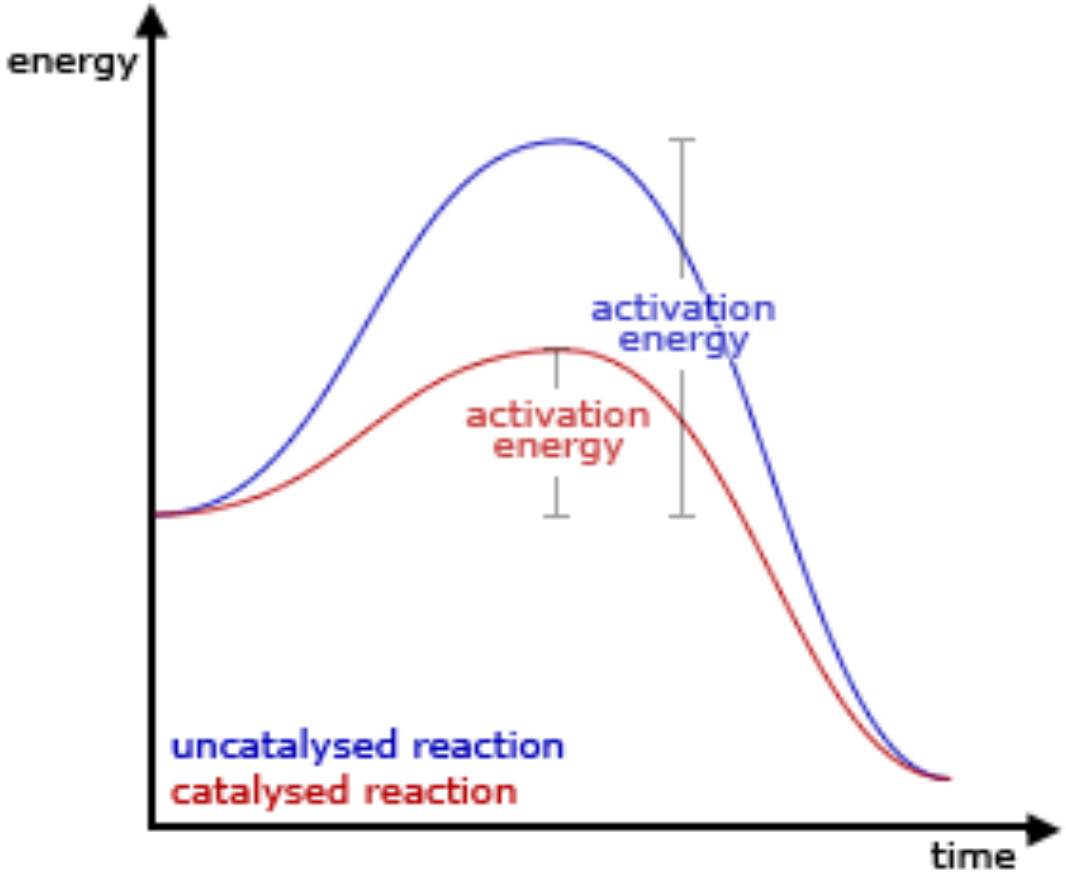
Principle 9: Catalysis

Catalytic reagents are _superior_ to stoichiometric reagents

- Catalysis is the acceleration of a chemical reaction by means of a substance, catalyst, which is itself not consumed by the overall reaction
- Advantages of catalysis:
  - Reduces energy
  - Increasing efficiency
  - Reduces by-product formation

