Catalytic Processes

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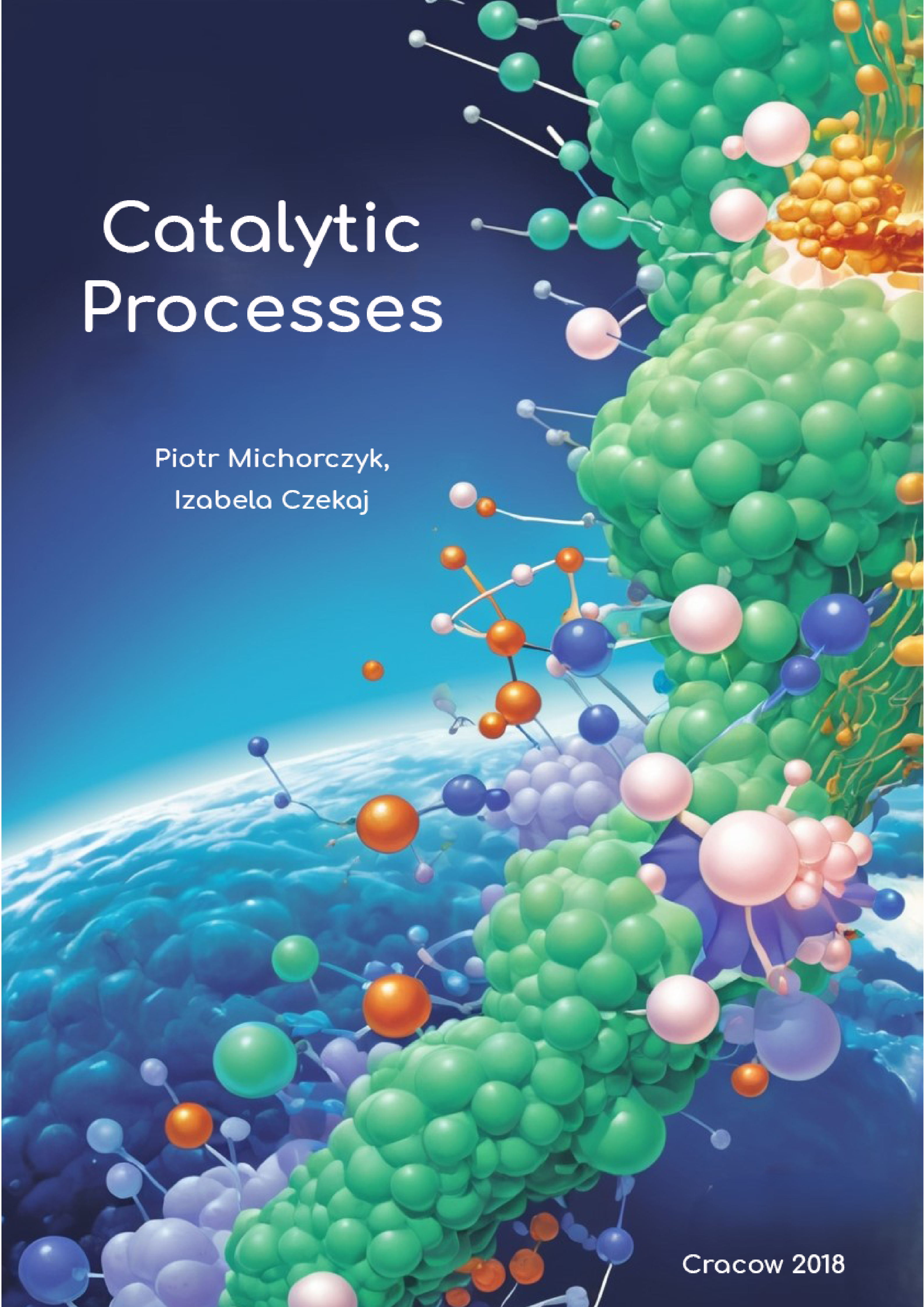

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Content

Preface

This book is intended to provide a comprehensive introduction to basic information about catalysis and catalytic processes which are important in modern industrial practice. Such principled information is necessary to know in order to work with catalysts in the laboratory, pilot and commercial plants.

1. Introduction: history and advantages of catalytic processes

As a result of catalytic processes, reactions that could take hundreds of years to complete in the uncatalysed “real world,” occur in seconds in the presence of a catalyst [1]. A catalyst is a substance that participates in a chemical reaction but is not consumed during the reaction. It provides a new mechanism of reaction, which has a lower activation energy than that of the same reaction without the catalyst. A catalyst changes neither the thermodynamics of the reaction nor the equilibrium composition. Catalysts only affect the rate of the reaction. Catalysts change the course of a reaction compared to non-catalytic reactions by forming a complex with the reactants/products, thus controlling the rate of the elementary steps in the process. This is evidenced by the fact that: the reaction activation energy is altered, the intermediates formed are different from those formed in non-catalytic reactions, the rates of reactions are altered (both the desired and undesired ones).

Catalytic processes have been influencing the development of humanity for thousands of years [2]. Early catalytic processes, such as producing alcoholic beverages using fermentation, vinegar using ethanol oxidation, and soap production using fat hydrolysis, have been known since Egyptian times. In the 8th century, Persian alchemist, Geber (Abu Mūsā Jābir ibn Hayyān), described the production of diethyl ether through the dehydration of ethanol. In the time of alchemistry, scientists concentrated on the search for a “magical catalyst” that could convert material into gold. In Europe, the first known description of the catalytic process dates from around 1540, when Valerius Cordus synthetized diethyl ether from alcohol using sulfuric acid (‘oil of vitriol’). The principles of catalysis were first presented by Elizabeth Fulhame in 1794 in the book "An Essay On Combustion with a View to a New Art of Dying and Painting, wherein the Phlogistic and Antiphlogistic Hypotheses are Proved Erroneous", based on her novel work in oxidation-reduction experiments [3]. In 1812 Kirchhoff, while hydrolysing starch to sugars, observed that the acids used in the reaction were not affected by the reaction. The next important year was 1817, when Humphry Davy observed that combustible gases mixed with oxygen and exposed to heated platinum could explode below the ignition temperature [4]. In the same year Johann Wolfgang Döbereiner discovered trends in certain properties of selected groups of elements (e.g. sulphur, selenium, and tellurium) "triads" and the use of platinum group metals as catalysts (oxidation of ethanol to acetic acid over Pt). Döbereiner also demonstrated the combustion of hydrogen and oxygen at room temperature over platinum, which led him to the construction of the hydrogen lamp [5]. Also, Michael Faraday studied catalytic processes such as the oxidation of hydrogen in the presence of platinum. In 1834, Eilhard Mitscherlich concluded that only a small amount of sulfuric acid was required to convert large amounts of ethanol into ether. He also introduced the term "*contact catalysis*" to the field of heterogeneous catalysis. In 1836 Jöns Jacob Berzelius, who is known as the inventor of the term 'catalysis', published a work about considerations respecting a new mechanism which acts in the formation of organic bodies [6]. In that year, the era of only empiric investigations ended and the new 'scientific' period of research concerning catalytic processes began. In 1894 Wilhelm Ostwald defined a catalyst as a substance that increases the rate at which a chemical reaction approaches equilibrium, but is not consumed in the process without changing the final position of the thermodynamic equilibrium. The birth of the industrial catalytic processes is generally agreed to have occurred during the period between 1898 - 1918. In 1909 Alwin Mittasch developed the first industrial catalyst for the production of ammonia from hydrogen and nitrogen. In 1918 Fritz Haber received the Nobel Prize in chemistry for the synthesis of ammonia. The catalytic developments in the years 1918-1945 were dominated by the petroleum industry, which facilitated a dramatic increase in global mobility.

Nowadays, catalysis and catalysts play one of the key roles in new technology development. Around 90% of chemical processes involve catalytic processes to enhance production efficiency and reduce energy use. More than 20% of all industrial products employ underlying catalytic steps. For example, petroleum refining consists almost entirely of catalytic processes. From an environmental point of view catalytic processes make a reaction possible under achievable conditions, reduce the necessity of expensive and dangerous conditions, generate high yields and high product purity, reduce the amount of side-product and waste created and make the chemical process more environmentally friendly.

Several important advantages of catalytic processes are essential for industry; achieving better process economics and productivity (increase reaction rates, simplify the reaction steps - lower investment costs, carry out the reaction under mild conditions e.g. low T, P, - low energy consumption), reducing waste (improving selectivity toward the desired products - less raw material required, less waste, replacing harmful/toxic materials with readily available ones), producing certain products that may not have been possible without catalysts, having better control of the process (safety, flexible etc.), encouraging the application and advancement of new technologies and materials.

