

Catalysts

A computer graphic of the crystal structure of a zeolite

Catalysts are both vitally important for life and critically important for our society. This article looks at what catalysts are, how they work, where they are used and how and why many scientists still study them.

Every second of every day thousands of catalysts are at work in your body. They are critical in helping you to live. They break down the food you eat in your digestive system so that you can absorb it. They build it back up again so that you can grow. They are involved in most of the molecular processes which occur in every living thing. These catalysts are called enzymes.

Catalysts are also critical in virtually every industrial chemical process. Fertilisers could not be made without them. Neither could petrol or plastics. In a single day you will encounter many products which are either made themselves using catalysts or produced using materials which are formed in catalytic reactions.

The first person to express ideas about catalysts was a Swedish chemist, Jöns Jacob Berzelius. He recognised that catalysts are able to make reactions happen at a lower temperature than they would otherwise. Current understanding is that a catalyst will take part in a chemical reaction and increase its rate, but without being used up.

Key words

catalyst
activation energy
Haber process
Nobel Prize
zeolite

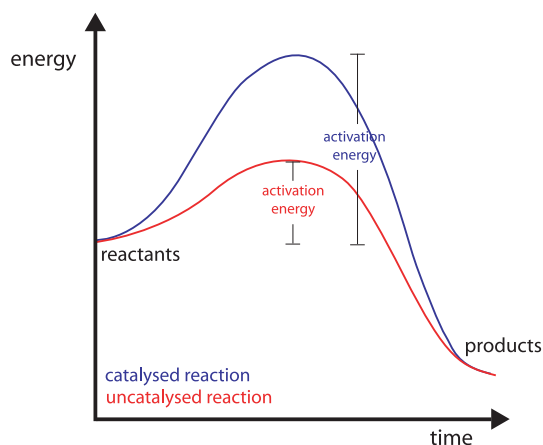
Box 1

The two types of Catalyst

- Heterogeneous (*hetero* means different) catalysts are in a different state to the reactants and products. Often the catalyst is a solid and the reactants and products are liquids or gases.
- Homogeneous (*homo* means the same) catalysts are in the same state as the reactants and products. They are often all dissolved in a solvent. The catalyst may be an acid.

How do catalysts work?

There is no single answer to this question as different catalysts work in different ways. All of them, though, give an alternative reaction pathway which has a lower energy barrier or activation energy than the uncatalysed reaction.



This diagram shows how the activation energy required for an uncatalysed reaction (top plot in blue) can be higher than the activation energy for a catalysed reaction (bottom plot in red.)

Diagram 1 shows an energy profile for a typical exothermic reaction. The products have less energy than the reactants and so the reaction gives out energy in the form of heat (it will get hot). However, for the reaction to get started, some of the bonds in the reactants have to be broken. This can take a lot of energy and leads to the 'hump' in the profile. The amount of energy required to break some bonds and get the reaction started is called the 'activation energy.' In general, the higher the activation energy the slower the reaction is.

A catalyst will help the reaction to take place via a different pathway. This may mean that it helps to form a very unstable and short lived molecule called a 'transition state.' If the transition state has less energy than the original activation energy then the barrier to the reaction is lower – see Diagram 1. This speeds up the rate at which the reaction can take place.

Making fertilisers

Most plants need a supply of nitrogen in the form of nitrates in order to grow well. In areas which are farmed frequently, this can be depleted from the soil. Fertiliser containing easily accessible nitrogen must be added or plants will not grow well. This fertiliser can be natural (for example, animal manure) but in the developed world it is often artificial.

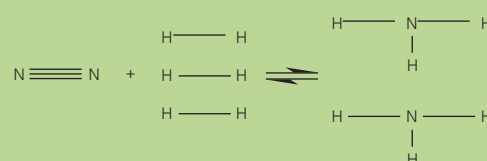
In the late 1800s, natural deposits of nitrogen salts were being used to make fertilisers but it was clear that they were going to run out. The population of the world was increasing and fertilisers were vital to ensure that there was enough to eat and to avoid widespread famine.

Nitrogen gas, N_2 , is plentiful; it is about 78% of the air we breathe. The trouble is that the two nitrogen atoms are held together by a very strong triple bond and a lot of energy is required to break them apart. A method for catalysing the bond breaking was urgently required and chemists around the world were working on a solution.

Box 2

Forming Ammonia

The reaction of nitrogen and hydrogen to form ammonia



A German chemist called Fritz Haber finally solved the problem in 1905. He realised that iron would act as a catalyst for the reaction between nitrogen and hydrogen, producing ammonia gas (see Box 2). It was developed into an industrial process by another German chemist, Carl Bosch, in 1914. The Haber-Bosch process is still used today to manufacture over 100 million tons of fertiliser a year. It is often claimed that this process saved the world from starvation by ensuring that there was a supply of ammonia for fertiliser manufacture. Ammonia can also be used to make explosives and so it is also possible that the process lengthened World War I as well as it meant that Germany could keep fighting.

Fritz Haber won the Nobel Prize in Chemistry in 1914 for his work on the synthesis of ammonia.



Fritz Haber who discovered that iron would catalyse the reaction between nitrogen and hydrogen to form ammonia and won the Nobel Prize in Chemistry in 1914.

Emilio Segre Visual Archives/American Institute Of Physics/SPL

Reactions at the surface

Although iron had been used successfully for decades to manufacture ammonia, by the mid-1970s it was still unknown how it worked. Another German Chemist, Gerhard Ertl, took up the challenge and decided to find out. He showed that the nitrogen's strong triple bond broke on the surface of the iron – in other words that the nitrogen molecule broke apart into nitrogen atoms before meeting a hydrogen molecule.