Green Chemistry and Catalysis



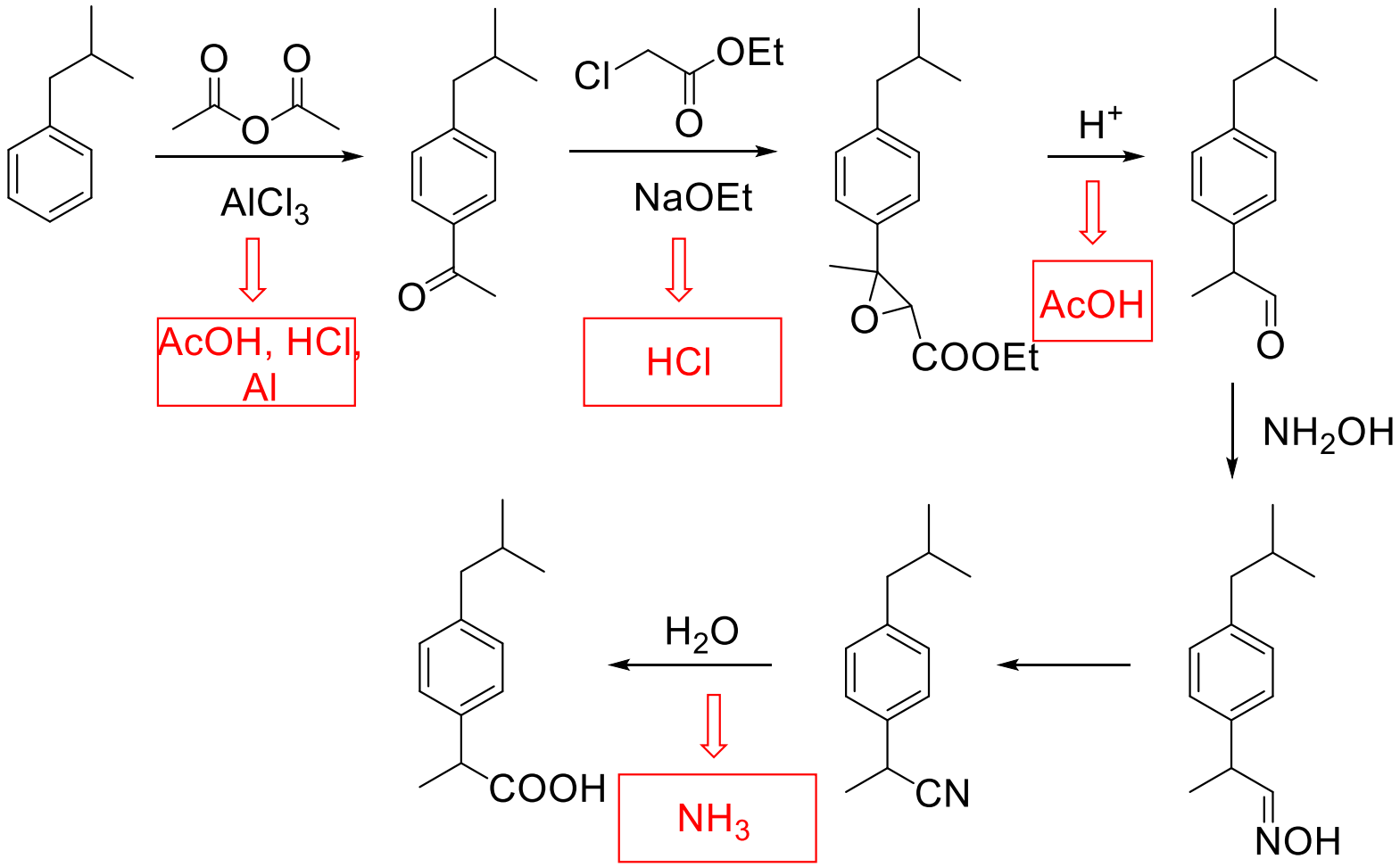
How is Catalysis Green?

