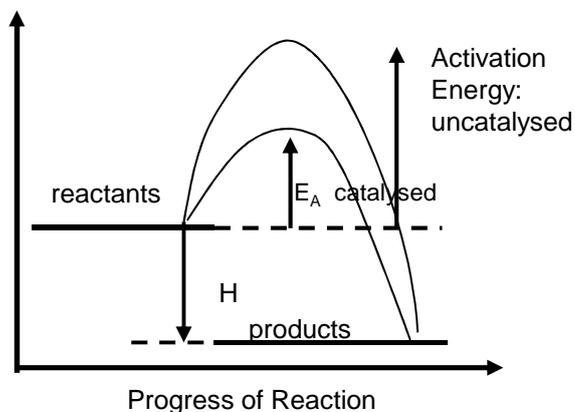


Catalysts

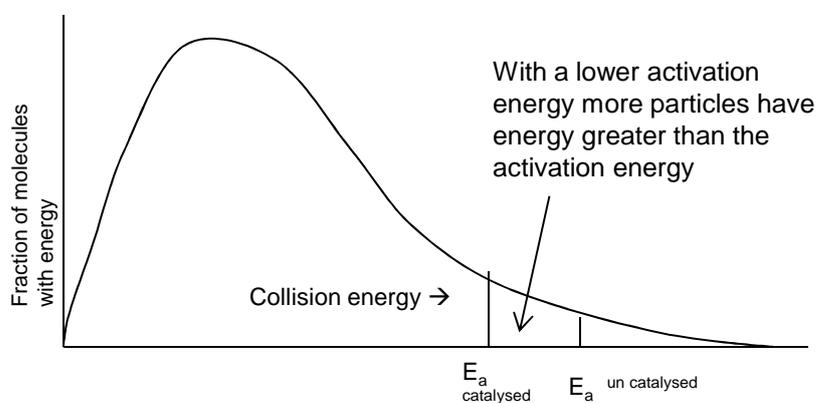
Definition: Catalysts increase reaction rates without getting used up.

Explanation: They do this by **providing an alternative route or mechanism** with a **lower activation energy**

Comparison of the activation energies for an uncatalsed reaction and for the same reaction with a catalyst present.



If the activation energy is lower, **more particles will have energy > E_A**, so there will be a higher frequency of effective collisions. The reaction will be faster



Transition metals and their compounds can act as heterogeneous and homogeneous catalysts.

A **heterogeneous catalyst** is in a different phase from the reactants

A **homogeneous catalyst** is in the same phase as the reactants

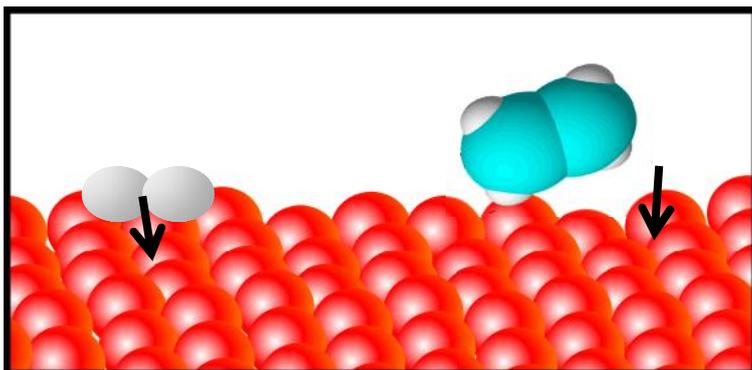
Heterogeneous catalysis

Heterogeneous catalysts are usually solids whereas the reactants are gaseous or in solution. The reaction occurs at the surface of the catalyst.

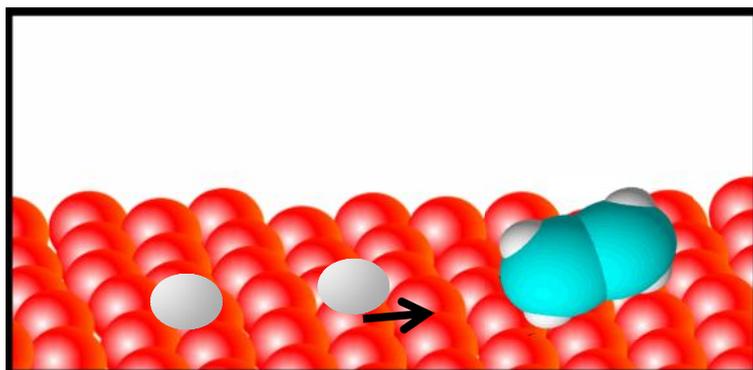
Steps in Heterogeneous Catalysis

1. Reactants form bonds with atoms at **active sites** on the surface of the catalyst (adsorbed onto the surface)
2. As a result bonds in the reactants are weakened and break
3. New bonds form between the reactants held close together on catalyst surface.
4. This in turn weakens bonds between product and catalyst and product leaves (desorbs).

