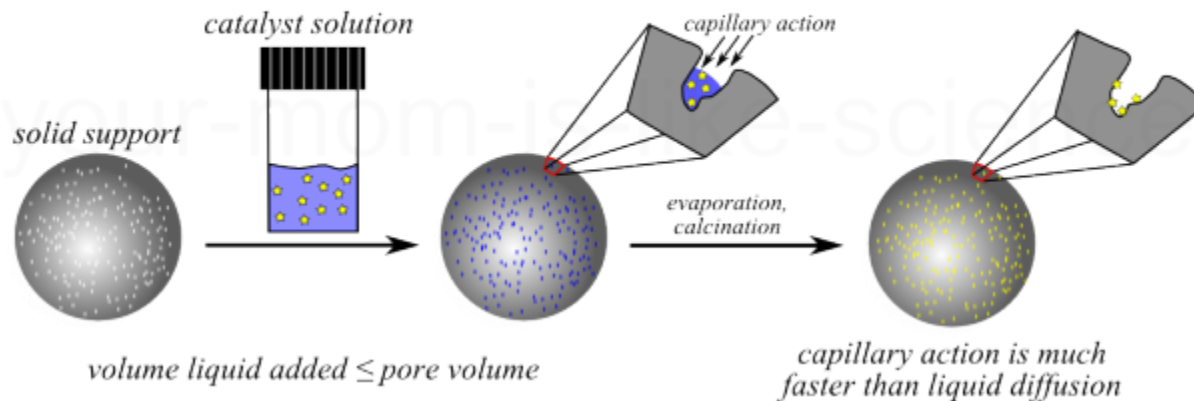
NOTE: a failed two-component bulk material recipe may effectively give you a 'supported' catalyst.

- 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

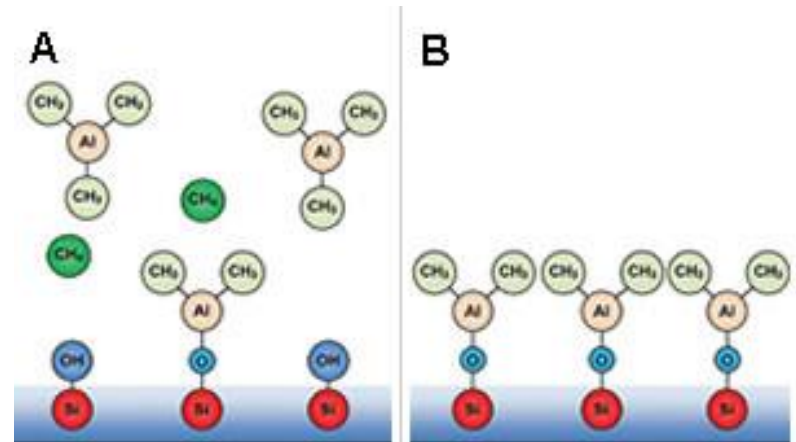
Grafting

- 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

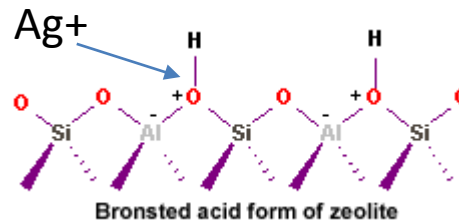
- If precursor can't react with itself or adsorbed version

- ALD is a gas-phase version, in some cases
- Presence of a contaminant, e.g. H_2O , 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!