

## CATALYSIS AND BIOCATALYSIS

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### Summary

This chapter presents a survey of catalysis and biocatalysis. Catalysis is a kinetic phenomenon, e.g. increasing the rate of a chemical reaction (catalysis) in the presence of a substance (catalyst) which does not appear in the overall stoichiometric equation of this chemical reaction. Catalysis is of crucial importance for chemical engineering, which focuses on the design and maintenance of chemical processes for large-scale manufacture. The number of catalysts applied in industry is very large and catalysts come in many different forms, from heterogeneous catalysts in the form of porous solids to homogeneous catalysts dissolved in the liquid reaction mixture to biological catalysts in the form of enzymes. Similarities and specificities of heterogeneous, homogeneous and biocatalysis are discussed in the chapter.

### 1. Brief History

When the rate of a certain process is measured, especially if it is of practical relevance, it is always important to know to accelerate its rate. It is even possible to imagine a situation that for a system demonstrating low velocity or complete inertness, introduction of a foreign substance could enhance the rate dramatically. Conversion of starch to sugars in the presence of acids, combustion of hydrogen over platinum, decomposition of hydrogen peroxide in alkaline and water solutions in the presence of

metals, etc., were critically summarized by a Swedish scientist J. J. Berzelius in 1836, who proposed the existence of a certain body, which “effecting the (chemical) changes does not take part in the reaction and remains unaltered through the reaction”. He called this unknown force, catalytic force, and defined catalysis as decomposition of bodies by this force.



Jöns Jakob Berzelius



Wilhelm Ostwald and Svante Arrhenius

Photo 1. Jöns Jakob Berzelius; Wilhelm Ostwald and Svante Arrhenius

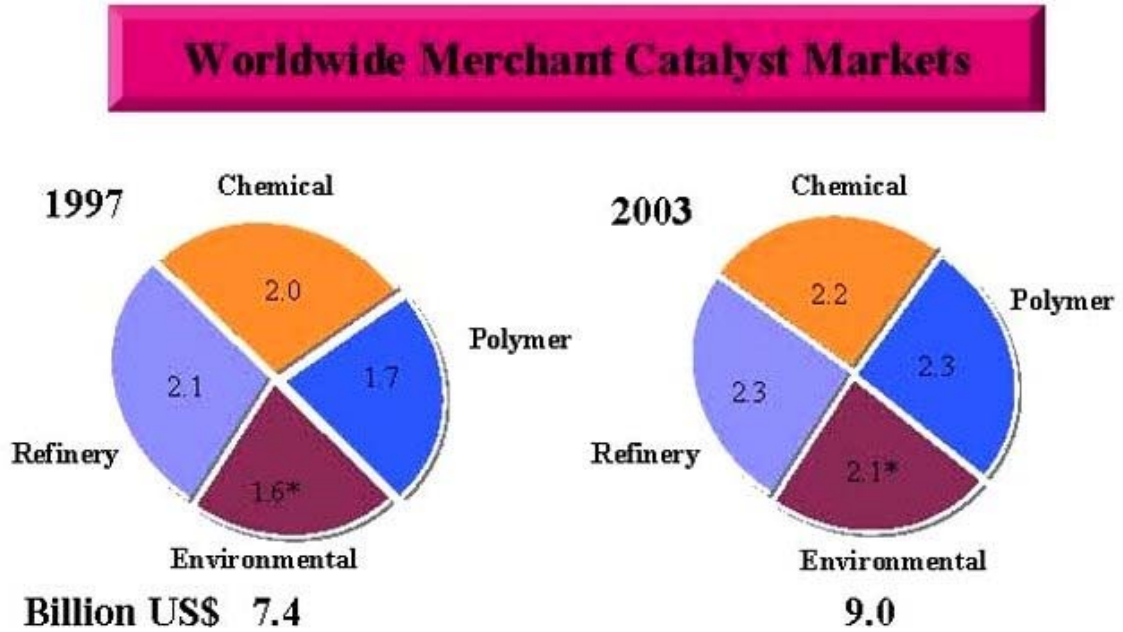
This new concept was immediately criticized by J. Liebig, as this notion was putting catalysis somewhat outside other chemical disciplines. A *catalyst* was later defined by W. Ostwald as a compound, which increases the rate of a chemical reaction, but which is not consumed by the reaction. This definition allows for the possibility that small amounts of the catalyst are lost in the reaction or that the catalytic activity is slowly lost.

