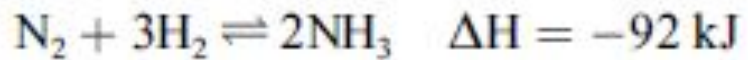

Green Chemistry

DSE-8, SLIDE-6

Catalysis and Green Chemistry

CONSIDER THE GIVEN REACTION



AT ROOM TEMPERATURE THE REACTION DOES NOT TAKE PLACE.

UNDER WHAT CONDITIONS OF TEMPERATURE AND PRESSURE WILL THE PRODUCT FORMATION BE FAVOURED?

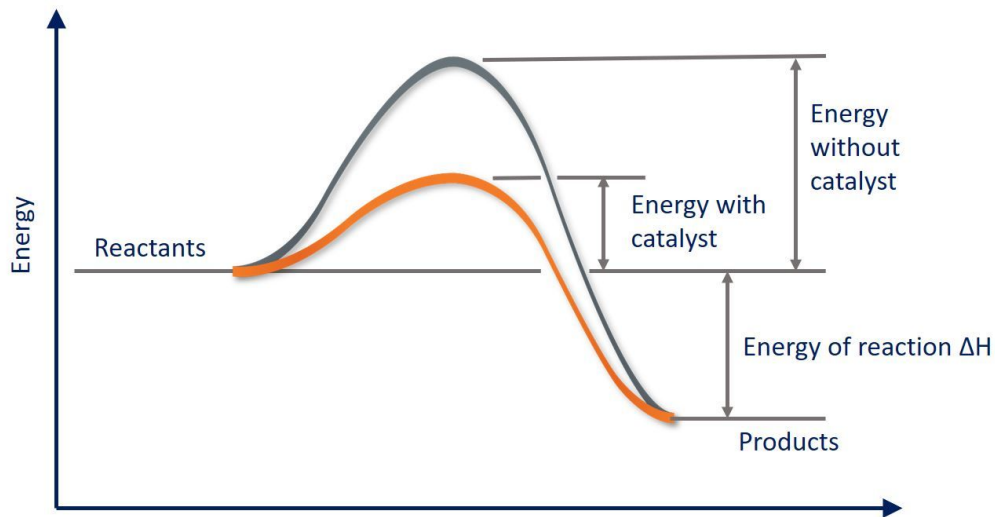
According to Le Chatelier's principle the equilibrium will be shifted to the right-hand side by high pressures and, since the reaction is exothermic, by low temperatures.

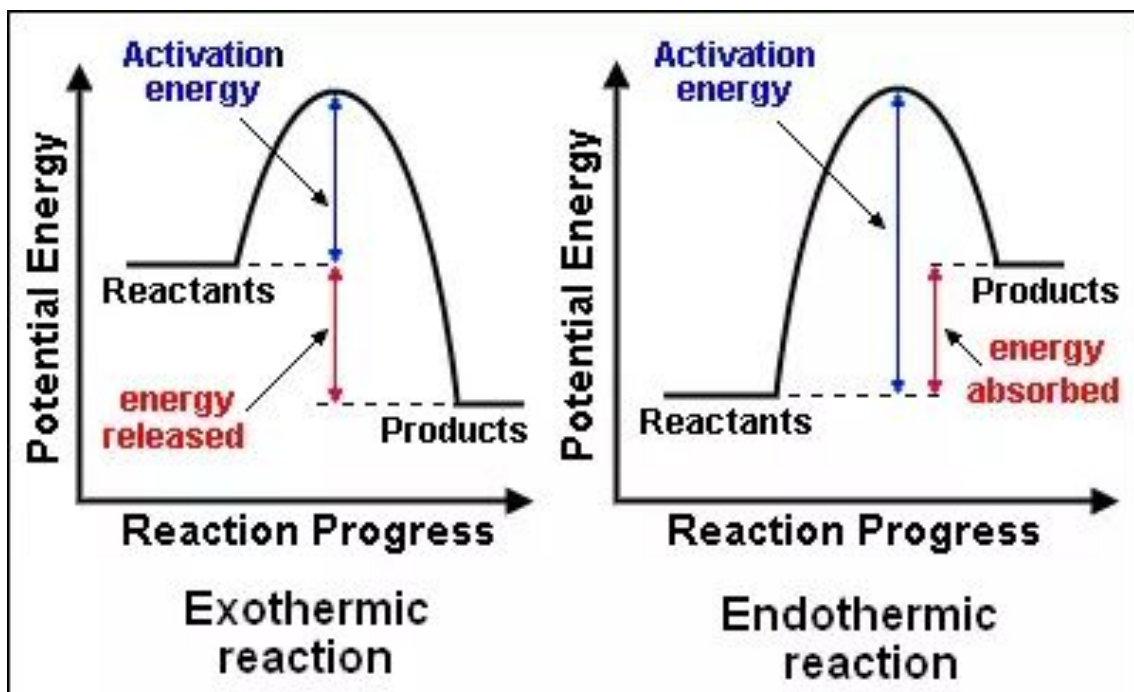
| TEMPERATURE | PRESSURE | AMMONIA AT EQUILIBRIUM |
|--------------------|----------|------------------------|
| 200 ⁰ C | 300 atm | 90% |
| 700 ⁰ C | 300 atm | 05% |