Research in catalysis involves a multi-discipline approach, which is an additional advantage of the catalytic processes. A multi-discipline approach involves not only the catalytic process itself (like energy balance and the efficiency of the process, heat and mass transfer), but also; catalyst development (material synthesis, stability of catalysts, preparation techniques), reaction kinetics and mechanisms (reaction paths, intermediate formation and reactivity, behaviour under various conditions, reaction types, prediction of catalyst performance), reaction modelling (elementary reactions and rates, quantum mechanics/chemistry), characterization techniques (adsorption/desorption techniques, microscopic and spectroscopic techniques, conditions development), reactor modelling (numerical methods, micro-kinetics, reactor design, mathematical representation).

2. Types of catalytic processes

Catalytic processes can be divided into two main types based on the ways catalysts work [7,8]; homogeneous (where the catalyst and all reactants/products are in the same phase gas or liquid) and heterogeneous (where the reaction system involves multi-phase (catalysts + reactants/products) processes. Based on the type of substances from which a catalyst is made the catalytic processes are classified as: (i) inorganic catalysts, where catalysts are in form of gases, metals, metal oxides, inorganic acids or bases, (ii) organic catalysts including the following substances: organic acids, enzymes.

Another classification is based on the mode of action of the catalyst and includes the following processes: acid-base catalysis, photocatalysis, enzymatic catalysis or electrocatalysis [7].

In acid-base catalysis [9] a chemical reaction is catalysed by an acid (the proton donor) or a base (the proton acceptor), known as a Brønsted acid and base, respectively. An examples of acid-base catalysis, where proton transfer is observed is the esterification reaction.

Photocatalysis is based on a photoreaction in the presence of a catalyst [10]. The mechanism of photocatalytic reactions is based on the formation of free radicals, which react further. An example of a photocatalytic reaction is water photolysis over titanium dioxide. The TiO_2 material is a very good photocatalyst due to its electronic structure (e.g. able to create electron-hole pairs).

Enzymatic catalysis [11] is based on a series of reactions with the presence of enzymes, which form energetically favorable intermediates. The most important one is the formation of an enzyme-substrate complex that provides a gain in energy sufficient to accelerate the whole process. An example of an enzymatic catalyst is dehydrogenase NAD, which converts primary alcohols to aldehydes.

Electrocatalysis is a form of catalysis which modifies the rate of an electrochemical reaction occurring on an electrode surface [12]. An electrocatalyst is a catalyst which takes part in electrochemical reactions. Electrocatalysts may be heterogeneous (platinum surface or supported nanoparticles) or homogeneous (complex or enzyme). The electrocatalyst: i) assists in transferring electrons between the electrode and reactants, ii) facilitates an intermediate chemical transformation described by an overall half-reaction.

3. Thermodynamics and kinetics of chemical reactions

Catalysis is a phenomenon of increasing the rate of a chemical reaction or/and directing it to one of thermodynamically possible pathways resulting in different products in the presence of small amounts of substances referred to as catalysts [13]. These substances chemically react with the reaction substrates and form unstable bonds, however, they are not consumed in the reaction and do not appear in its stoichiometric equation. Neither does a catalyst affect the chemical equilibrium, it only increases the velocity of reaching the equilibrium.

The essence of catalysis may be explained on the basis of the active complex theory (Fig. 1). According to this theory, a reaction occurs when, at the moment of a collision, the colliding molecules form an active complex, which is a system of interacting molecular entities. In order for the collision to be effective, the molecular entities must be provided with energy that is higher or equal to the reaction activation energy (for a non-catalysed reaction it equals E_a), which is required, inter alia, to overcome the intermolecular repulsive forces, regrouping of atoms or loosening the bonds in the reacting substrates.

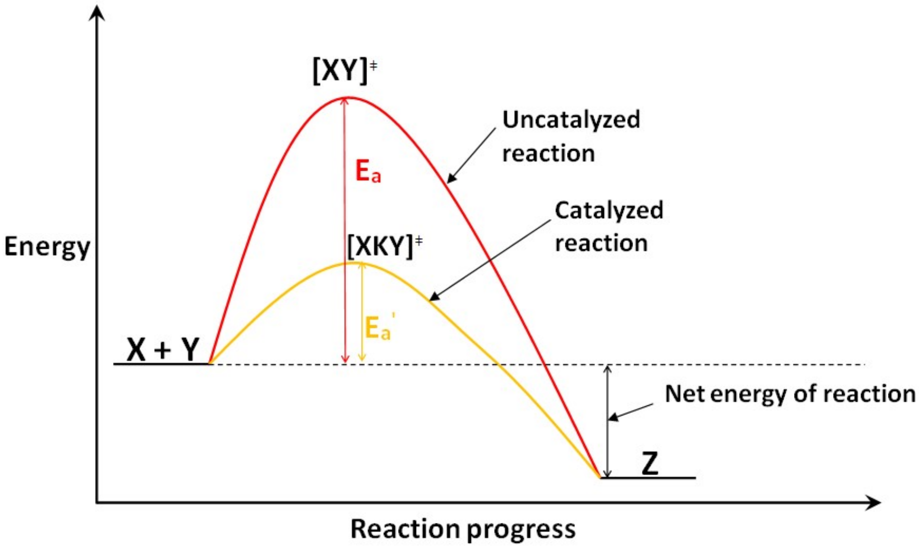

Figure 1. The essence of catalysis on the basis of the active complex theory. Key: X and Y – substrates, *Z* – reaction product, E_a and E_a' – activation energy of a non-catalysed and catalysed reaction, respectively, $[XY]^‡$ and $[XKY]^‡$ – transitional complex in a non-catalysed and catalysed reaction, respectively.

In a catalysed reaction there occurs a new, alternative pathway of "Z" product generation. The energy required for the generation of an active complex $[XKY]^‡$ is lower than in a non-catalysed process, which means that statistically more molecular entities will be able to react.

Statistically, the distribution of energy among the molecular entities (molecules) has been also described using the Maxwell-Boltzmann equation. In Figure 2, there is a graphical presentations of the functions of kinetic energy distribution for molecules in three different temperatures and indication of a sample energy threshold above which reactions take place (reaction activation energy).

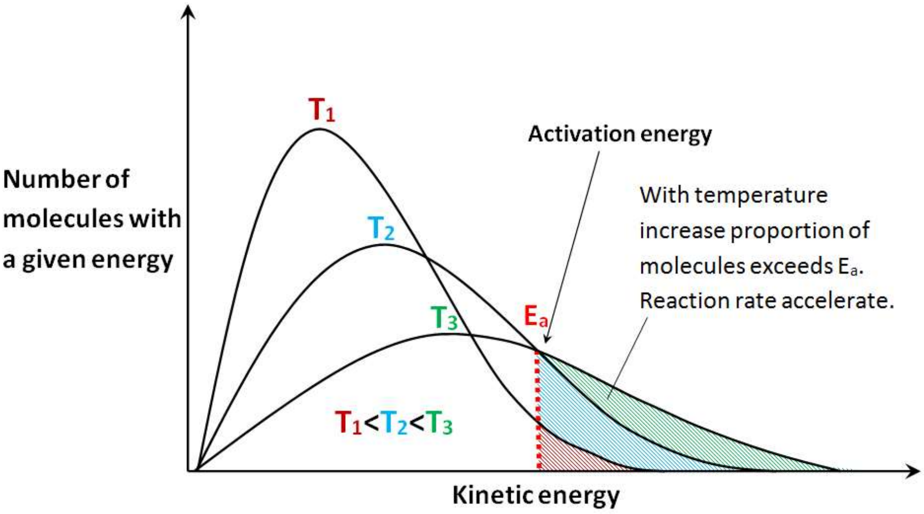

Figure 2. A diagram of the molecular kinetic energy distribution in three different temperature values.

The Maxwell-Boltzmann equation is a probability density function for speed (u).

$$f(u) = \left[\frac{M}{2\pi RT}\right]^{3/2} \cdot 4\pi u^2 \cdot e^{-Mu^2/2RT}$$

where: M – the atomic or molecular mass in kg/mole, R – the gas constant in J/K·mol, and temperature T.

Arrhenius equation shows the effect of a change of temperature on the rate constant.

$$k = Ae^{-\frac{E_a}{RT}} \quad or \quad ln\ k = -\frac{E_a}{RT} + ln\ A$$

where: k – chemical reaction rate, A – pre-exponential factor, Ea – activation energy, R – gas constant, T – temperature in Kelvin.