## 2. Catalysis-Overview

Already from these definitions it is clear that there is a direct link between chemical kinetics and catalysis, as according to the very definition of catalysis it is a kinetic process. Despite the fact that catalysis is a kinetic phenomenon, there are quite many issues in catalysis which are not related to kinetics. Mechanisms of catalytic reactions, elementary reactions, surface reactivity, adsorption of reactants on the solid surfaces, synthesis and structure of solid materials, enzymes, or organometallic complexes, not to mention engineering aspects of catalysis are obviously outside the scope of chemical kinetics.

Catalysis is of crucial importance for the chemical industry and thus chemical engineering, the number of catalysts applied in industry is very large and catalysts come in many different forms, from heterogeneous catalysts in the form of porous solids to homogeneous catalysts dissolved in the liquid reaction mixture to biological catalysts in the form of enzymes. Catalysis is a multidisciplinary field requiring efforts of specialists in different fields of chemistry, physics and biology to work together to achieve the goals set by the mankind. Knowledge of inorganic, organometallic, organic chemistry, materials and surface science, solid state physics, spectroscopy, reaction engineering, and enzymology is required for the advancements of the discipline of catalysis.

The immense importance of catalysis in chemical industry is manifested by the fact that roughly 85-90% of all chemical products have seen a catalyst during the course of production.



The Catalyst Group: The Intelligence Report: Global Shifts in the Catalyst Industry

Figure 1. Worldwide catalyst market

Figure 1 demonstrates applications of catalysis in industry. In the last years there is an increase of catalytic applications also for non-chemical industries: treatment of exhaust gases from cars and other mobile sources, as well as power plants (Figure 2).

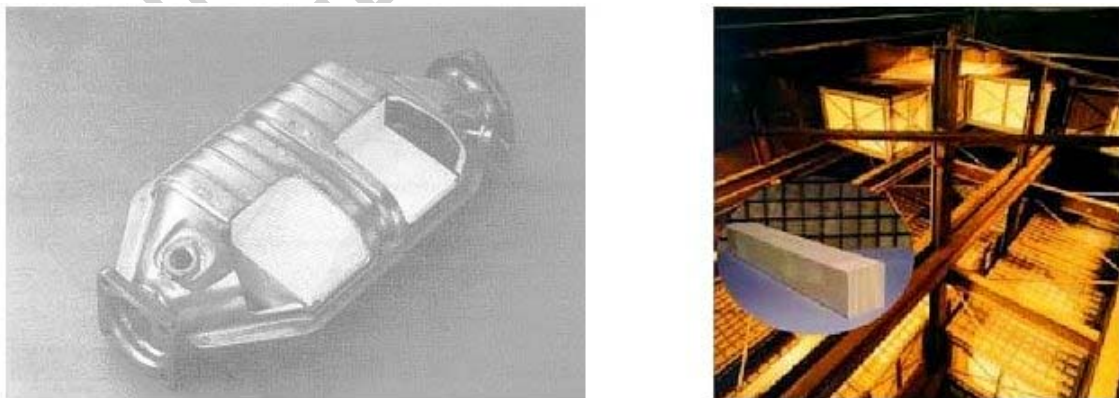


Figure 2. Catalytic treatment of NOx in a) mobile b) stationary sources

A great variety of homogeneous catalysts are known: metal complexes and ions, Brønsted and Lewis acid, enzymes. Homogeneous transition metals are used in several industrial processes; a few of them are given in Table 1.