But to overcome energy barrier, 1000⁰C temperature is required. Which can only be done if a catalyst is employed.

Definition

catalyst is commonly defined as: A material which changes (usually increases) the rate of attainment of chemical equilibrium without itself being changed or consumed in the process.





There are three important parameters that impact on both the commercial viability and the inherent greenness of a particular catalyst:

1. **Selectivity** – the amount of substrate converted to the desired product as a percentage of total consumed substrate (a catalyst will be of limited benefit if it also enhances the rate of by-product formation).
2. **Turnover frequency** – the number of moles of product produced per mole of catalyst per second (low turnover frequencies will mean large amounts of catalyst are required, resulting in higher cost and potentially more waste).
3. **Turnover number** – the amount of product per mole of catalyst (this is related to catalyst lifetime and hence to cost and waste).

Table 1. Hydrogenation^a of olefins and arenes by RuO₂ nanoparticles pre-catalyst

| Entry | Substrate | Product(s) | Medium | Time (h) | Conv. ^b (%) | TOF ^c (h ⁻¹) |
|-------|------------------------|--------------------------------------|---------------------|----------|------------------------|-------------------------------------|
| 1 | 1-hexene | hexane | None | 0.2 | 99 | 3300 |
| 2 | 1-hexene | hexane | BMI.BF ₄ | 3.0 | 98 | 218 |
| 3 | 1-hexene | hexane | BMI.PF ₆ | 1.2 | >99 | 556 |
| 4 | cyclohexene | cyclohexane | None | 0.4 | >99 | 1668 |
| 5 | cyclohexene | cyclohexane | BMI.PF ₆ | 3.0 | >99 | 222 |
| 6 | 1-methyl-1-cyclohexene | methylcyclohexane | None | 1.8 | >99 | 370 |
| 7 | 1-methyl-1-cyclohexene | methylcyclohexane | BMI.PF ₆ | 5.4 | 97 | 120 |
| 8 | 2,3-dimethyl-2-butene | 2,3-dimethylbutane | None | 0.5 | >99 | 1334 |
| 9 | 2,3-dimethyl-2-butene | 2,3-dimethylbutane | BMI.PF ₆ | 20.0 | 89 | 30 |
| 10 | benzene | cyclohexane | None | 2.5 | >99 | 267 |
| 11 | benzene | cyclohexane | BMI.BF ₄ | 24.0 | 3 | <1 |
| 12 | benzene | cyclohexane | BMI.PF ₆ | 15.0 | 97 | 43 |
| 13 | toluene | methylcyclohexane | None | 13.0 | 98 | 50 |
| 14 | p-xylene | 1,4-dimethylcyclohexane ^d | None | 17.0 | 64 | 25 |

^aConditions: catalyst/substrate ratio = 1/667, temperature = 75 °C, hydrogen pressure = 4 atm; ^bMeasured by GC; ^cCatalytic turnover frequency; moles of substrate transformed per mole of catalyst per hour. ^dcis/trans=2.1.

Types of catalysts

HETEROGENEOUS AND HOMOGENEOUS

- Heterogeneous catalysts, sometimes referred to as surface catalysts or contact catalysts owing to their mode of action, are in a different phase to the reaction medium.
- Heterogeneous catalysts are widely used industrially.
- In most cases the catalyst is a solid with the reactants being in the gaseous phase.
- The actual reaction takes place on the surface of the catalyst, which may be the external surface or, more effectively, a surface within internal pores of the solid.