It can be noticed that the activation energy is independent from the reaction temperature. In low temperature, there is little involvement of molecules with the kinetic energy necessary for the reaction to take place and thus the reaction rate is low. Most molecules will undergo elastic collisions without losing any energy. Moreover, it can be noticed that the involvement of molecules with energy equal or higher than E_a grows along with temperature increase, which is illustrated by the growing area under the curve (AUC) in Figure 2. Quantitative interdependence between reaction rate and temperature is also described by Arrhenius equation.

The effect of catalyst introduction has been presented in the diagram of molecular kinetic energy distribution (Figure 3). As it was mentioned above, a catalyst activates a new, alternative reaction pathway with a lower energetic barrier. Because the diagram illustrates the probability distribution of molecules with a certain kinetic energy, it shows that the shift of activation energy to the left leads to statistical increase of the involvement of molecules with energy equal to or higher than this threshold value.

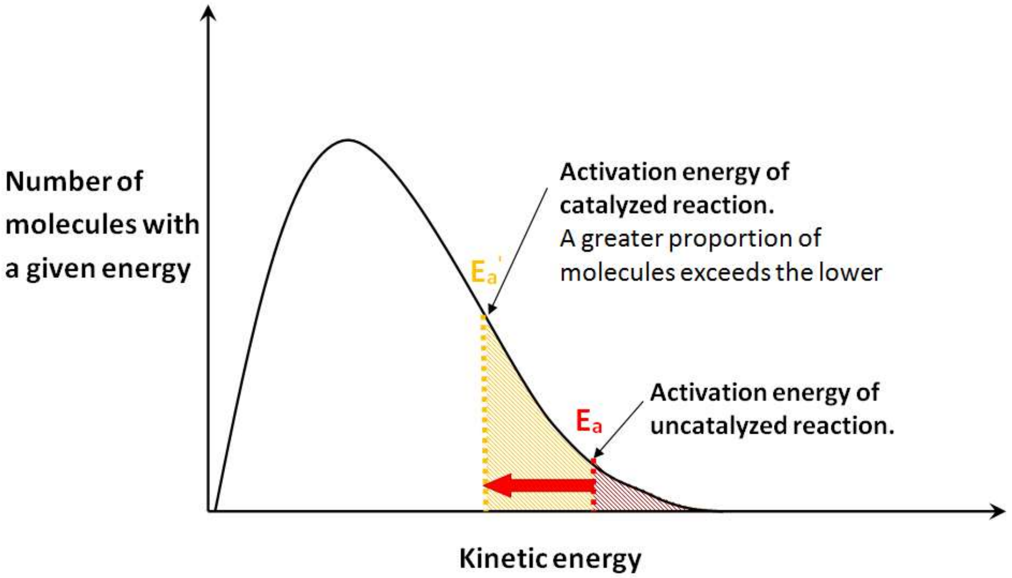

Figure 3. The diagram of molecular kinetic energy distribution with the threshold value of non-catalysed and catalysed reaction activation.

It should be noted here that the introduction of a catalyst does not affect the activation energy of the non-catalysed reaction, which is taking place simultaneously with the catalysed reaction.

4. Adsorption at solid surfaces

Adsorption is a process in which molecules from a gas (or liquid) phase land on, interact with and attach to solid surfaces [14]. The reverse process of adsorption, i.e. the process in which adsorbed molecules escape from solid surfaces, is called ***Desorption***. Molecules can attach to surfaces in two different ways because of the different forces involved. These are ***Physisorption*** (Physical adsorption) & ***Chemisorption*** (Chemical adsorption). Adsorption is usually exothermic (in special cases *dissociated* adsorption may be endothermic). The heat of physisorption is in the same order of magnitude as condensation heat. The heat of chemisorption is in the same order of magnitude as chemical reaction heat.

Adsorption is a very important step in solid catalysed reaction processes. Adsorption in itself is a common process used in industry for various purposes: purification (removing impurities from a gas / liquid stream), depollution, decolourization, deodourization, solvent recovery, trace compound enrichment. Usually adsorption is only applied to a process dealing with a small capacity. The operation is usually batch type and requires the regeneration of saturated adsorbent. Common adsorbents are: molecular sieve, active carbon, silica gel, activated alumina. Physisorption is a useful technique for determining the surface area, the pore shape, pore sizes and size distribution of porous solid materials (BET surface area).

Table 1. Comparison of physical and chemical adsorption [15]

	Physisorption	Chemisorption
force	van de Waal	chemical bond
adsorption heat	low (10-40 kJ/mol)	high (>40 kJ/mol)
temperature to occur	low	high
number of adsorbed layers	multi	only one layer
selectivity	low	high
example	attraction of a fluid (N_2 gas) to any surface	chemical bond formation (e.g. CO and surface site)
adsorption energy	low (10-40 kJ/mol)	high (~100- 500 kJ/mol)

5. Mechanisms of catalytic process at the surface

Reactions on surfaces are reactions which involve the adsorption of one or more reactants. This causes the existence of different reaction mechanisms, which include different kinetics and adsorption modes [16]. There are three types of surface reaction mechanisms used in the field of heterogeneous reactions (Figure 4): a) Eley-Rideal mechanism, b) Langmuir-Hinshelwood mechanism and c) Mars-Van Krevelen mechanism.

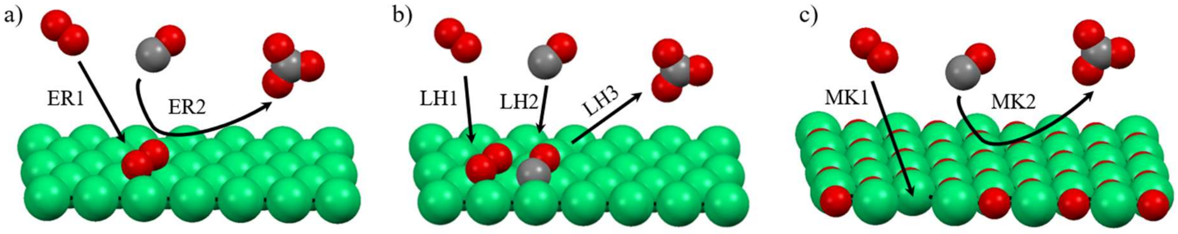

Figure 4. Reaction steps in certain mechanisms: a) Eley-Rideal, b) Langmuir-Hinshelwood, c) Mars-Van Krevelen mechanism.

Eley-Rideal mechanism. Only one of the reactants adsorbs onto the surface (reaction ER1) [17]. The other reactant interacts with the adsorbed species directly from the gas phase. The desorption of the reaction product (reaction ER2). An example of a reaction following the Eley-

Rideal mechanism is: the hydrogenation of CO_2 during formate synthesis, in which H_2 is the adsorbed species.

Langmuir-Hinshelwood mechanism. Both reactants first adsorb onto the surface before a reaction takes place (reactions LH1 and LH2) [18]. Surface diffusion facilitates interaction between the adsorbed molecules. The reaction at the surface is the rate limiting step. The reaction product desorbs from the surface (reaction LH3). The reactivity is highest when a stoichiometric amount of the reactant is adsorbed on the surface, and both reactants are fully dispersed over the surface. An example of a Langmuir-Hinshelwood mechanism is the reduction of NO by CO into N_2 on Pt(100).

Mars-Van Krevelen mechanism. The surface itself plays an active part in the reaction [19]. One reactant forms a chemical bond with the catalytic surface (reaction MK1) forming a thin surface layer of metal-reactant. Another reactant then reacts directly from the gas phase with the atoms from the chemically bonded reactant on the surface (reaction MK2). When the reaction product desorbs, a vacancy is left behind on the surface. This vacancy will be filled again by the first reactant (reaction MK1). The vacancy created by the reaction is filled by a reactant atom from the bulk, rather than from the gas phase. An example of a Mars-Van Krevelen reaction mechanism is CO-oxidation over RuO_2.

6. Steps of catalytic reactions

Several physical and chemical processes take place when a heterogeneous catalytic reaction occurs due to the fact that the reactants and catalyst are present in different phases [20]. Catalytic reaction takes place at the surface, however, the reactants need to diffuse through fluid phases, catalyst pores and be adsorbed at the surface. The sequence of physical and chemical steps is schematically illustrated in Figure 5 for a solid-catalysed liquid reaction [21].