Process	World capacity (million t/a)	Catalyst	Temperature (K)	Pressure (bar)
Acetaldehyde	2.5	Pd/Cu	375-405	3-8
Acetic acid	4.0	Rh	425-475	30-60
Oxo-alcohols	7	Co or Rh	335-470	200/30
Dimethyl terephthalate	3.3	Co	415-445	4-8
Terephthalic acid	9.4	Co	450-505	15-30

Table 1. Some homogeneous transition metals

Metal complexes can have a very sophisticated structure with a variety of ligands. An example of such ligands for Rh catalyzed hydroformylation is given in Figure 3.

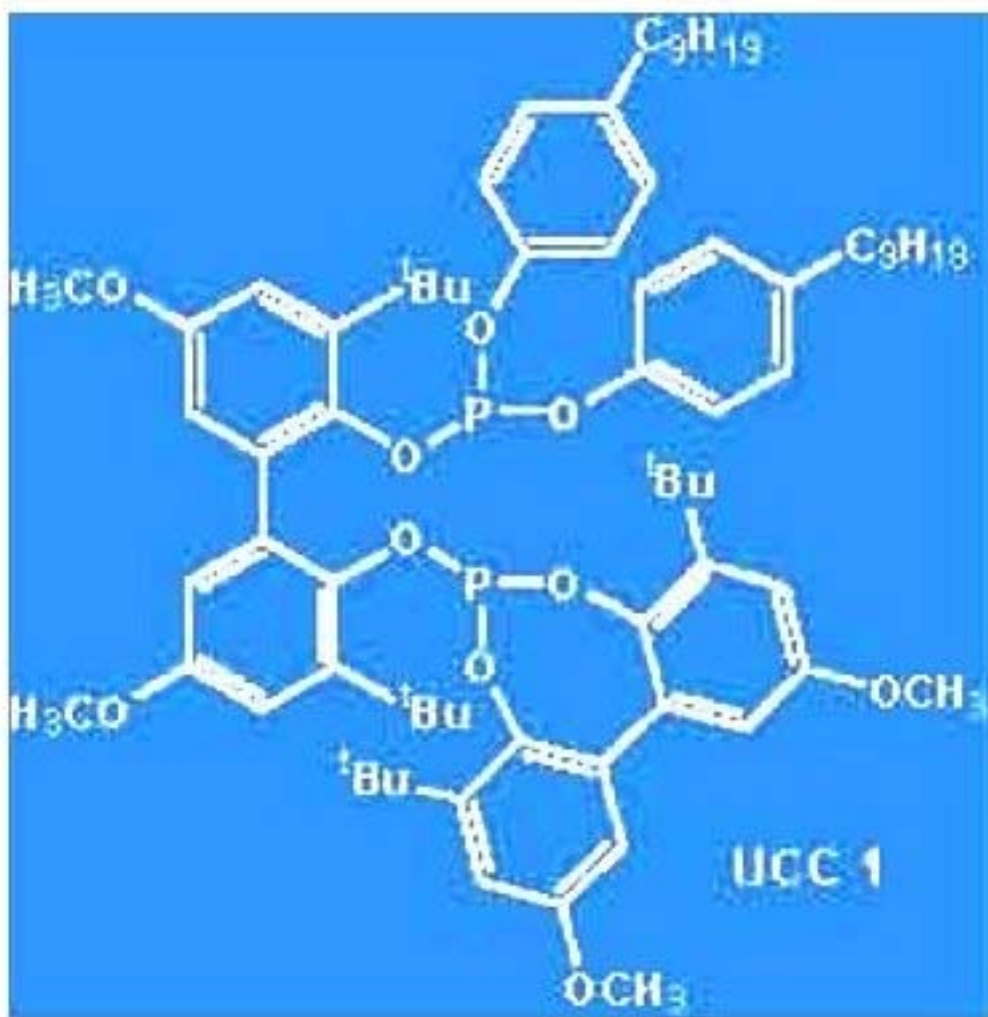


Figure 3. A ligand for Rh catalyzed hydroformylation

A comparison between homogeneous and heterogeneous catalysts (coming in variety of form, Figure 4) from the viewpoint of a homogeneous catalysis expert is presented in Table 2.