Homogeneous catalysts are in the same phase as the substrate and are uniformly distributed. In almost all cases the reaction takes place within the liquid phase, the catalyst being dissolved in the reaction medium.

Catalysts

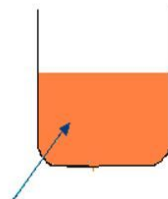
Catalysts may be either homogeneous or heterogeneous

A **homogeneous** catalyst is in the same phase as the substances reacting.

A **heterogeneous** catalyst is in a different phase

Homogeneous Catalyst

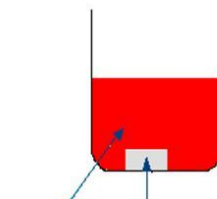
Single Phase



Single Liquid Phase

Heterogeneous Catalyst

Two Phases



Liquid Phase
Solid Phase

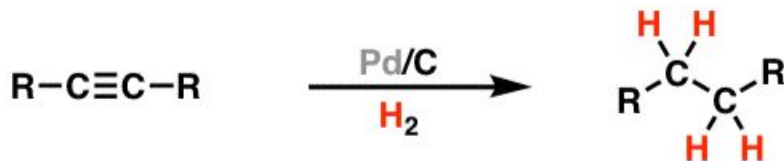
Table 4.1 *Comparison of heterogeneous and homogeneous catalysts*

| <i>Heterogeneous</i> | <i>Homogeneous</i> |
|--|---|
| Usually distinct solid phase | Same phase as reaction medium |
| Readily separated | Often difficult to separate |
| Readily regenerated and recycled | Expensive/difficult to recycle |
| Rates not usually as fast as homogeneous | Often very high rates |
| May be diffusion limited | Not diffusion controlled |
| Quite sensitive to poisons | Usually robust to poisons |
| Lower selectivity | High selectivity |
| Long service life | Short service life |
| Often high-energy process | Often takes place under mild conditions |
| Poor mechanistic understanding | Often mechanism well understood |

Examples

The "Concerted Pathway for Alkynes" - What Works?

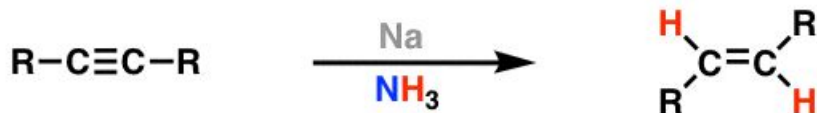
1. Hydrogenation (although Pd/C / H₂ adds *twice* to alkynes)



Note: partial hydrogenation can be achieved using Lindlar's catalyst or nickel boride to give syn hydrogenation



The anti product can be formed using Na/NH₃ (although this is not a concerted reaction)

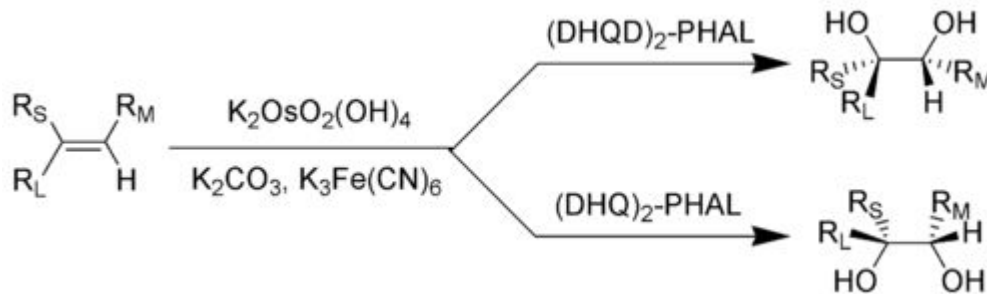
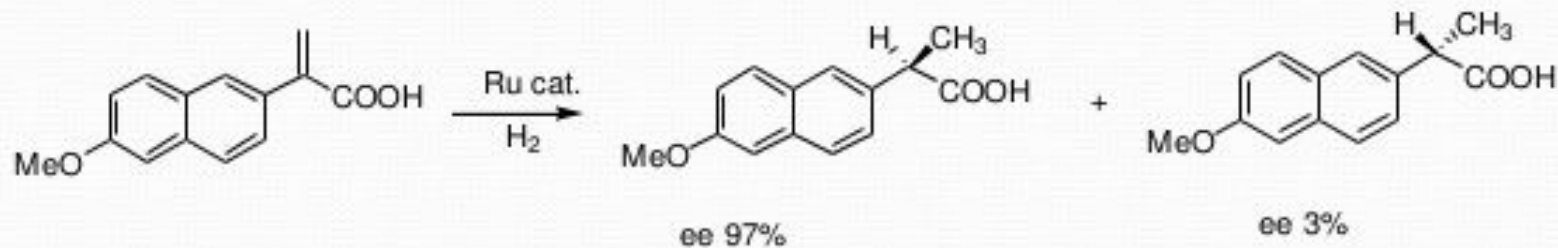