The catalyst particle can only be effective if the reactants reach the external and internal catalytic surface. The long journey for reactant molecules during the catalytic process includes several steps: (1) mass transfer within the gaseous phase (diffusion) and (2) cross gas-liquid phase boundary (adsorption and diffusion), (3) mass transfer of both reactants (gas and liquid) from the bulk liquid to the external surface of the catalyst particle (diffusion through a stagnant external layer surrounding the catalyst particle), (4) mass transfer of reactants into the porous catalyst (internal diffusion), (5) adsorption of reactants at the active phase surface following either step 3 or 4; (6) surface reaction; (7) desorption and transfer of product(s) by (8) internal and (9) external diffusion to the bulk liquid or gaseous phase. The transport steps (1-4, 8, 9) depend mainly on temperature, pressure, composition, flow rates and pore size. The chemical steps (5, 6, 7) are dependent on the temperature, pressure and composition of the catalyst. The surface reaction depends on the types of active sites and electronic structure of the active phase, which is discussed in detail in chapter 8 in "Catalyst composition and active sites".

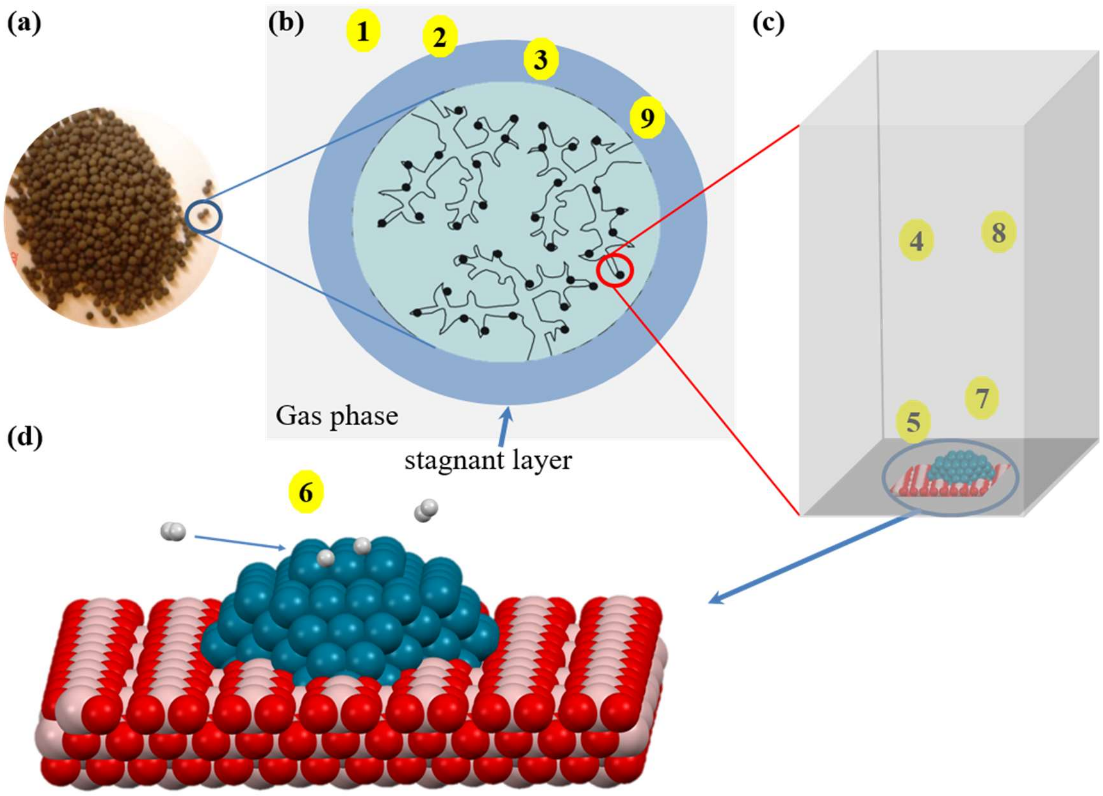

Figure 5. Sequence of physical and chemical steps of catalytic reactions: (a) catalyst pellets, (b) metal particles on a porous support, (c) catalyst pore, (d) active metal nanoparticle at the support surface.

7. Catalytic properties

In the case of heterogeneous catalysts, their catalytic properties are characterised with three parameters, i.e.:

– activity,
– selectivity,
– stability (in correlation with lifetime).

From the user's point of view (industry) other parameters are also important, such as:

– price,

– toxicity.

Activity defines the rate of reaction taking place in the conditions in the reactor (temperature, pressure, reagent concentration) in the presence of catalyst "r_K". Usually, in experimental conditions, the total reaction rate "r" is measured that comprises non-catalysed reaction rate "r_N" and catalysed reaction rate "r_K".

$$r = r_K + r_N \quad (mol \cdot s^{-1}) \qquad (4)$$

Because the non-catalysed reaction rate is much lower than the catalysed one ($r_K >> r_N$), for the sake of simplification it can be assumed that the experimentally measured value (in kinetic conditions) equals the catalysed reaction rate. Obviously, such assumption is not always valid.

$$r = r_K \qquad (5)$$

Usually, the reaction rate refers to the catalyst mass ($m_{cat.}$) or its specific surface ($S_{cat.}$). The value determined in this way is referred to as the catalyst's "proper activity", which is defined in the equations (6 and 7) [22].

$$A_w = \frac{r}{m_{cat.}} \quad (\mathrm{mol \cdot s^{-1} \cdot kg^{-1}}) \ (6)$$

$$A_w = \frac{r}{S_{cat.}} \quad (\mathrm{mol \cdot s^{-1} \cdot m^{-2}}) \ (7)$$

The figures determined in this way give an average result (assuming surface homogeneity in terms of activity) and refer to the activity of individual active centres, which usually constitute a very small proportion of the forms present on the surface of the heterogeneous catalyst. More precise evaluation of the activity may be obtained by referring the reaction rate "r" to the number of specific centre types determined using spectroscopic or other techniques, e.g. temperature-programmed desorption of ammonia, temperature-programmed reduction with hydrogen, etc. By determining the number of specific forms and assuming that their activity is dominant, the reaction rate per individual centre (active centre) may be established. Thus, using the results of quantitative analysis of the catalyst surface and reagent content, it is possible to establish the TOF (Turnover Frequency) value, which is defined in homogeneous and heterogeneous catalysis as the quantity of substrate moles transformed on a single active centre within a unit of time (s, min, h). It must be kept in mind that, in case of heterogeneous catalysts, such calculations are very rough and may lead to overestimation.

Specific activity in propene metathesis calculated based on measurement in microreactor [23]:

$$r_{\mathrm{Mo}}(\mathrm{C_3H_6}) = \frac{\dot{V}_{\mathrm{F}}[x_{\mathrm{out}}(\mathrm{C_3H_6})]N_{\mathrm{A}}}{V_{\mathrm{M}}S_{\mathrm{BET}}m_{\mathrm{Cat}}\omega_{\mathrm{Mo}}}$$

where: x_{out} (C_3H_6), $\dot{V}_F$, m_{Cat}, V_M, S_{BET}, N_A, and ω_{Mo} stand for outlet mole fraction of propene, volumetric feed flow rate ($cm^3 s^{-1}$), catalyst mass (g), molar volume ($cm^3\ mol^{-1}$), specific surface area ($m^2\ g^{-1}$), Avogadro's number (mol^{-1}) and Mo apparent surface density ($Mo\ m^{-2}$), respectively.

In many cases, when activity of a number of catalysts is compared, simpler measuring methods can be used based on the determination of the degree of conversion (8) in the function of temperature. The degree of conversion is defined as the amount of substrate, in moles, that has reacted to the total amount of moles of the substrate introduced into the reactor at the same time. Usually the numerical value of the degree of conversion is expressed in percentage or mole/mole and determined on the basis of the correlation (8 and 9).

$$X = \frac{n_{Ao} - n_A}{n_{Ao}} \quad (\mathrm{mol \cdot mol^{-1}}) \qquad (8)$$

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$$X = \frac{(n_{Ao} - n_A)100\%}{n_{Ao}} \quad (\%) \qquad (9)$$

This idea is presented in Figures 6a and 6b. The first method consists in the designation of the degree of substrate conversion change curves in the function of reaction temperature keeping the other process parameters (pressure, catalyst load and supply mixture composition). For example, Figure 9a presents curves for two catalysts (X and Y). The figure shows that identical degree of conversion for catalyst X was obtained in lower temperature than in case of catalyst Y, which demonstrates that material X is characterised with higher catalytic activity in the examined process. Analogical method can be used to determine so called isoconversions for a series of catalysts in the function of contact time (Figure 6b).