	Homogeneous	Heterogeneous
Activity	high	variable
Selectivity	high	variable
Conditions of reaction	mild	harsh
Life time of catalyst	variable	long
Sensitivity to deactivation	low	high
Problems due to diffusion	none	difficult to solve
Recycling of catalyst	usually difficult	can easily be done
Steric and electronic properties	easily changed	no variation possible
Mechanism	realistic models exist	not obvious

Table 2. Comparison between homogeneous and heterogeneous catalysts

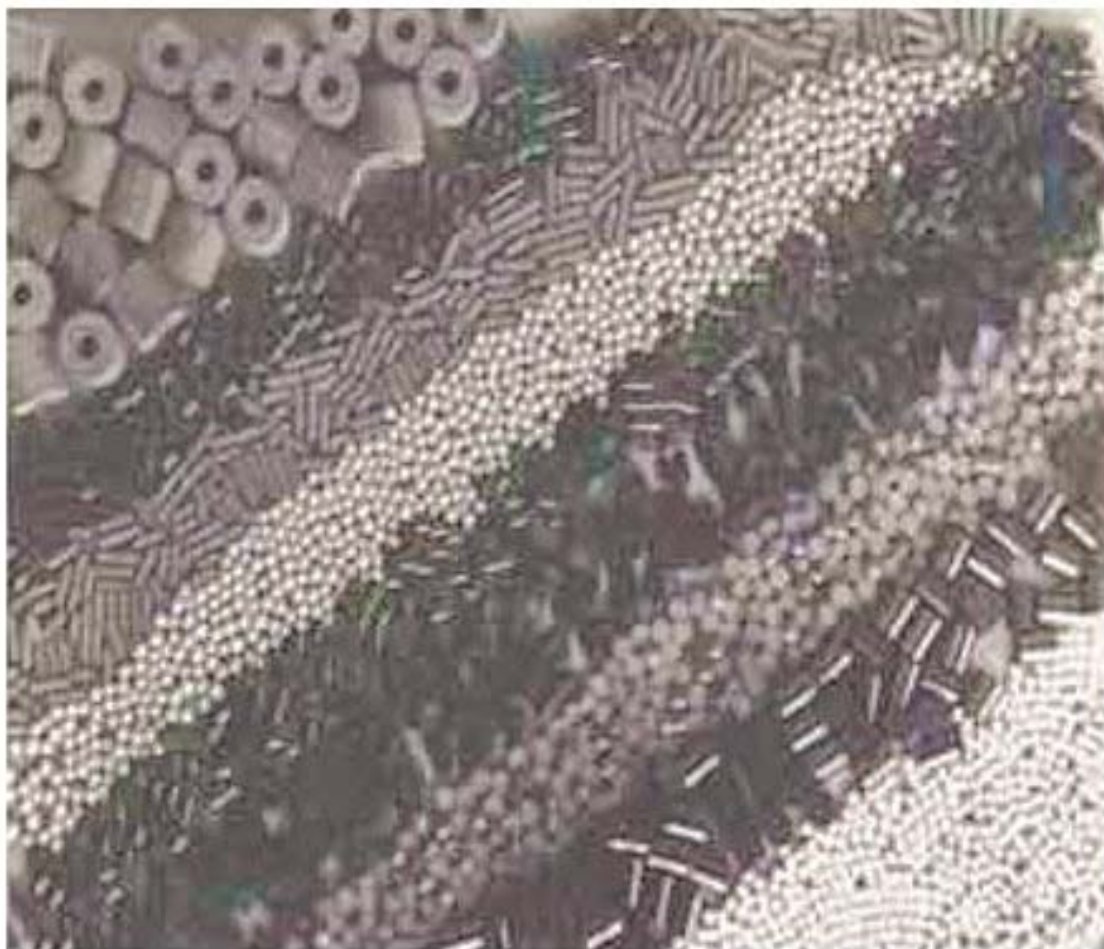


Figure 4. Images of heterogeneous catalysts.

