

26.2 HOMOGENEOUS AND HETEROGENEOUS CATALYSTS

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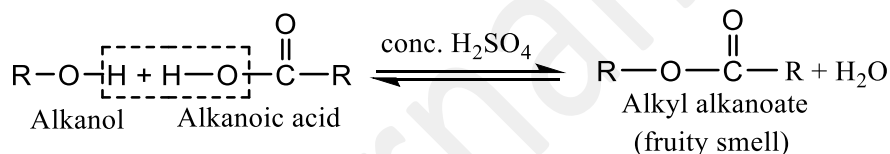
Learning outcomes

Candidates should be able to:

1. Explain that catalysts can be homogeneous or heterogeneous
2. Describe the mode of action of a heterogeneous catalyst to include adsorption of reactants, bond weakening, and desorption of products, for example:
 - (a) Iron in the Haber process
 - (b) palladium, platinum, and rhodium in the catalytic removal of oxides of nitrogen from the exhaust gases of car engines
3. Describe the mode of action of a homogeneous catalyst by being used in one step and reformed in a later step, for example:
 - (a) Atmospheric oxides of nitrogen in the oxidation of atmospheric sulfur dioxide
 - (b) Fe^{2+} or Fe^{3+} in the $\text{I}^-/\text{S}_2\text{O}_8^{2-}$ reaction

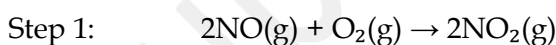
Homogeneous catalysts

In homogeneous catalysis, the catalyst and reactants are in the same phase, and the catalyst participates in the reaction mechanism before being regenerated. For example: hydrogen ions catalyse the hydrolysis of esters.

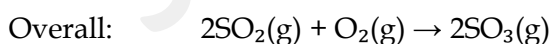


In this reaction, the reactants, products and catalyst are all in the aqueous phase.

Atmospheric oxides of nitrogen in the oxidation of atmospheric sulfur dioxide

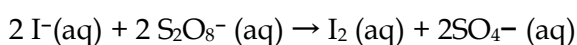


 **NO is regenerated in Step 2 and can enter Step 1 again. Therefore, NO acts as a catalyst.**

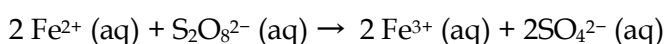
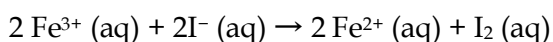


The iodide-peroxydisulfate(VI) reaction

Iodide reacts slowly with aqueous peroxydisulfate(VI) ions to produce iodine and sulfate ions:



The reaction is catalysed by the addition of some transition metal cations, for example $\text{Fe}^{3+}(\text{aq})$:



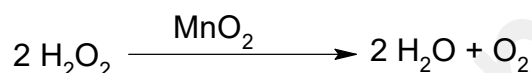
How does Fe^{3+} act as a catalyst?

Fe^{3+} is used up in the first step, and Fe^{2+} is produced. Fe^{2+} is then used in the second step to regenerate Fe^{3+} . Thus, the iron ions participate in the reaction mechanism but are regenerated and are not consumed overall.

Transition-metal ions can act as catalysts because they can readily change oxidation state and provide an alternative reaction pathway.

Heterogeneous catalysts

Heterogeneous catalysis occurs when the catalyst is in a different phase to the reaction mixture. For example, the decomposition of aqueous hydrogen peroxide is catalysed by manganese(IV) oxide.

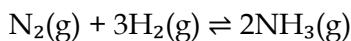


The manganese(IV) oxide is in the solid phase, whereas the hydrogen peroxide is in aqueous solution.

Principles of Heterogeneous Catalysis

The Haber Process

In the Haber process, nitrogen reacts with hydrogen to form ammonia:



Iron is used as a heterogeneous catalyst to increase the rate of reaction. The iron catalyst is **promoted** with small amounts of potassium oxide and aluminium oxide. Because the iron is a solid and is in a different phase from the reactants, which are gases, it is a heterogeneous catalyst. Finely divided iron has a large surface area, providing more active sites where reactant molecules can be adsorbed.

The way the catalyst works is not completely understood. Nitrogen and hydrogen molecules are adsorbed onto the iron surface. Their bonds are weakened, allowing the atoms to react more easily. Ammonia is then formed on the surface and desorbs from the catalyst. Breaking the nitrogen-nitrogen triple bond needs a lot of energy and is thought to be the rate-determining step.

How does a heterogeneous catalyst work?

1. **Adsorption:** Reactant molecules attach to the catalyst surface.
2. **Bond weakening:** Bonds in the adsorbed molecules become weaker.
3. **Reaction:** The reactants react more easily on the surface.
4. **Desorption:** Products leave the surface, freeing the active sites.

The process can be summarised as:

Reactants → Adsorption → Bond weakening & reaction → Desorption of products

Catalytic converter

Platinum, palladium and rhodium are used as catalysts in catalytic converters. Exhaust gases pass over the catalyst surface, where nitrogen oxides are adsorbed. Their bonds are weakened and reactions occur on the surface. The nitrogen oxides react on the catalyst surface to form less harmful products, including N_2 . These products then desorb from the surface, leaving the active sites available again.

Remember

A catalyst increases the rate of a reaction by providing an alternative reaction pathway with lower activation energy. It is regenerated at the end of the reaction.

Summary

Feature	Homogeneous	Heterogeneous
Phase of catalyst	Same phase as reactants	Different phase from reactants
How it works	Participates in reaction steps and is regenerated	Reactants adsorb onto catalyst surface
Key idea	Used $\rightarrow$ regenerated	Adsorb $\rightarrow$ react $\rightarrow$ desorb
Example	$\text{Fe}^{2+}/\text{Fe}^{3+}$ in solution	Fe in Haber process

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