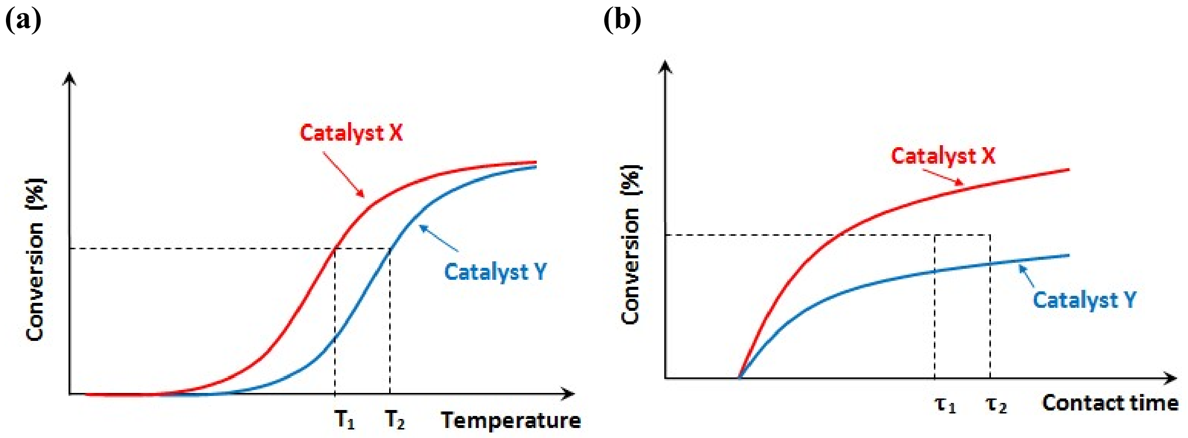


Figure 6. A graphical way of comparing the activity of a series of examined catalysts (according to [22]).

In this case the variable is the contact time, which is defined as the proportion of catalyst deposit bulk volume (V_{cat}) to volumetric raw material flow rate (F)(10).

$$\tau = \frac{V_{kat.}}{F} \quad \text{(s, min, h...itd)} \qquad (10)$$

The inverses of the contact time "$1/\tau$" can also be used in the calculations, that is GHSV (Gas Hourly Space Velocity) or LHSV (Liquid Hourly Space Velocity) when liquid raw material flow is included in the calculations (11).

$$GHSV(LHSV) = \frac{1}{\tau} \quad (\text{s}^{-1}, \text{min}^{-1}, \text{h}^{-1}\text{...itd}) \qquad (11)$$

Selectivity is another feature of a catalyst. It defines what part of the reacted substrate is converted to particular reaction products. The selectivity to product "S_p" is expressed in percentage on the basis of a simple correlation presented below (12).

$$S_P = \frac{n_P |\nu_P|}{(n_{A_0} - n_A)/|\nu_A|} \text{x}100\% \quad (\%) \qquad (12)$$

where: n_p – number of moles of a product, n_{Ao} – initial number of moles of a substrate, n_A – number of moles of a substrate that remained after the reaction, ν_A and ν_P – stoichiometric factors from the reaction equation for the substrate and the product, respectively.

This quantity is especially important from the industrial point of view because it provides quantitative information about substrate losses (side products). Usually, in industrial practice, even in the most selective processes taking place in the presence of heterogeneous catalysts, the selectivity to the intended products does not exceed 95%. Table 2 lists several example processes and performances obtained in industrial installations.

Table 2. Performance achieved in selected industrial processes [24–26].

Process	Substrate	Main product (desired)	Catalyst	Degree of conversion (%)	Main product selectivity (%)
Dehydrogenation (Oleflex)	propane	propylene	Pt-Sn/Al_2O_3	40	90
	isobutane	isobutylene		50	92
Dehydrogenation (Pacol)	saturated serial hydrocarbons n-C_{10}-C_{14}	non-saturated analogues with double terminal bond	Pt/Al_2O_3	13	90
Ethylene oxide synthesis (version with oxygen)	ethylene/oxygen	ethylene oxide	Ag/Al_2O_3	7–15	75–80
Methanol oxidising to formaldehyde	methanol/oxygen	formaldehyde	Fe_2O_3-MoO_3	95–99	91–94
Vinyl acetate synthesis (gas phase version)	acetic acid/ethylene/oxygen	vinyl acetate	Pd/SiO_2 Pd-Au/SiO_2	10 (ethylene)	94
Maleic anhydride synthesis	benzene/oxygen	maleic anhydride	V_2O_5	85–90	60–65

Side products may arise both in parallel and subsequent reactions, which is illustrated in Figure 7. In parallel reaction, the side products arise simultaneously with the main product of the reaction. While, in subsequent reactions, the intended product obtained in the main reaction may react further, which leads to the occurrence of side products.

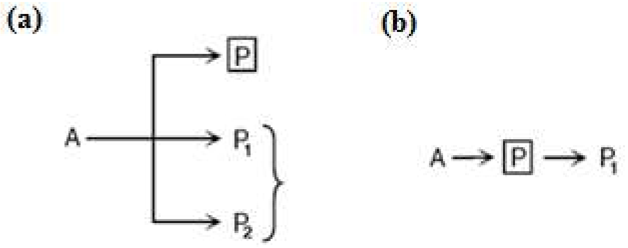


Figure 7. The manner of formation of the desired and side products in parallel (a) and subsequent (b) reactions [27].

For example, in the propane dehydrogenation reaction to obtain propylene, beside the main dehydrogenation reaction there also occur side reactions of propane cracking and hydrocracking, Moreover, in subsequent reactions, the more reactive propane is transformed into oligomers and carbon deposit (Figure 8).

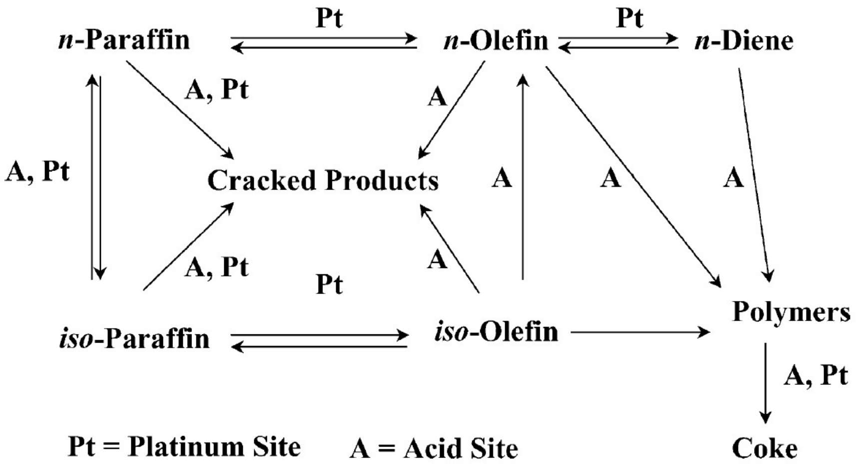


Figure 8. A diagram of reactions taking place during the process of alkane dehydrogenation to alkenes in the presence of Pt/Al_2O_3 catalyst [26].

Calculation of selectivity based on carbon balance for propane dehydrogenation reaction [28]:

$$S_i = \frac{a_i}{3} \cdot n_i \times \frac{100\%}{n_{C_3H_8,\mathrm{inlet}} - n_{C_3H_8,\mathrm{outlet}}}$$

where: $nC_3H_{8,\mathrm{inlet}}$ and $n_{C3H8,\mathrm{outlet}}$ are numbers of propane moles in inlet and outlet of reactor, respectively; a_i is a number of carbon atoms in a product, and n_i is a number of moles of a product.

Catalyst performance stability. This parameter is usually ignored in laboratory tests and it has a key significance in industrial applications. It happens that a very active and selective catalyst is not applicable in industrial conditions due to its low reaction stability. This parameter can be defined as the duration of time in which a catalyst retains performance efficiency in the reaction conditions without the need for its regeneration or replacement. Catalyst stability is strictly correlated with its deactivation, which can be classified as reversible and irreversible. Intuitively, the difference between these two types of deactivation is whether, after the loss of catalytic properties, the catalyst can regain activity, following certain actions (regeneration, e.g. deposit burning with air) regarding the installation where it is used, or not Reversible deactivation usually occurs much faster than irreversible deactivation. A good example if the process of fluid catalytic cracking (FCC), in which a catalyst loses its activity after just a few seconds due to reversible deactivation, It can only be regained following carbon deposit burning with air. In turn, the irreversible deactivation is a much slower process. Usually, in result of catalyst operation in high temperature (phase transformations, active ingredient redispersion), in the presence of toxins or mechanical damage (catalyst molecule friction) there occurs irreversible deactivation, which makes it necessary to replace the catalyst.