Enzymes represent a special type of homogeneous catalyst. They are large proteins (Figure 5) capable of increasing the reaction rates by a factor of  $10^6$  to  $10^6$  at mild reaction conditions and displaying very high specificity and capability of regulation.

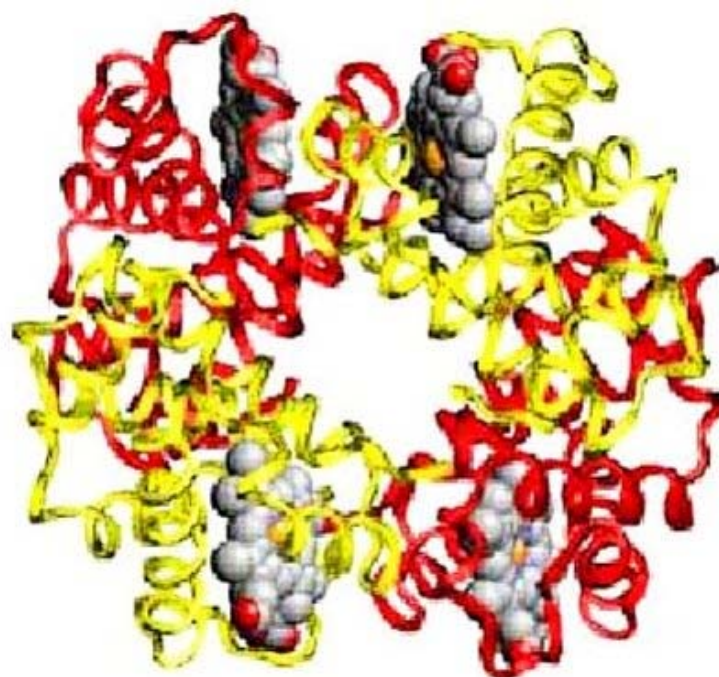


Figure 5. A schematic view on an enzyme structure.

Specificity (Figure 6) is controlled by the enzyme structure; more precisely a unique fit of substrate with the enzyme controls the selectivity for the substrate and the product yield.

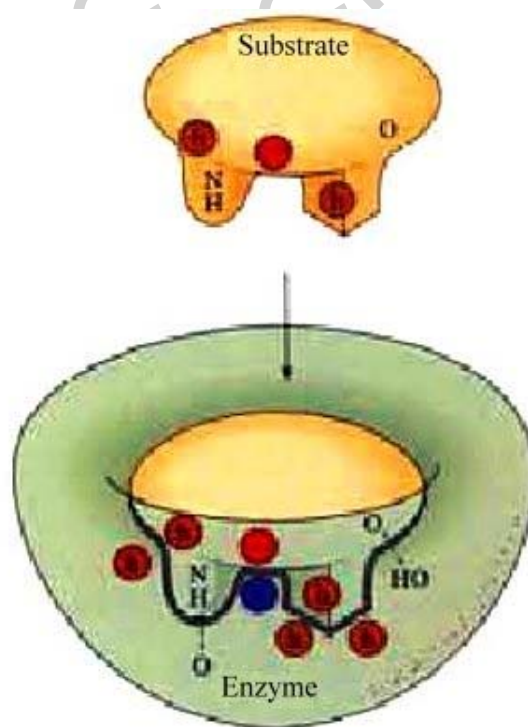


Figure 6. Specificity of enzyme catalysis.