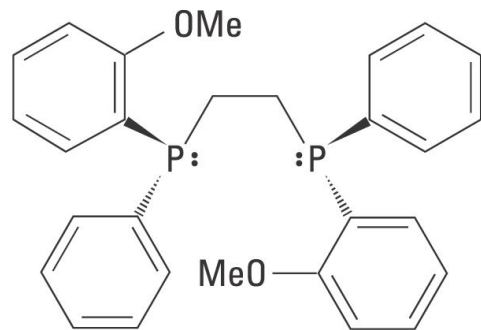
Other types (relevant as per green chemistry)

Asymmetric catalysts:

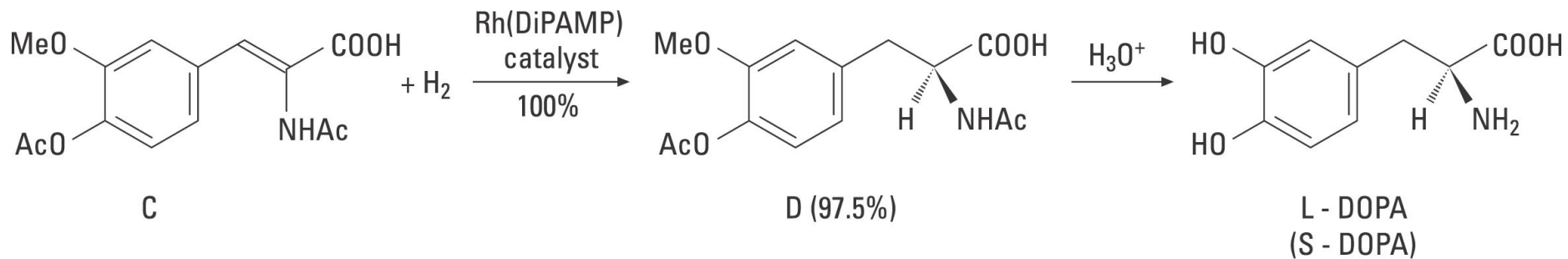
Asymmetric catalysis is a type of catalysis in which a chiral catalyst directs the formation of a chiral compound such that formation of one particular stereoisomer is favoured. These are still relatively rare in industrial processes but they are playing an increasingly important role in the development of pharmaceuticals. This is because they offer one of the most efficient, low-waste methods for producing enantiomerically pure compounds.

Examples





DiPAMP



Me = CH₃

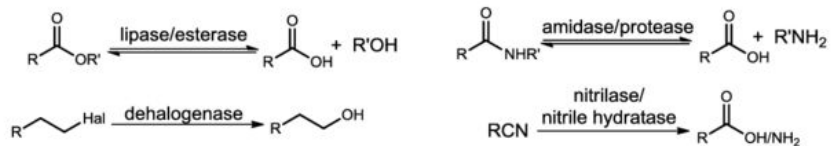
Ac = CH₃CO

Biocatalysts:

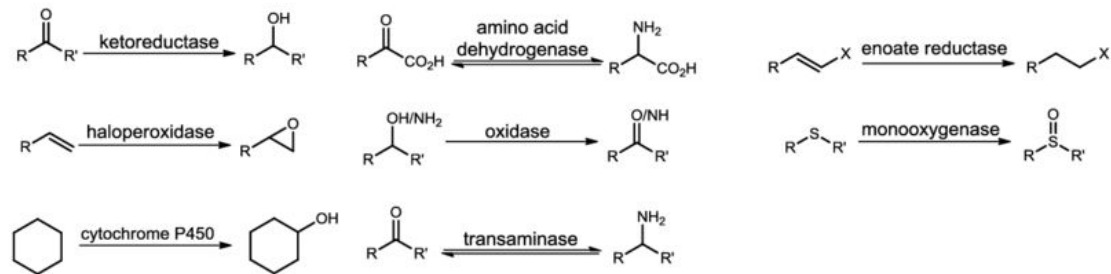
These are essential for life and play a vital role in most processes occurring within the body as well as in plants. In the laboratory biocatalysts are usually natural enzymes or enzymes produced in situ from whole cells. They offer the possibility of carrying out many difficult transformations under mild conditions and are especially valuable for producing enantiomerically pure materials. Their huge potential is currently largely untapped, partially due to the time and expense of isolating and screening enzymes.