Due to varied catalyst operation conditions, catalyst performance time is very diverse. Figure 9 presents a diagram of catalyst usage times in logarithmic scale in selected important industrial installations.

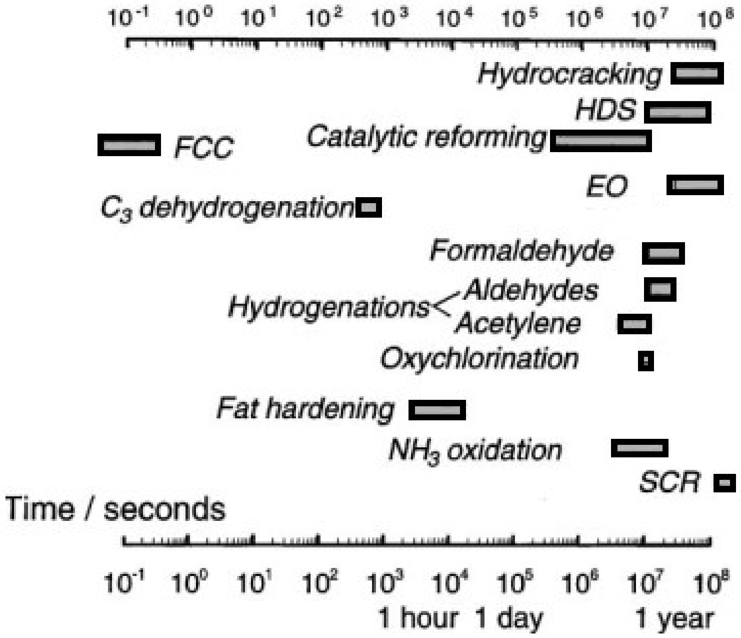


Figure 9. Deactivation times of selected industrial catalysts. FCC – fluid catalytic cracking, HDS – hydrodesulphurisation, SCR – selective catalytic reduction, EO – ethylene oxide synthesis (according to [29]).

A very wide catalyst operation time span can be observed. Beginning from fluid catalytic cracking processes, in which a USY-based catalyst becomes deactivated within a few seconds, through hydrocarbon dehydrogenation processes (propane, isobutane) lasting for several minutes, to, for example, ethylene oxygenation to ethylene oxide (EO), where the catalyst performance time is equal to the time in which the catalyst must be replaced.

8. Catalyst composition and active sites

Catalyst characteristics include composition, crystal structure, crystallite size, crystallite shape and heterogeneity. The elemental composition and crystal structure of catalyst phases may be established using X-ray Photoelectron spectroscopy (XPS) and X-ray diffraction (XRD), respectively. Surface area, pore volume and pore size distribution are the fundamental characteristics of catalyst architecture. They are measured using nitrogen adsorption methods. Crystallite shape may be measured where this is likely to arise, e.g. titanium oxide or zinc oxide. Catalyst composition is often assumed but it is good practice to verify batches. Even when the elemental composition is known, the phase composition may not be obvious, for example, 'alumina' may be one of several transition alumina types or the high temperature corundum phase, all having significantly different properties. Titanium oxide may occur in the form of rutile, anatase or brookite.

The composition and nature of the catalyst is essential for its activity and selectivity in the whole chemical process [30]. A catalyst is typically composed of different materials, which are complementary to each other (see Figure 10): active phase, promoter and support/carrier.

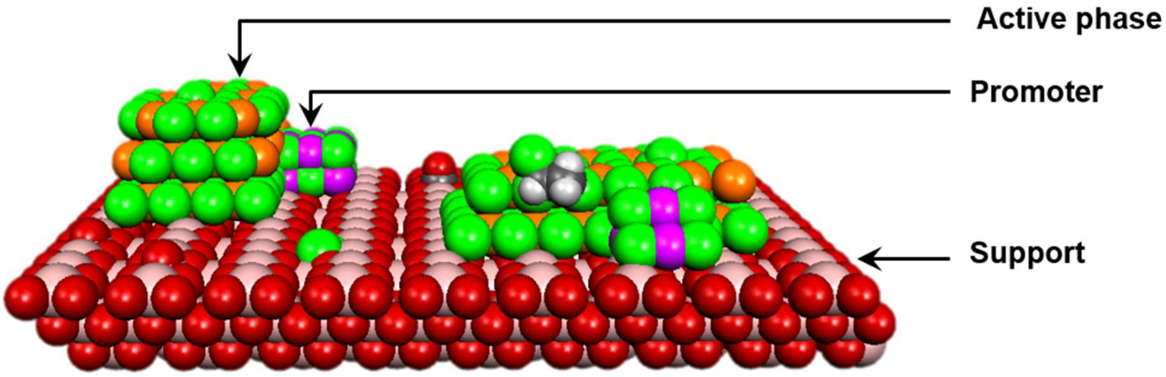


Figure 10. Catalyst composition.

Active phase: the phase where reaction occurs. For the most part the active phase is composed of metal, oxide or sulfide. Information concerning particle sizes and shapes of the active phase and its size distributions may be extracted from micrographs and structural information may also be obtained using electron-diffraction and lattice imaging techniques. Some examples of the active phases of catalysts are listed in Table 3.

Promoter: is added to a catalyst to improve its performance in a chemical reaction [32]. By itself, the promoter has little or no catalytic effect. Some promoters interact with the active phase of catalysts and alter their chemical effect on the catalysed substance. Different types of promoters are possible: textual promoter (e.g. Al - Fe for NH_3 production), electronic or crystal structure modifier, poison resistant promoters, reducer of the volatility of the catalyst active phase and melting point (e.g. KCl for $CuCl_2$ catalyst used for Deacon process). Often the addition of such stabilizers and activators reduces the active phase loss and/or improves the activity and selectivity of the process (e.g. $LaCl_3$ and $CeCl_3$ for $CuCl_2$ catalysts used for the Deacon process).

Table 3. Active phases of a mixed oxide catalyst [31]

Catalyst	Active phases	Industrial process
Nickel-alumina	Ni, $NiAl_2O_4$	methanation of biomass
Chromia – alumina	$Cr_xAl_{2-x}O_3$	dehydrogenation of light alkanes
Copper chromite	$CuCr_2O_4$, CuO	oxidations, hydrogenation, low-temperature CO conversion
Copper/zinc chromite	$Cu_xZn_{1-x}Cr_2O_4$, CuO	methanol synthesis (low pressure)
Iron molybdate	$Fe(MoO_4)_3$, MoO_3	methanol to formaldehyde
Zinc chromite	$ZnCr_2O_4$, ZnO	methanol synthesis (high pressure)
Zinc ferrite	$ZnFe_2O_4$	oxidative dehydrogenation

Table 4. Properties of typical catalyst supports [33]

Support	Crystal phases	Properties and applications
Al_2O_3	α and γ	inexpensive, thermally stable, SA 1 ~ 700, acidic, three-way catalyst, steam reforming, methanation and many other catalysts
TiO_2	anatase, rutile	SA 10 ~ 50, limited thermal stability; selective catalytic reduction catalyst
SiO_2	amorphous	inexpensive, SA 100 ~ 800, acidic, thermally stable; hydrogenation and other catalysts
Carbon	amorphous	SA up to 1000, unstable in an oxidative environment, hydrogenation catalyst
Zeolites	various	mixture of alumina and silica, often exchanged metal ion present, shape selective, acidic, highly defined pore system; shape selective; bifunctional

SA - surface area in m^2/g

Support / carrier: the support is typically used to increase the surface area and/or mechanical strength of the catalyst. The typical supports are listed in Table 4. The principle support material is inert during the catalytic reaction. However, in reality, in many catalytic reactions the support or interface between the support and the active phase plays an important part in the catalytic reaction and may influence the mechanism of reaction. The nature of the support influences the stability and activity of the catalyst.

Active Phase – Support Interactions: In supported catalysts the active phase undergoes active phase-support interactions [34-36]. The interactions depend on the surface free energy of the support and active phase as well as the interfacial free energy between the support and active phase. Transition and noble metals typically have high surface free energies [35]. For example, metal-support interactions (MSI) are the measure of metal particle-support interactions. MSI are defined as weak, medium or strong. Weak metal-support interactions are typically observed for non-reducible metal oxides (silica, alumina, magnesia, carbon). Medium interactions are observed in the case of zeolite support. Strong interactions are typically present in the case of reducible oxide supports (titania, zirconia, ceria). However, MSI also depends closely on the metal. For example, the MSI of supported Pt decreases in the order; $Al_2O_3 > SiO_2 > C$, while for Ag the order is; $SiO_2 > Al_2O_3 > C$ [37].