Despite the fundamental differences between elementary steps in catalytic process on surfaces, with enzymes or homogeneous organometallics there are striking similarities also in terms of chemical kinetics. Although superficially it is difficult to find something in common between the reaction of nitrogen and hydrogen forming ammonia on a surface of iron, D-fructose 6-phosphate with ATP involving an enzyme phosphofructokinase, or ozone decomposition in the atmosphere in the presence of NO<sub>x</sub>, all these transformations require that bonds are formed with the reacting molecules. Such a complex then reacts to products leaving the catalyst unaltered and ready for taking part in a next catalytic cycle. Figure 7 is an example of a catalytic reaction between two molecules A and B with the involvement of a catalyst

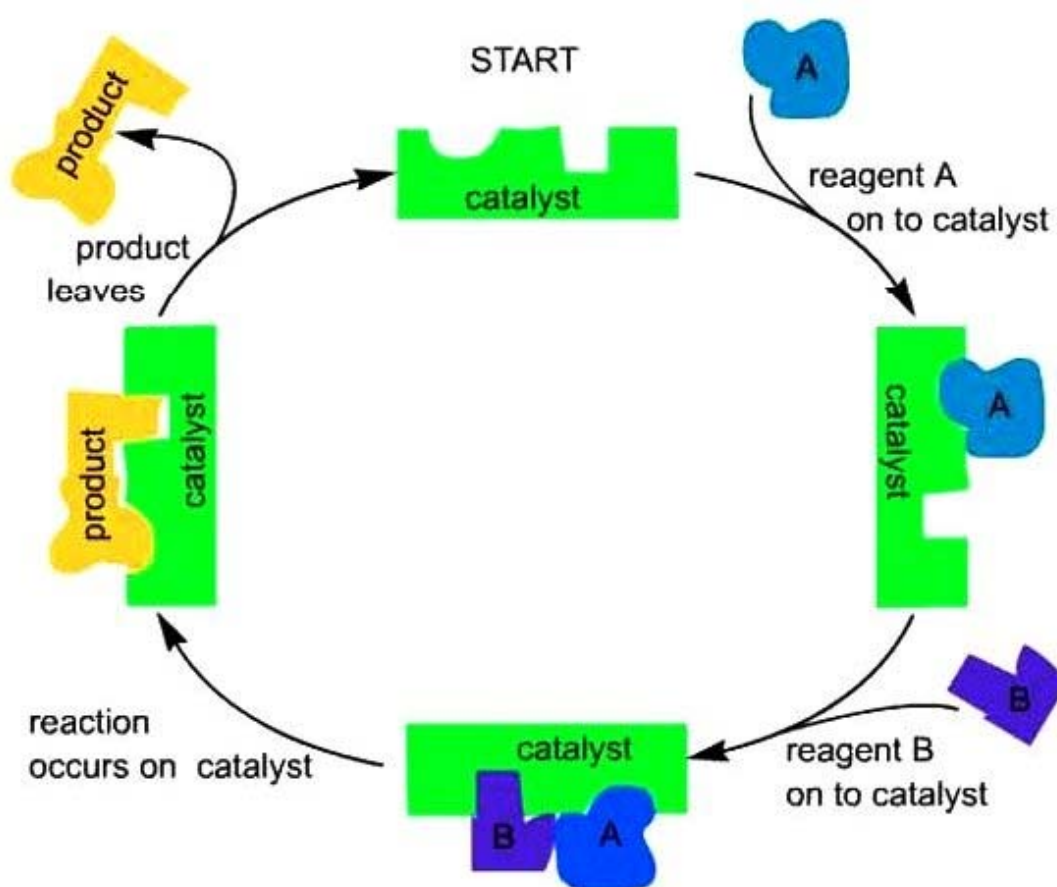


Figure 7. Catalytic cycle.

Figure 7 is somewhat simplified as it does not take into account possible bonding of the catalyst and reactant. In order for a catalyst to be effective, the energy barrier between the catalyst-substrate and activated complex must be less than between substrate and activated complex in the uncatalyzed reaction. The binding of substrate to an enzyme lowers the free energy of the catalyst-substrate complex relative to the substrate (Figure 8). This is a general feature of catalysis and is relevant for heterogeneous, homogeneous and enzymatic catalysis.

If the energy is lowered too much, without a greater lowering of the activation energy then catalysis would not take place, meaning that bonding between a catalyst and a



reactant should not be too strong. Alternatively if it is too weak, then the catalytic cycle could not proceed.