Examples

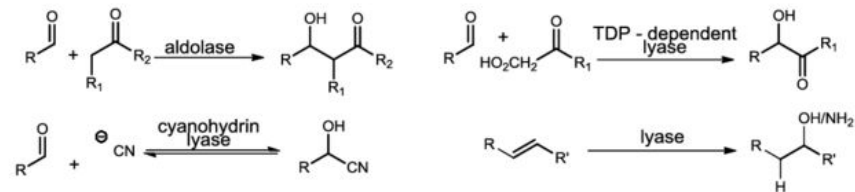
Hydrolysis/Reverse Hydrolysis



Oxidation/reduction

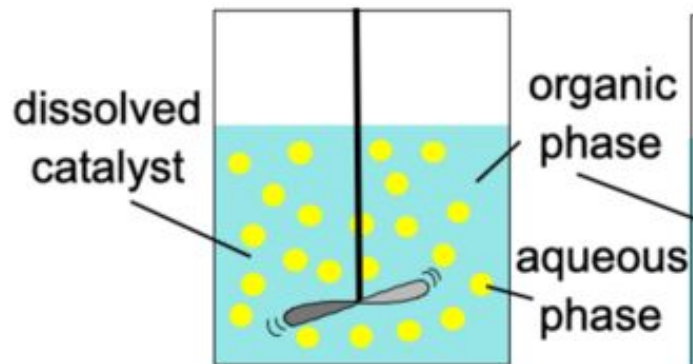


C-C and C-X Bond Forming



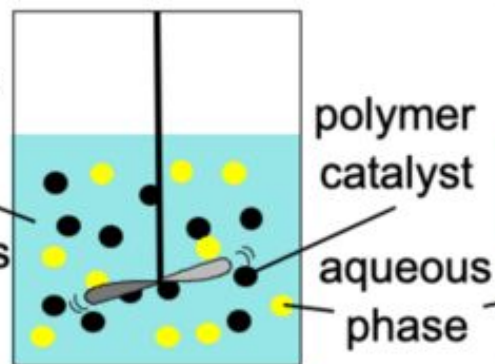
Phase transfer catalysts: These have been around for about 40 years and were developed as a means of increasing the rates and yields of reactions in which the reactants are in two separate phases. In these cases poor mass transport often limits the reaction. Phase transfer catalysts act by transporting the reactants from one phase into another, thus overcoming mass-transport limitations.

Phase Transfer Catalysis (PTC)



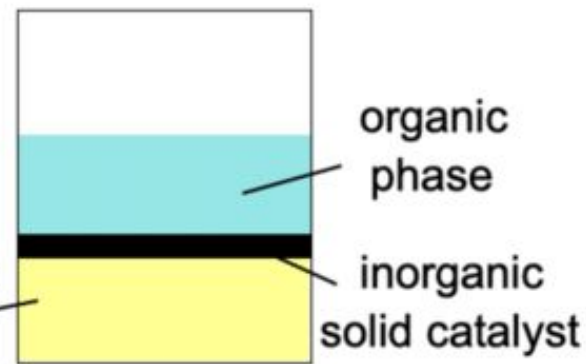
homogeneous catalysis under stirring condition