- Reduces the energy required for the reaction due to lower activation energy (e.g. lower temperature)
- Eliminates the use of stoichiometric reagents
- Reduces the amount of by-products (catalyst are unchanged at the end of the reaction) → Reduces waste
- Highly selective

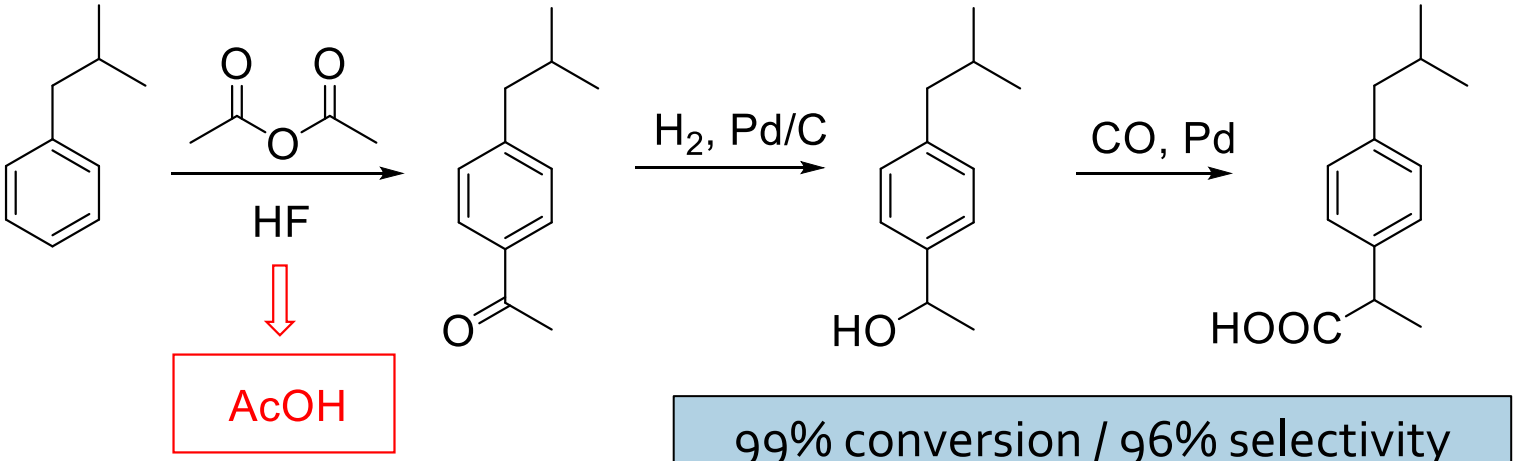
Which of the 12 principles of green chemistry does catalysis apply to?

- Principle 1: Prevent waste
- Principle 6: Design for energy efficiency
- Principle 9: Catalysis

Boots Synthesis of Ibuprofen



Hoechst Synthesis of Ibuprofen

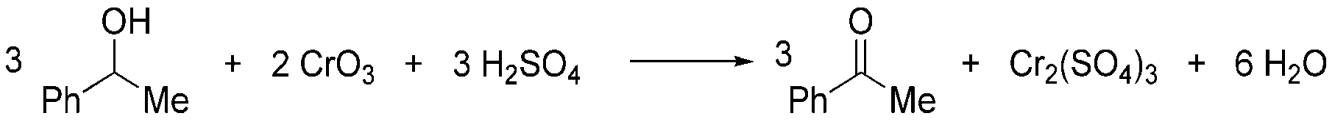


99% conversion / 96% selectivity
100% atom economy (steps 2 and 3)

- High conversion and high selectivity
- Less waste generated (by-products, solvents)

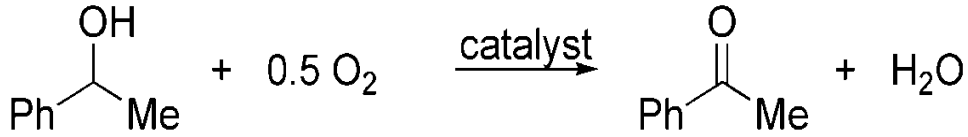
Stoichiometric vs Catalytic

Stoichiometric oxidation (Jones Reagent)



atom economy = 42 %
E-factor = ca. 1.5

Catalytic oxidation



atom economy = 87 %
E-factor = ca. 0.1

Principle 9: Catalytic reagents are superior to stoichiometric ones

Limitations of a Catalyst

- Catalyst mainly involve heavy metals (Pd, Ru, Rh) which may have toxicity issues

- Factors to consider regarding a catalyst:
  - Separation of catalyst from product
  - Ability to recycle catalyst
  - Catalyst degradation
  - Toxicity

Generally, it is greener to use a catalyst!

Catalyst

Parameters impacting both commercial viability and inherent greenness of a particular catalyst:

1. Selectivity

Amount of substrate converted to desired product as percentage of total consumed substrate

2. Turnover number

Amount of product produced per mole of catalyst

3. Turnover frequency

Number of moles of product produced per mole of catalyst per second

Types of Catalysis

Heterogeneous catalysis

- Reagents and catalyst are in different phase.
- Usually in refining/ bulk chemical syntheses.

Homogeneous catalysis

- Reagents and catalyst are in the same phase.
- Usually in fine chemicals and pharmaceuticals.

Types of Catalyst

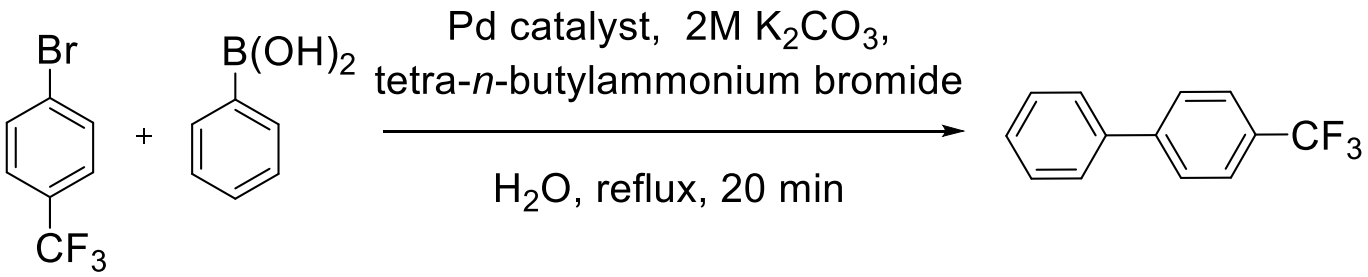
Asymmetric catalysts

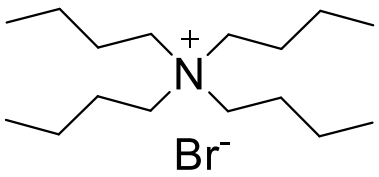
- Relatively rare in industrial process
- Increasing important in pharmaceutical industry
- One of the most efficient, low waste methods to produce enantiomerically pure compounds

Types of Catalyst

Phase transfer catalyst

- Increase rate and yield of reaction when reactants in separate phases
- Act as transporting reactants from one phase to another





Types of Catalyst

Photocatalysts

- Harness energy from sun for chemical transformation
- Energy efficient catalysts useful to destroy harmful waste and water clean-up

Types of Catalyst

Biocatalysts

- Catalysis by enzymes
- Essential for life and vital in most process in body and plants
- Natural enzymes or enzymes produced *in situ* from whole cells
- Carry out difficult transformation under mild conditions
- Produce enatiomerically pure materials

Enzyme catalysis is GREEN!

Properties	**Relevance to Green Chemistry**
Fast reaction due to correct catalyst orientation	Faster throughput
Orientation of site gives high stereospecificity	Possibility of asymmetric synthesis
High degree of substrate specificity due to limited flexibility of active site	High degree of selectivity
Water soluble	Opportunity for aqueous phase reactions
Naturally occurring	Non-toxic, low hazard catalyst
Natural operation under conditions found in body	Energy efficient reactions under moderate conditions of pH, temperature, etc
Possibility for tandem reactions when using whole organisms	Possibility for carrying out sequential one-pot synthesis

Homogeneous vs Heterogeneous Catalysis

	Homogeneous	Heterogeneous
Activity	High	Low
Selectivity	High	Low
Catalyst separation / recycling	Difficult	Easy

Fluorous-tagged catalysts