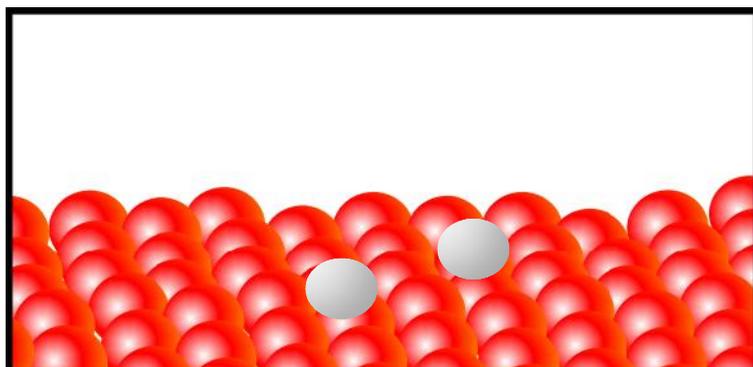
How do Heterogeneous Catalysts Work?



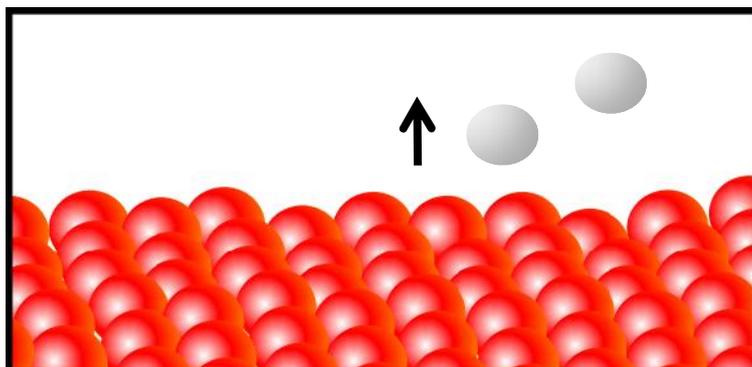
Reactants adsorb on to atoms on the **surface of the catalyst**.



This can result in the bonds within the reactant molecules becoming weaker and may break



New bonds form between the reactants held close together on catalyst surface



This in turn weakens bonds between product and catalyst and product leaves

Adsorption of reactants at active sites on the surface may lead to catalytic action. The **active site** is the place where the **reactants adsorb** on to the **surface of the catalyst**. This can result in the bonds within the reactant molecules becoming weaker, or the molecules being held in a more reactive configuration. There will also be a higher concentration of reactants at the solid surface so leading to a higher collision frequency.

Transition Metals can use the 3d and 4s e- of atoms on the metal surface to form weak bonds to the reactants.

Strength of adsorption

The strength of adsorption helps to determine the effectiveness of the catalytic activity. Some metals e.g. **W** have **too strong** adsorption and so the products cannot be released. Some metals e.g. **Ag** have **too weak** adsorption, and the reactants do not adsorb in high enough concentration. Ni and Pt have about the right strength and are most useful as catalysts.

Surface area:

Increasing the surface area of a solid catalyst will improve its effectiveness. A support medium is often used to maximise the surface area and minimise the cost (e.g. Rh on a ceramic support in catalytic converters).

Examples of heterogeneous catalysts

V_2O_5 is used as a catalyst in the Contact Process.

Overall equation : $2SO_2 + O_2 \rightarrow 2SO_3$

step 1 $SO_2 + V_2O_5 \rightarrow SO_3 + V_2O_4$

step 2 $2V_2O_4 + O_2 \rightarrow 2V_2O_5$

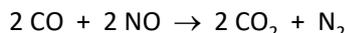
Note the oxidation number of the vanadium changes and then changes back. It is still classed as a catalyst as it returns to its original form.

Cr_2O_3 catalyst is used in the manufacture of methanol from carbon monoxide and hydrogen.
 $CO + 2H_2 \rightarrow CH_3OH$

Fe is used as a catalyst in the Haber Process
 $N_2 + 3H_2 \rightarrow 2NH_3$

Catalytic converters

These remove CO, NO_x and unburned hydrocarbons (e.g. octane, C₈H₁₈) from the exhaust gases, turning them into 'harmless' CO₂, N₂ and H₂O.



Converters have a ceramic honeycomb coated with a thin layer of catalyst metals **Platinum, Palladium, Rhodium** – to give a large surface area.

Leaded petrol cannot be used in cars fitted with a catalytic converter since lead strongly adsorbs onto the surface of the catalyst.

Poisoning Catalysts

Catalysts can become poisoned by impurities and consequently have reduced efficiency.

It is important to ensure the purity of the reactants if poisoning can occur.

Poisoning has a cost implication e.g. poisoning by sulphur in the Haber Process and by lead in catalytic converters in cars means that catalysts lose their efficiency and may need to be replaced.