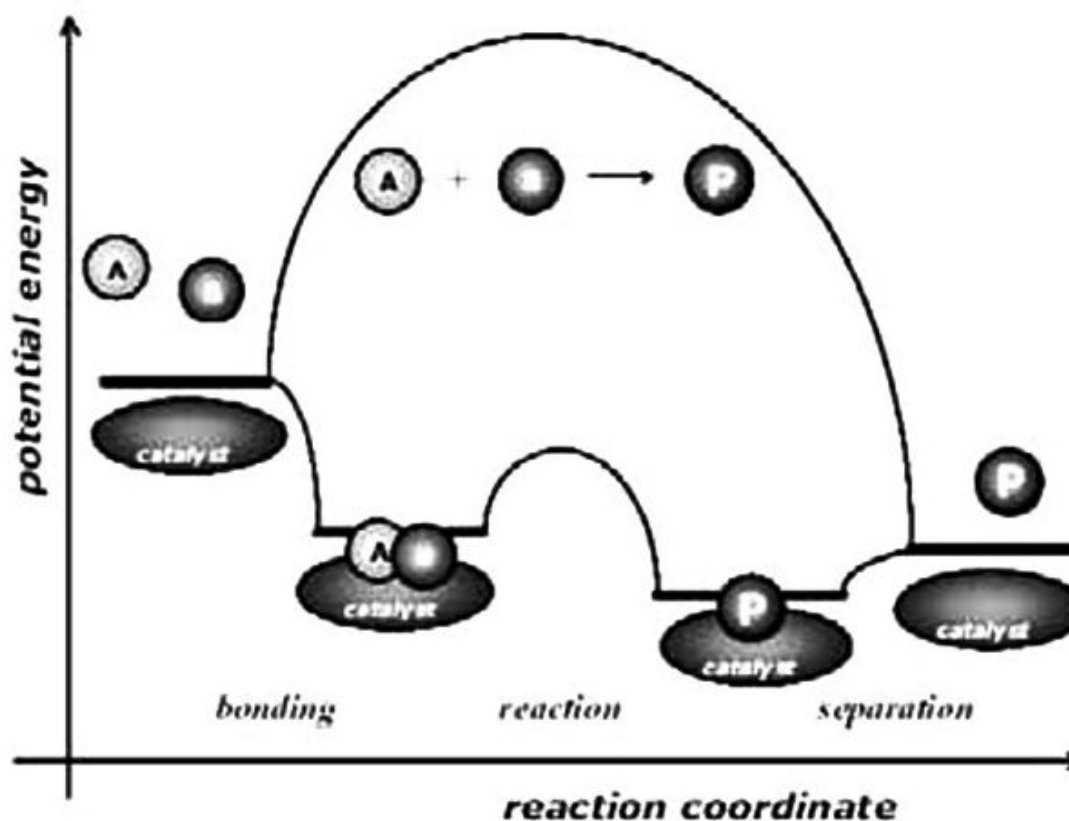


Figure 8. Potential energy diagram of a heterogeneous catalytic reaction (I.Chorkendorff, J.W. Niemantsverdriet, *Concepts of Modern Catalysis and Kinetics*, Wiley, 2003).

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### Biographical Sketch

**Dmitry Yu. Murzin** was born in Moscow; he received his M.Sc. in Chemical Engineering (1986) from Moscow Mendeleev University of Chemical Technology and PhD (1989), as well as Doctor of Science (1999) degrees from Karpov Physico-Chemical Institute (Moscow). After postdoctoral stays (1992-1994) in France (Universite Louis Pasteur, Strasbourg) and Finland (Åbo Akademi University, Turku/Åbo) he joined BASF in 1995, where he was involved in research and engineering, technical marketing and sales, as well as management. Since 2000 Dr. Murzin is full professor at Åbo Akademi University, holding the Borgström Chair in Chemical Technology. Main activities of Prof. Murzin are in catalysis and catalytic kinetics. He is an author of one book and authored ca. 350 scientific publications in referred journals and is a member of Editorial Boards of several journals.