Ertl also studied the reactions which form the basis of a catalytic converter in a car's exhaust. Platinum metal forms the main part of the catalyst and Ertl studied how the carbon monoxide and oxygen molecules react together on the surface to produce the much less toxic carbon dioxide.



A catalytic converter from a car exhaust

For the many catalysts which are solids, the reactions will take place on their surface. As the importance of catalysts are recognised, surface science is becoming increasingly significant.

Gerhard Ertl won the Nobel Prize in Chemistry in 2007 for his work on the chemistry of surfaces.

Zeolites – crystals with huge surfaces

As reactions take place on the surface of catalysts, it follows that the more surface which is available, the more efficient the catalyst. One group of catalysts which have huge surface areas are the zeolites. It has been estimated that for some zeolites a single teaspoonful could provide a surface area of up to 500 square metres which is equivalent to two tennis courts.

The reason for this incredible surface area to volume ratio is the way that the zeolites are constructed. They consist of a series of interconnected channels or pores which are between 0.3 and 1 nm wide. They are constructed so that almost every atom in the zeolite crystal is at a surface, which gives huge potential for catalysing reactions. Naturally occurring zeolites are mainly made of a lattice of SiO_4 units, with aluminium ions sometimes taking the place of the silicon. Chemists now make synthetic zeolites and have incorporated



Marie Curie

Box 3 Nobel Prizes

The Nobel prizes are awarded each year for outstanding achievement in Physics, Chemistry, Literature, Peace and Physiology or medicine. There is also a related prize for Economics. The prizes are considered to be the highest award in Science and have a great deal of prestige. The prize winners receive about £750 000 and a medal.

The awards were set up in the will of Alfred Nobel who left his entire estate for the purpose and were first awarded in 1901. They are given in a ceremony each year on the 10th December, the anniversary of the death of Alfred Nobel.

Many famous scientists have won a prize including Ernest Rutherford, Albert Einstein, Francis Crick and James Watson. Only four people have ever won two prizes. These include Marie Curie who won both the chemistry and the physics prizes. Her daughter was also a prize winner.

several other elements such as zinc, germanium and phosphorus. In the synthetic zeolites, the precise shape of the pores can be controlled and designed. The size and shape of the pores control which substances can pass through and how fast they can do so. This allows chemists great control when trying to catalyse complex reactions and zeolites have been used to help synthesise new and advanced materials.

Zeolites are also used in the petrochemical industry to crack large hydrocarbons. Crude oil contains a mix of many different sized hydrocarbons but there are not many uses for the larger ones. These are broken (or cracked) into smaller ones which are useful as fuels in, for example, petrol. The catalysts which are used for this are zeolites. They are also used in isomerisation reactions, turning straight chain hydrocarbons into branched hydrocarbons or vice versa.

Although catalysts have been known about for over 100 years, they are still being studied in many research laboratories today. New catalysts are being discovered and these are assisting in the development of new materials and new processes. Catalysts help to make reactions 'greener' or more environmentally friendly by enabling them to take place at lower temperatures and use less starting materials.

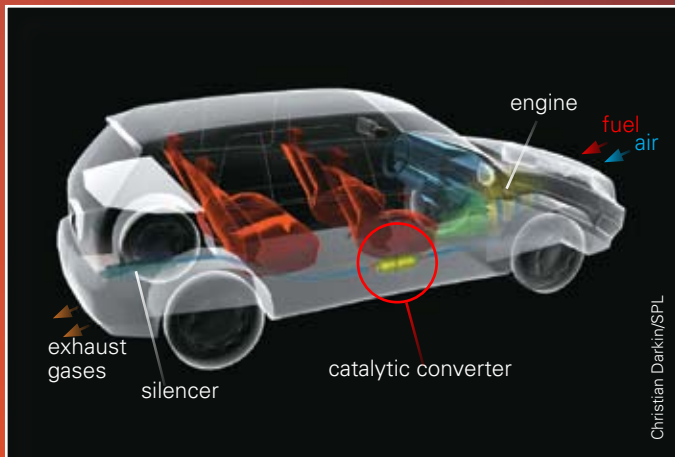
Vicky Wong teaches chemistry and is an editor of CATALYST.

1 nm is one nanometre, 0.000 000 001 m or 10^{-9} m

Hydrocarbons are compounds which contain hydrogen and carbon only.

Catalytic converter

A *catalytic converter* is part of a vehicle's exhaust system. It removes harmful substances from the exhaust gases.



Reactions in the engine:

- Hydrocarbon fuel burns with oxygen:
 $\text{hydrocarbon} + \text{oxygen} \rightarrow \text{carbon monoxide} + \text{carbon dioxide} + \text{water}$
- Nitrogen from the air is also oxidised:
 $\text{nitrogen} + \text{oxygen} \rightarrow \text{nitrogen oxides (NO}_x\text{)}$

Exhaust gases contribute to urban smog. Carbon monoxide is poisonous. Nitrogen oxides cause acid rain.

Reactions in the converter:

- Unburned hydrocarbons are oxidised:
 $\text{hydrocarbon} + \text{oxygen} \rightarrow \text{carbon dioxide} + \text{water}$
- Carbon monoxide is oxidised:
 $\text{carbon monoxide} + \text{oxygen} \rightarrow \text{carbon dioxide}$
- Nitrogen oxides are reduced:
 $\text{nitrogen oxide} \rightarrow \text{nitrogen} + \text{oxygen}$

What's inside?

Inside the catalytic converter, hot exhaust gases and oxygen pass over unreactive metals (platinum, palladium, rhodium). These metals are coated on a ceramic or steel honeycomb, to give a large surface area. They catalyse the reactions which reduce the toxicity of the exhaust gases.

On the surface

The chemical reactions in the catalytic converter take place on the surface of the precious metal catalysts. A large surface area and a high temperature speed up the reactions.