Homogeneous catalysis

When catalysts and reactants are in the same phase, the reaction proceeds through an intermediate species.

The intermediate will often have a different oxidation state to the original transition metal. At the end of the reaction the original oxidation state will reoccur. This illustrates importance of variable oxidation states of transition metals in catalysis.

Explaining homogeneous catalysis using E values

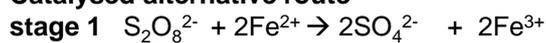
The reaction between I^- and $\text{S}_2\text{O}_8^{2-}$ catalysed by Fe^{2+}
overall $\text{S}_2\text{O}_8^{2-} + 2\text{I}^- \rightarrow 2\text{SO}_4^{2-} + \text{I}_2$



The uncatalysed reaction is very slow because the reaction needs a collision between **two negative ions**. **Repulsion** between the ions is going to hinder this – meaning **high activation energy**

For a substance to act as a homogenous catalyst its electrode potential must lie in between the electrode potentials of the two reactants, so it can first reduce the reactant with the more positive electrode potential and then in the second step oxidize the reactant with the more negative electrode potential

Catalysed alternative route



Both of the individual stages in the catalysed mechanism involve collision between positive and negative ions and will have lower activation energies.

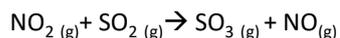
Using E values to find a catalyst only shows that catalysis is possible. It does not guarantee that the rate of reaction will be increased

Fe^{3+} ions can also act as the catalyst because the two steps in the catalysed mechanism can occur in any order

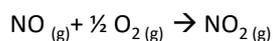
Catalytic role of atmospheric oxides of nitrogen in the oxidation of atmospheric sulfur dioxide

Nitrogen dioxide catalyses the conversion of sulphur dioxide to sulphur trioxide.

The first step of the reaction is



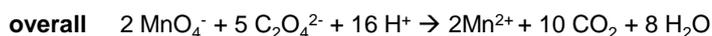
The second step of the reaction is



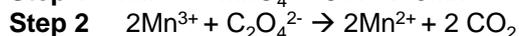
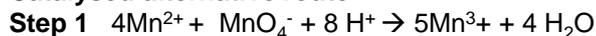
The nitrogen dioxide is regenerated at the end of the reaction so is classed as a catalyst.

Autocatalytic Reaction between Ethanedioate and Manganate ions

The autocatalysis by Mn^{2+} in titrations of $\text{C}_2\text{O}_4^{2-}$ with MnO_4^-



Catalysed alternative route

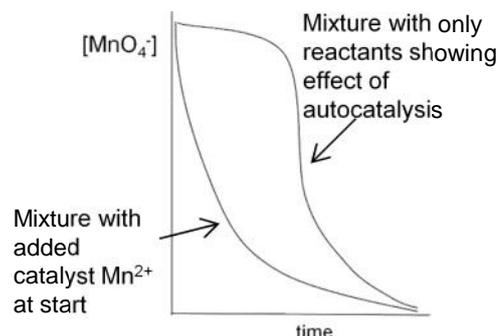


The initial uncatalysed reaction is **slow** because the reaction is a collision between **two negative ions** which **repel each other** leading to a **high activation energy**.

The Mn^{2+} ions produced act as an **autocatalyst** and therefore the reaction starts to speed up because they bring about the alternative reaction route with lower activation energy.

The reaction eventually slows as the **MnO_4^- concentration drops**.

This is an example of **autocatalysis** where one of the products of the reaction can catalyse the reaction.



Following the reaction rate

This can be done by removing samples at set times and titrating to work out the concentration of MnO_4^- .

It could also be done by use of a spectrometer measuring the intensity of the purple colour. This method has the advantage that it **does not disrupt the reaction mixture**, using up the reactants and it leads to a much **quicker determination of concentration**.

Constructing a catalysed mechanism for a reaction

Example

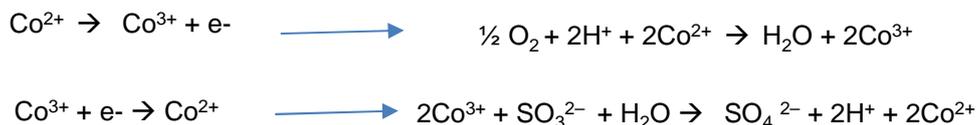
The following reaction is catalysed by Co^{2+} ions in an acidic solution. $\text{SO}_3^{2-} + \frac{1}{2} \text{O}_2 \rightarrow \text{SO}_4^{2-}$.

Write a mechanism for the catalysed reaction by writing two equations involving Co^{2+} and Co^{3+} ions.

Split the full equation into its two half equations



Add in cobalt to make two new redox equations. Making sure the oxidised cobalt equation is combined with the original reduced half equation and vice versa



Check your two mechanism equations add up to the original full non-catalysed equation.