As a consequence of active phase-support interactions, small particles or crystallites tend to agglomerate to reduce their surface area. It was found that the electronic properties of small metal particles depend not only on their size but also on their shape. Thus, the surface structure of the particles is closely related to their chemisorption properties. In an atomic-level scheme, a free, single metal atom has its electrons distributed in known, discrete orbitals. When more equivalent atoms are agglomerated forming a small cluster aggregate, the atomic levels split into molecular levels depending on the inter-atomic interactions. The split levels of one atomic orbital start to overlap energetically with those from another atomic orbital. As long as the aggregate has a molecular character ("metallic molecule"), an energy gap is left between the occupied and unoccupied levels, and the electron motion is still confined and quantized. This situation is typically valid for aggregates up to several hundreds of atoms. For larger aggregates metallic bands are formed and there is no longer a gap between the occupied and unoccupied levels as in an infinitive periodic metallic solid (Figure 11) [38].

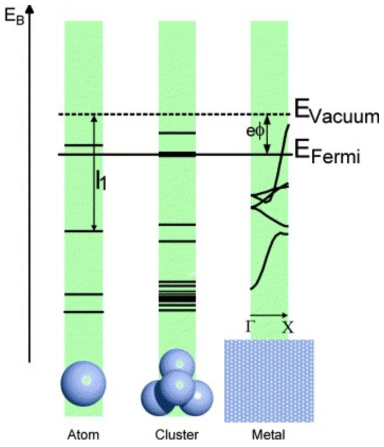


Figure 11. Diagram illustrating the transition from an atom to a metal (E_B, binding energy; I_1, first ionization energy; e: electron charge; : work function; Γ, X: symmetry points in the Brillouin zone) [38].

When single atoms or very small metal particles with up to about 100 atoms (with sizes of about a few Å) are deposited onto a surface of support, they are not only influenced electronically by the atom/molecule-metal transition described above, but their geometrical and/or their electronic structures may be additionally influenced by the support. The origin of this may be a possible lattice mismatch between the metal and the support leading to a distortion of the clusters, or an electronic interaction between both. However, when larger clusters consisting of several atomic layers are considered, the clusters may relax leading to aggregates with electronic and geometrical structures relatively similar to the pure solid and thus (almost) independent of the support.

In this sense, a realistic model system mimicking a commercial catalyst must consider several surface scenarios, especially the presence of both small clusters and larger agglomerates. Experimentally, both of these scenarios may be obtained e.g. by a careful control of the deposition rate and the deposition conditions leading to only small clusters or only large agglomerates. For theoretical modelling, small particles (with sizes in the range of about 0.1 nm to 1 nm) require studies including cluster-support interactions, while in the case of larger agglomerates just a (pure) metal model provides a valid description.

So far, the knowledge concerning the molecular structure of complex catalytic systems and the role of their components (nanoparticle shape and size, support, role of the interface between support and nanoparticles in the activation of catalytic reactions) is still limited. Understanding the effect of the support on the properties of metal nanoparticles is still a challenging subject.

It has been recognized that the presence of a support plays an important role in the control of particle morphology. The intrinsic heterogeneity of the supported model catalysts have to be taken into account to understand the catalytic reactions in detail. Three different theoretical growth modes during metal deposition have been suggested (Figure 12) [39,40]: “Volmer-Weber” mode, where the deposited metal forms clusters immediately on the support; “Frank van der Merwe” mode describes a layer-by-layer growth; and “Stranski-Krastanov” mode, which includes transition from an initial layer-by-layer to a consecutive three dimensional cluster growth at a critical layer thickness.

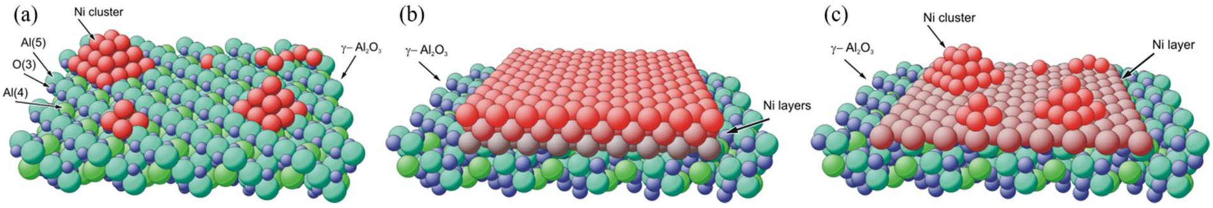


Figure 12. Models of Ni deposition at γ-Al_2O_3 (100) surface: (a) Volmer-Weber model, (b) Frank-Van der Merve model, (c) Stranski-Krastanov model.

Figure 13 shows the scheme of necessary steps of molecule adsorption to be considered in the combined nanoparticle/support system: A) adsorption at metallic nanoparticles, B) adsorption at modified nanoparticles (e.g. metal oxides), C) adsorption at support, D) adsorption at interface between nanoparticles and support.

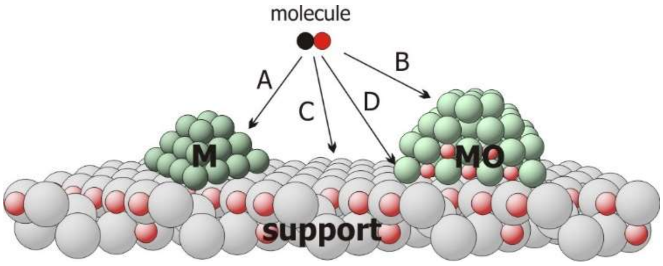


Figure 13. Scheme of different options of molecule adsorption in the case of a metal nanoparticle/support system.

The influence of the interface between the nanoparticle and the support on the reaction mechanism may be presented using an example of the oxidation of methane over a palladium catalyst supported on γ-Al_2O_3. The Pd/PdO catalyst is one of the most important catalytic materials currently used in industry. [41,42]. Palladium undergoes Pd–PdO transformations during catalytic reactions. The choice of a palladium catalyst provides greater performance for catalytic combustion in boilers and gas turbines, and a higher activity towards CO and CH_4

oxidation [43]. In the catalytic redox reaction of palladium/support systems, PdO is an additional source of oxygen. The transformation between the metallic and oxidized phase of palladium leads to strong transformations not only at the surface and in the PdO bulk [44], but also at the interface between the palladium nanoparticles and the support. Pd/PdO nanoparticles were stable on a γ-alumina support. It has been shown that the support greatly facilitates the initial steps of the oxidation of Pd nanoparticles by attracting one oxygen atom and creating a bridging interface between the support and the nanoparticle.

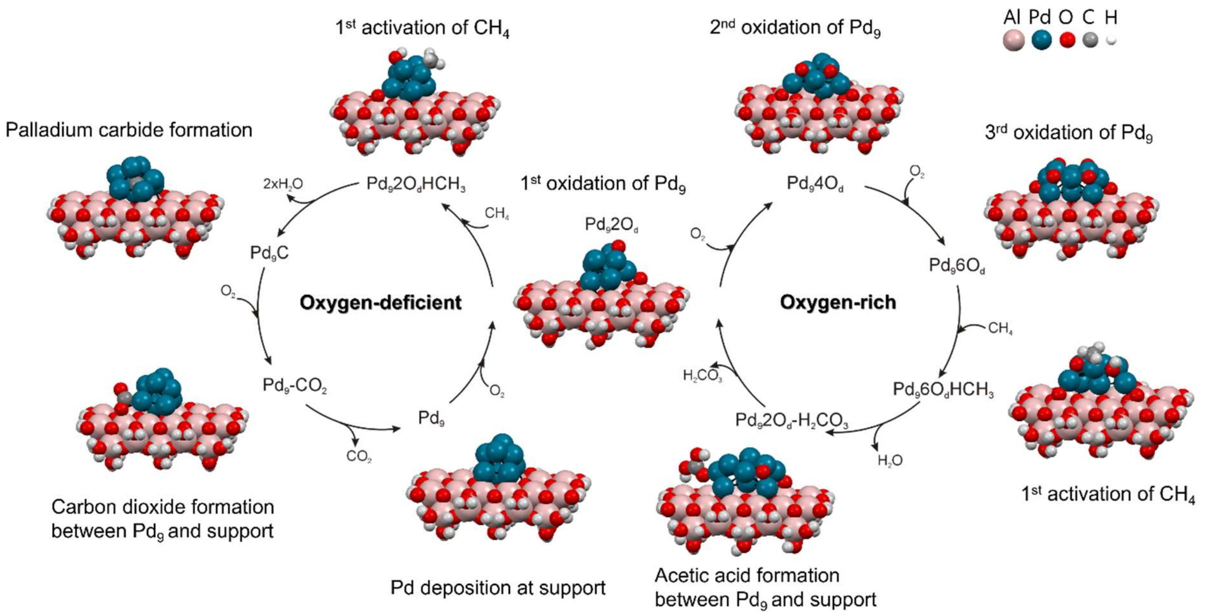


Figure 14. Oxidation of methane over Pd/γ-Al_2O_3 [45]. Two different oxidation cycles: oxygen-deficient (left) and oxygen-rich (right).

