Catalysts and the environment

# apropos Catalysts

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#### The concept

The term catalysis (from the Greek meaning "dissolution") means that a particular substance (= catalyst) accelerates a chemical reaction without itself being changed by that reaction.

#### Occurrence in nature

The phenomenon of catalysis also occurs in nature. All enzyme reactions, e.g. in the various metabolic reactions and processes which take place in organisms, occur in accordance with this principle (example: alcoholic fermentation). Enzymes can speed up reactions or processes which would otherwise occur only very slowly or not at all. Enzymes are highly selective, i.e. they affect only certain substances or reactions.

This property of enzymes is turned to advantage in the field of biotechnology ( $\rightarrow$  biocatalysts). In recent years this has been implemented on an industrial scale, e.g. in the production of ascorbic acid (vitamin C).

#### History

The first catalytic reaction was observed in 1816: the reaction of air with hydrogen and hydrocarbons on a platinum wire. In 1900 the German chemical firm BASF was the first to use a catalytic process to produce sulphuric acid. Other milestones in the large-scale exploitation of catalytic processes include the hardening of fats (1901), the Haber-Bosch process (1908) and the Fischer-Tropsch synthesis for liquefying coal (1925). Nowadays, the majority of industrial processes for the production of input substances and semi-finished materials, especially for the chemical industry, are catalytic processes.

# Fields of application and industrial significance

In the chemical industry catalysts play an extremely important role in a wide variety of areas. Technical catalysts are noted for their versatility.

The vast majority of production processes for input substances, particularly in the petrochemical industry and in the manufacture of plastics and polymers, are catalytic processes. But catalysts are also used in the foodstuffs industry, e.g. to harden fats in the making of margarine. A further application is to clean up exhaust gases in incineration plants, absorbers and motor vehicles.

In 1984 catalysts with a total value of US\$ 3.7 billion were produced worldwide. Although catalytic converters for car exhaust systems make up a large share of the market (about 30% of turnover), in sheer numbers they play a subordinate role to industrial catalysts. Whereas 1 kg of catalyst is required per car, a plant for the production of ammonia — an important input substance for industry — requires some 50 tonnes of catalyst, which have to be replaced about every two years.

### Nature and properties

We distinguish between two types of catalyst: homogeneous and heterogeneous.

Homogeneous catalysts are present in the same form as the reactants (e.g. liquid/liquid), whereas heterogeneous catalysts are usually solids and the other reactants are present in gas and/or liquid form.

Heterogeneous catalysts are generally heavy metals or their oxides or metal oxide mixtures. In some cases the active layer is applied to a ceramic carrier. Some examples are copper, nickel, chromium, platinum, palladium, rhodium, silver, tin, molybdenum, vanadium, iron, zinc, bismuth, tungsten, cobalt, titanium and their oxides.

Homogeneous catalysts were developed much more recently than heterogeneous ones and are characterised by their high degree of selectivity (= their efficacy in special types of reactions).

These are the so-called complex or cluster compounds of heavy metals, which are noted for their high degree of solubility.

These compounds may include the following metals: chromium, tungsten, iron, vanadium, molybdenum, copper, silver, mercury, cobalt, nickel, lead and manganese.

To date, the processes occurring on the surface of the catalayst have been only partially explained. As a result, the methods for producing catalysts — with the exception of a few standard catalysts — require very special know-how. Moreover, long and comprehensive testing is needed to find the right catalyst for a particular process. Some 20,000 catalysts had to be tested, for example, in the development of the Haber-Bosch process (used to produce ammonia from air, water and coke).

Certain substances can inhibit a catalyst by blocking its surface. These catalytic poisons include carbon monoxide as well as sulphur and arsenic compounds. It is sometimes possible to remove these substances and to regenerate the catalyst; if this is unsuccessful, the catalyst must be removed and disposed of.

#### Ecological aspects and toxicity

Catalytic processes are advantageous not only from an economic point of view (lower energy bills, precise control over reactions, higher process efficiency), but also from an ecological one: lower energy consumption conserves resources, for instance, and catalysts are often used to clean up exhaust gases (e.g. flue gas desulphurisation (FGD), nitrogen oxides stripping (DENOX)), thus reducing air pollution.

But it must be remembered that catalysts, too, have a toxic potential, whether inherent in the heavy metals themselves, in the substances (e.g. sulphur and arsenic compounds, tarry deposits, carbon monoxide and other deposits) which adhere to the catalyst's surface, or due to the formation of by-products.

Between 1953 and 1960, for instance, some 100 inhabitants of the area around Mitamata Bay in Japan fell ill (and by 1965 41 of them had died) as a result of severe mercury poisoning. The contamination stemmed from a chemical factory, where mercury oxide had been used as a catalyst in the production of acetic aldehyde (a basic substance for synthesis of acetic acid and other compounds). This oxide had formed methyl mercury which was pumped into the bay in the effluent, absorbed by fish and finally reached the human inhabitants of the bay via the food chain.

When disposing of catalysts it is important to ensure that no heavy metals are introduced into the environment, especially the soil, as these can be flushed out and cause water pollution. In this respect the homogeneous catalysts are more critical because of both their higher solubility and reactivity. Via entrainment in the soil and/or water heavy metals can eventually find their way into the food chain, too.

The toxic effect of catalysts lies in their ability to break down proteins and inhibit the action of enzymes. If excessive amounts are resorbed, symptoms of poisoning in tissues such as the gastric and intestinal mucosa and the bone marrow manifest themselves. These substances build up in the liver and kidneys and may also damage the nerve tissue.

## Disposal

Catalysts can be disposed of in a variety of ways. Precious metals such as platinum, palladium, rhodium and silver are usually recovered. The other catalysts are either regenerated, reactivated or consigned to a waste-disposal site. The latter is the normal method of disposing of irreversibly poisoned catalysts, the recycling of which is not (yet) economically viable.

#### Tips for the underwriter

From the insurer's point of view catalytic processes are interesting for a variety of reasons.

## Property insurance – business interruption

Since catalysts are crucial to the production of so many basic substances, major business interruption losses can occur if the catalyst is spoiled (e.g. deactivated as a result of a plant malfunction), if it is not available in the right amounts or even if the quality of the catalyst is not up to the usual standard. Interdependency losses in downstream processes should not be overlooked either. The actual property damage involved can be relatively minor. This also applies to FGD and DENOX facilities in power plants, where a slight deficiency in a catalyst may require the entire plant to be shut down for violating emission limits.

Catalysts may also involve an enhanced fire risk, as they accelerate reactions and because some of them (e.g. nickel catalysts) can react violently with atmospheric oxygen.

## Liability: Environmental damage

Liability losses can occur:

- o as a result of the catalytic process itself;
- when waste water is contaminated with heavy metals (e.g. byproducts);
- when pollutants are emitted owing to an ineffective catalyst (e.g. in the case of absorbers);
- o when a catalyst is replaced;
- o during disposal.

#### Branches of industry affected:

- o mineral oil processing;
- chemical industry (especially basic substances and petrochemicals);
- facilities using catalytic clean-up of exhaust gas (e.g. DENOX, FGD in power plants);
- o parts of the foodstuffs industry (e.g. hardening of fats);
- o waste-disposal companies;
- o manufacturers of catalysts.

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