Triphase Catalysis (TPC)



heterogeneous catalysis under stirring condition

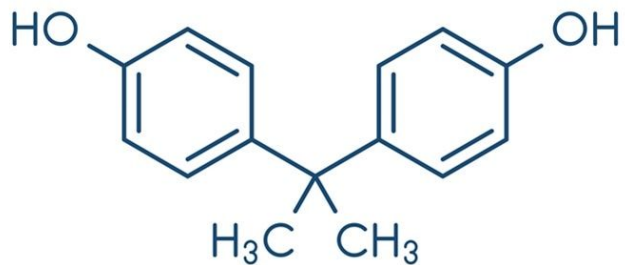
Phase Boundary Catalysis (PBC)



heterogeneous catalysis under static condition

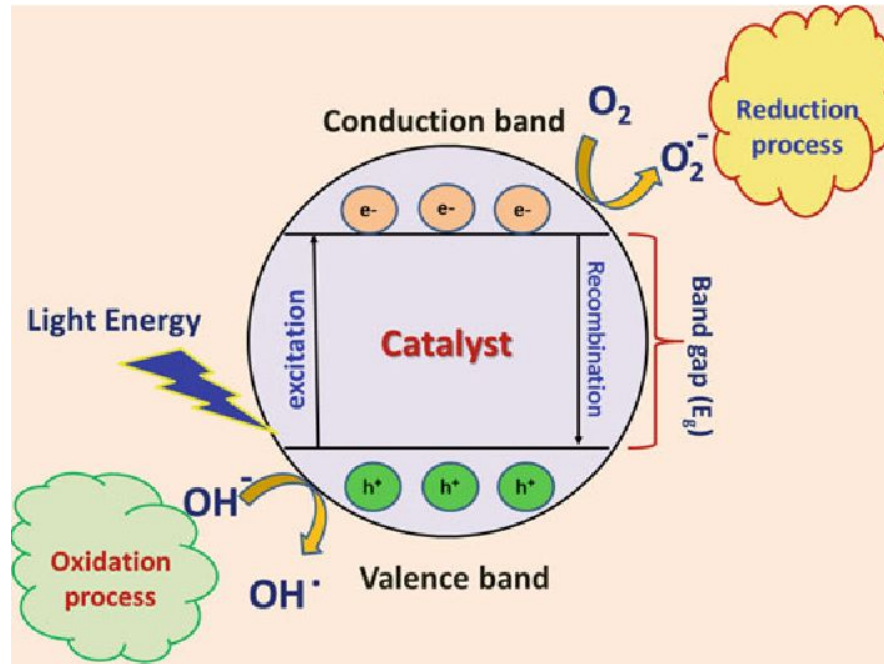
EXAMPLES

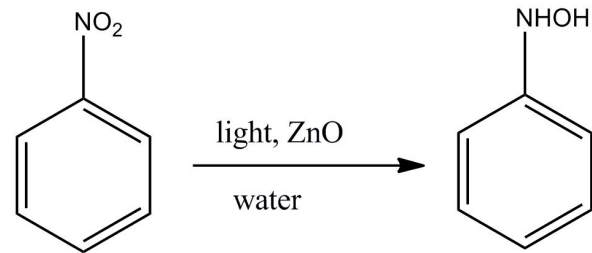
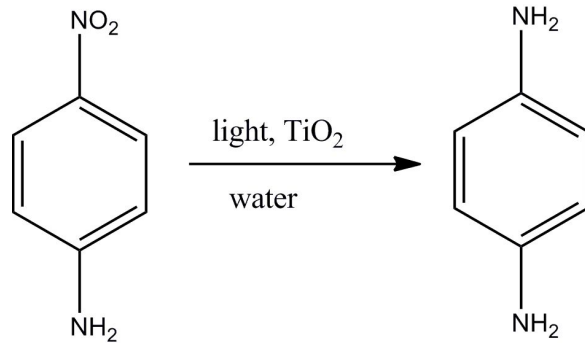
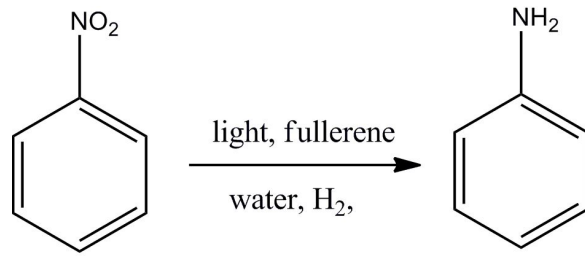
1. Polyesters are prepared from acyl chlorides and bisphenol-A.
2. One of the more complex applications of PTC involves asymmetric alkylations, which are catalyzed by **chiral** quaternary ammonium salts derived from **cinchona alkaloids**.



bisphenol A

Photocatalysts: These harness energy from the sun to carry out chemical transformations. These energy-efficient catalysts are proving especially beneficial in destroying harmful waste and for water clean-up.





THANK YOU