In the case of the low oxidation of Pd nanoparticles, an activation of methane is observed, whereby hydrogen is adsorbed at one oxygen atom (Figure 14, left cycle). Two molecules of water were formed. Due to the lack of oxygen, Pd_3C is formed and after the additional adsorption of oxygen, CO_2 is produced. During further oxidation of palladium nanoparticles carbon was transferred to the surface of the nanoparticles and the formation of carbon dioxide in the interface between the nanoparticle and support was observed. In the final step, CO_2 was desorbed from the interface between the support and the nanoparticle. When the Pd-nanoparticle is more strongly exposed to oxidative conditions, adsorption of methane is also possible (Figure 14, right cycle). The initial step in the activation of methane was carried out in a similar way, hydrogen is adsorbed on the oxygen and CH_3 at the palladium center. In the next steps of the reaction, carbonic acid was formed at the interface between the Pd nanoparticles and support. Again, the interface between the nanoparticle and the support has an essential role in the formation of carbonic acid.

Another important issue in catalyst science are structures at the catalyst surface that are active during chemical processes. The active sites of heterogeneous catalysts, which were introduced by Taylor, are not uniform [46]. Many types of sites are exposed on the surface of a material. Active sites include metal cations, anions, Lewis and Brønsted acids, acid – base pairs, organometallic compounds, vacancies and immobilized enzymes. Each type of site may serve a unique function during catalysis. Selected active sites at the flat metal surface are presented in Figure 15.

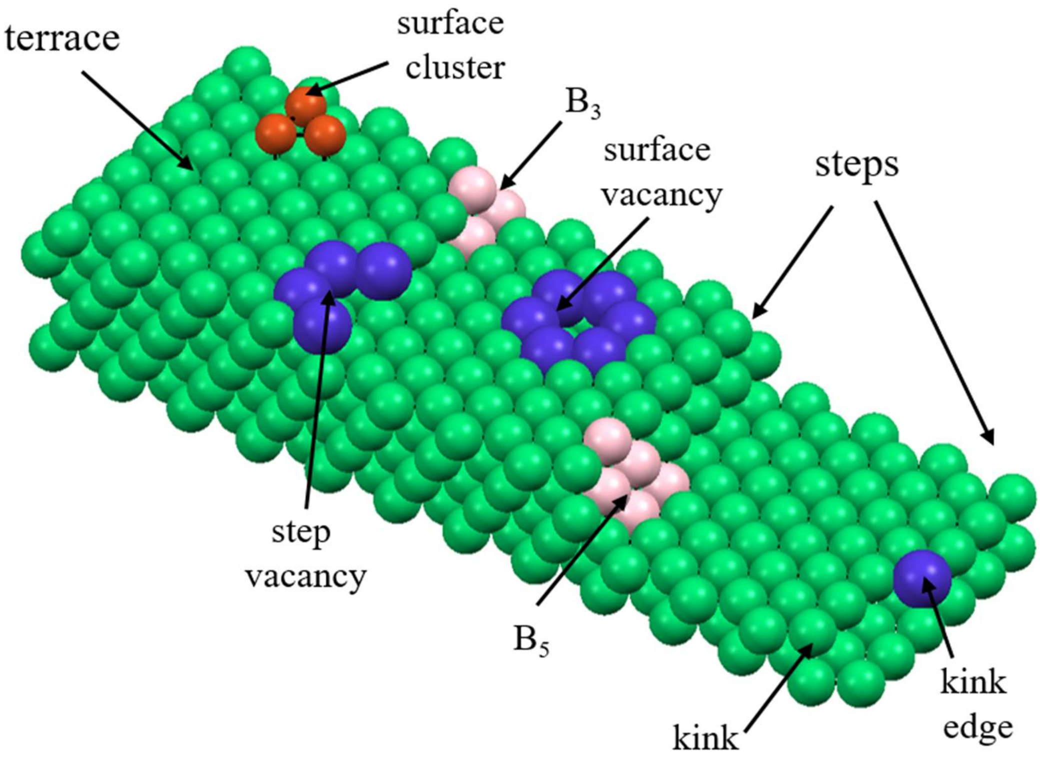


Figure 15. Selected active sites at the flat catalyst surface.

The electronic structure of the flat surface, steps, kinks or vacancies is different and presents the possibility of breaking different bonds [37]. Active sites may include more than one species (or atom) to form surface clusters.

The H_2 molecule dissociates on the metal surface at step and kink sites or at a single metal atom, while it does not dissociate on a smooth terrace. C–C bond breaking was found to occur at kink sites on noble metals. The N≡N bond requires high seven-coordinated sites, which appear at Fe surfaces. For ammonia synthesis and decomposition [47] as well as for CO chemisorption [48], it was reported that these reactions are structure-sensitive and the special importance of steps as catalytically active sites was recognized.

In the case of ammonia synthesis, the observed reactivity was correlated with a special arrangement of a step site, namely with the so-called B_5 sites. These were originally postulated by Van Hardeveld and Van Montfoort [49] analysing marble models of fcc crystals with cubo-octahedral morphology while investigating the adsorption and dissociation of nitrogen on Ni, Pd and Pd crystallites. The B_5 sites described consist of five metal atoms in a certain three-dimensional arrangement exposing a three-fold hollow site and a bridge site on a step edge close together. An example of the existence of B_5 sites as well as the significant effect of the support on the topology and the reactivity of active sites at the metal nanoparticle is a carbon-supported ruthenium catalyst. Carbon-supported Ru catalysts exhibit very good catalytic properties and are applied in the Haber–Bosch process [50], Fischer–Tropsch synthesis [51], hydrogenation reactions [52], the methanation of CO/CO_2 [53], as well as to the conversion of biomass to methane in supercritical water. It was recognized that the above-mentioned reactions are structure-sensitive, and the special role of crystal edges has been referred to in the literature [54].

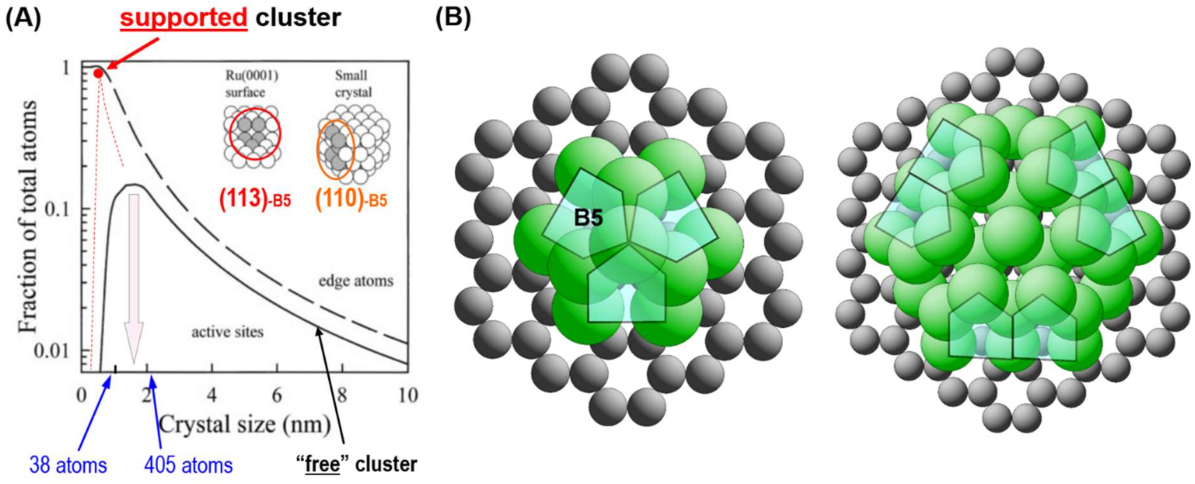


Figure 16. B5 sites at Ru/carbon catalyst: (A) Fraction of edge atoms and active sites on small Ru crystals relative to the total number of atoms as a function of crystal size, as obtained by Jacobsen et al. [47]. (B) Stable ruthenium cluster at carbon support: graphene and graphite type. