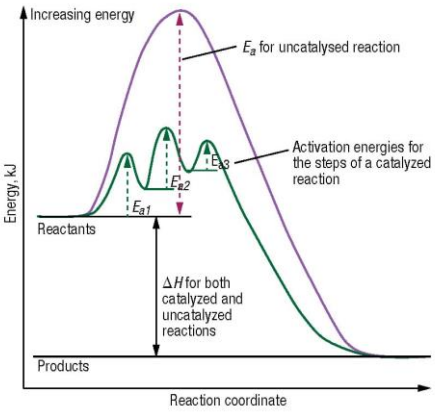
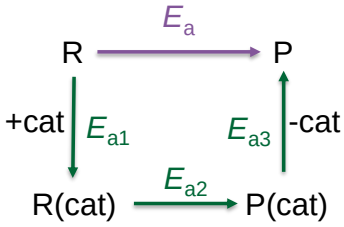
Catalysis





Catalyst

- affects reaction kinetics ($\Delta G^{\ddagger}$)

- does not affect thermodynamic equilibrium (ΔG, K_{eq})

- takes part, but is not "consumed"

Catalysts affect kinetics, not thermodynamics

$CH_4(g) + CO_2(g) = 2CO(g) + 2H_2(g)$

$\Delta G°_{373}$= 151 kJ/mol (100 °C)

$\Delta G°_{973}$ = -16 kJ/mol (700 °C)

- At 100°C, $\Delta G°_{373}$=151 kJ/mol > 0. There is no thermodynamic driving force, the reaction won't proceed with or without a catalyst

- At 700°C, $\Delta G°_{373}$= -16 kJ/mol < 0.
  The reaction is thermodynamically favoured. However, the reaction barrier precludes the reaction of bare CH_4 and CO_2. When Pt/ZrO_2 or Ni/Al_2O_3 is present in the reactor at the same temperature, equilibrium conversion can be achieved (<100%).

Why do we need catalysis?

- Catalysts should reduce
  - energy (low T, P)
  - number of reaction steps
  - stoichiometric reagents
  - by-products
  - waste

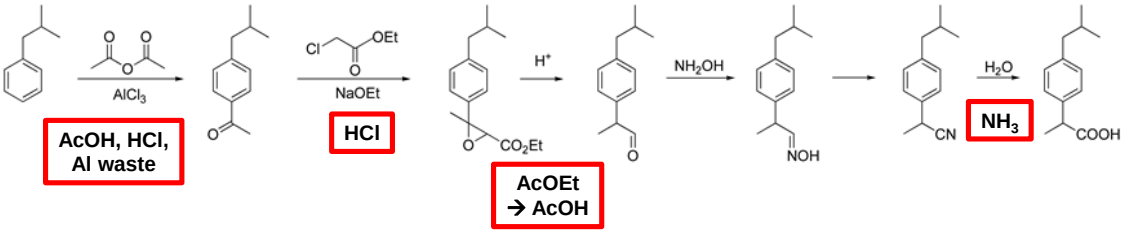
→ Catalysis is green

Disadvantages?

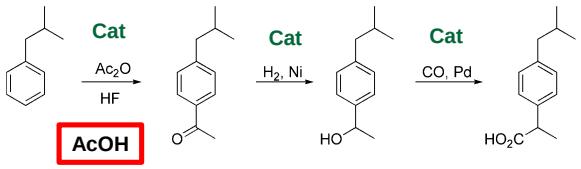
- many catalysts → based on heavy metals and may be toxic
  - separation of catalysts
  - recycling of the catalysts
  - degradation of the catalysts
  - toxicity of the catalysts and its degradation products

- Compare synthesis of Ibuprofen

Classical, stoichiometric approach



Catalysis approach



The last two steps together:
99% conversion
96% selectivity

- Basic terms
  - Homogeneous catalysis
    - Reagents and catalyst are all in the same phase (typically solution)
  - Heterogeneous catalysis
    - Reagents are in a different phase from catalyst (catalyst is typically solid, reagents are liquids or gases)
  - Biocatalysis
    - Catalysts are enzymes

- Types of catalysis

heterogeneous catalysis	heterogeneous catalysis	organocatalysis	transition-metal catalysis
catalysis by main-group element compounds	enzyme catalysis	photocatalysis	nanocatalysis
electrocatalysis	cooperative catalysis	tandem catalysis	biocatalysis

Homogeneous vs. Heterogeneous

Phase

- Homogeneous – liquid, if a reactant is gas, then it reacts as gas dissolve in the liquid phase (see the example of CO_2 reduction)
- Heterogeneous – liquid, gas, solid

Temperature

- Homogeneous – generally low temperatures limited by the solvent or by a stability of the catalyst, higher temperatures could be achieved at higher pressures
- Heterogeneous – only limited by the stability of the catalyst under harsh conditions

Diffusivity and heat transfer

- Homogeneous – high under proper stirring
- Heterogeneous – diffusivity depends on the surface area, heat transfer depends on the heat capacities of the reactants and the catalyst

Catalyst separation and recycling

- Homogeneous – expensive (tricks – biphasic systems)
- Heterogeneous – simple, the catalyst might need a reactivation

Active site

- Homogeneous – usually well defined (often a transition metal atom stabilized by ligands)
- Heterogeneous – mainly not well defined, the active sites might be only a few percent of the metal, different zones of a catalyst may have different catalytic properties

Catalyst modification

- Homogeneous – easy – tuning electronic and steric properties at the metal site by ligand design
- Heterogeneous – difficult – control of active sites or particle size at the molecular level is difficult

Reaction mechanisms

- Homogeneous – many available techniques, defined conditions, direct investigation of the intermediates (NMR and EPR spectroscopy, IR/UV-Vis spectroscopy, mass spectrometry, X-ray diffraction methods, computational methods)
- Heterogeneous – usually indirect methods – looking at reactants/products (IR spectroscopy for determination of the species absorbed on the active site, electron microscopy – ex-situ determination of particle size, X-ray absorption – ex-situ and in-situ study of the active sites – supported by computational models, computational methods)

Selectivity

- Homogeneous – high – achieved by the ligand design and by the understanding of the mechanisms
- Heterogeneous – low – difficult reactivity tuning, less understood mechanisms

Homogeneous vs. Heterogeneous in a nutshell

Homogeneous	Heterogeneous
Difficult to separate ×	Readily separated ✓
Difficult to recover ×	Readily recycled / regenerated ✓
Short service life ×	Long-lived ✓
Expensive ×	Cheap ✓
Very high rates ✓	Lower rates (diffusion limited) ×
Robust to poisons ✓	Sensitive to poisons ×
Highly selective ✓	Lower selectivity ×
Mild conditions ✓	High energy process ×
Mechanisms often known ✓	Poor mechanistic understanding ×

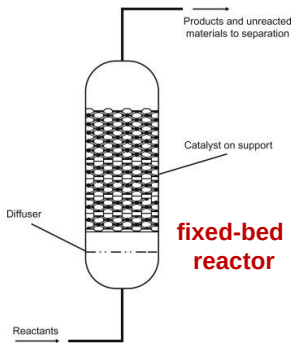
Ultimate goal: to combine the fast rates and high selectivities of homogeneous catalysts with the ease of recovery /recycle of heterogeneous catalysts

Catalytic Reaction Processes

A catalytic reaction can be operated in a ***batch* manner**

- Reactants and catalysts are loaded together in reactor
- Catalytic reactions (homo- or heterogeneous) take place in pre-determined temperature and pressure for a desired time / desired conversion
- Type of reactor is usually simple, basic requirements
  - Withstand required temperature & pressure
  - Stirring to encourage mass and heat transfers
  - Provide sufficient heating or cooling

Catalytic Reaction Processes



fixed-bed reactor

Catalytic reactions are commonly operated in a ***continuous*** **manner**

- Reactants are fed to a flow reactor in *steady* rate (e.g. mol/h, kg/h, m^3/h)
- Usually a *target conversion* is set for the reaction
- Reactants are mostly in gas phase or liquid phase (easy transportation, the heat & mass transfer rates in gas phase are much faster than those in liquid
- Catalysts are pre-loaded (a solid catalyst) or fed together with reactants (catalyst & reactants are in the same phase and pre-mixed)
  - Solid catalysts are easiest to separate from unreacted reactants and products
  - Note: In a chemical process separation usually accounts for ~80% of cost. That is why engineers always try to put a liquid catalyst on to a solid carrier (immobilization).
  - A pre-loaded solid catalyst can be used for number cycles (months or years), but some catalysts need a *regeneration*

