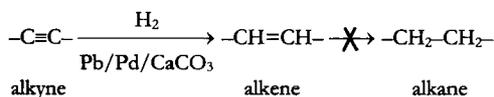


Catalysts – Myths and Realities

A modern dictionary (1) definition of a catalyst as ‘a substance that increases the rate of a chemical reaction without itself undergoing any permanent chemical change’ does not completely describe what occurs. *Changing* the rate of a chemical reaction, as opposed to just *increasing* it, broadens the scope of catalysis. Indeed the dictionary acknowledges this extension by introducing concepts of ‘positive catalysts’ (increased reaction rates) and ‘negative catalysts’ (reduced reaction rates).

A commercial example of a negative catalyst is Lindlar’s catalyst. Here, controlled amounts of lead (Pb) are added to a palladium on calcium carbonate (Pd/CaCO₃) powder catalyst to inhibit alkane production from the reduction of alkynes.



In the reaction A → B or C, catalysts can often be designed to favour the formation of B (with inhibition of C) or promote the production of C (with inhibition of B) – catalyst selectivity.

If a catalyst did not undergo any ‘permanent chemical change’, then presumably it could last indefinitely. In practice every catalyst has a finite lifetime. There are two main reasons why a catalyst deactivates: *agglomeration* of active sites and *poisoning* (both chemical and physical).

Agglomeration. Over time, the metal surface area of a platinum group metal (pgm) heterogeneous catalyst (and hence its activity) will fall due to metal crystallite agglomeration. A compromise has often to be made between increased reaction rate (high temperature) and low agglomeration rate (low temperature). A similar effect can occur with mononuclear pgm homogeneous catalysts at much lower temperatures when polynuclear clusters may form. This is inhibited to some extent by excess free ligand being present.

Chemical poisoning. A typical mode of chemical poisoning is when an impurity in the reagents reacts irreversibly with the active metal. It is thus

common practice to ensure that the feedstocks are as pure as possible – often achieved by installing upstream purification units.

Physical poisoning – external. Another mode of catalyst deactivation is when the active sites become covered by ‘dirt’ from external sources (perhaps oil drops (from compressors) or condensed spray from upstream wet scrubber units). Installation of a sacrificial filter immediately upstream of the catalytic reactor can often be beneficial.

Physical poisoning – internal. Sometimes, physical masking of catalytic sites can be caused by solid deposition from an internal side reaction. In the petrochemical industry, one factor affecting catalyst lifetime in hydrocarbon reforming is the rate of elemental carbon lay-down. Such carboniferous deposits may be removed by controlled burning. The resulting exotherm must be limited to ensure minimal metal crystallite agglomeration. Such catalysts never attain 100% of their original activity, so in practice the number of reactivations is limited.

Metal loss can clearly be an important factor in reaction efficiency. In gas-phase heterogeneous catalysis, pgm loss can occur by volatilisation of metal or by abrasion/dusting losses from the surface of individual pellets. In liquid-phase reactions, metal loss can occur by dissolution from the support into the reaction medium. A possible loss mechanism (also can occur with homogeneous catalysts) is the soluble pgm salt plating out onto the reactor wall.

At some stage the process operator will decide that the overall reaction performance is unsatisfactory. Then, spent catalyst residues can be returned to the manufacturer for pgm recovery and (if required) conversion to fresh catalyst for reuse.

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Reference

- 1 “Oxford Dictionary of Chemistry”, 4th Edn., ed. J. Daintith, Oxford University Press, Oxford, 2000

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