In most cases, catalytic reactions are carried out with catalyst in a fixed-bed reactor, with the reactant being gases or liquids

General requirement for a good catalyst

- Activity – it must promote the rate of the desired reaction
- Selectivity – it should promote only the rate of the desired reaction
  (not the undesired reactions

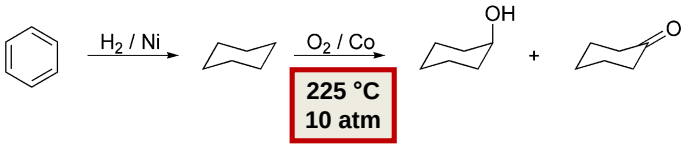
  The selectivity is sometimes considered to be more important than the activity and sometime it is more difficult to achieve

  (e.g. selective oxidation of NO to NO_2 in the presence of SO_2)

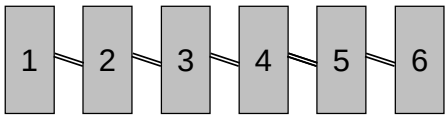
- Stability - a good catalyst should resist to deactivation, caused by
  - the presence of impurities in feed (e.g. poisoning of car catalysts by lead impurities).
  - thermal deterioration, volatility and hydrolysis of active components
  - attrition due to mechanical movement or pressure shock
- A large surface area of solid catalysts increases a number of active sites - this is usually achieved by making the solid into a porous structure.

Example: Synthesis of cyclohexanol

Traditional synthesis



For selectivity reasons, the reaction is run at low conversions
(approx 6% per tank) and the hot cyclohexane stream is continuously recycled.



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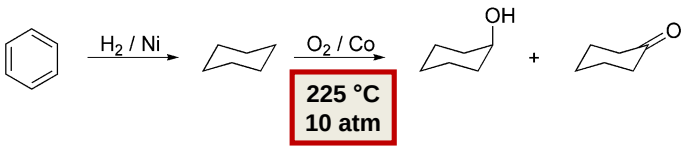

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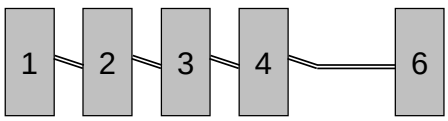
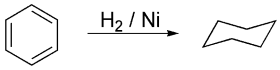


Flixborough 1974
- tank 5 removed for repairs
- temporary pipework between tanks 4 and 6 ruptured and cyclohexane cloud exploded
  → -28 deaths

Example: Synthesis of cyclo

Traditional synthesis



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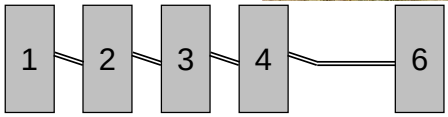

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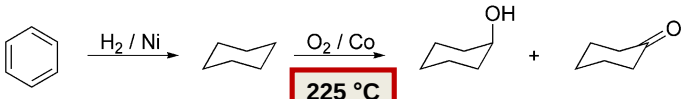
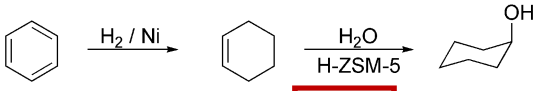
Traditional synthesis



225 °C
10 atm

For selectivity reasons, the reaction is run at low conversions
(approx 6% per tank) and the hot cyclohexane stream is continuously recycled.

Zeolite - Asahi cyclohexanol process:



100 °C

98 % selectivity

- Learning objectives
  - You should be able to:
    - Explain what catalysis is and why it is green.
    - Describe the difference between heterogeneous and homogeneous catalysis and formulate what are their pros and cons.
    - Describe possible operations of catalytic processes
    - Formulate requirements for a good catalyst

Do the quiz and
see you in the class!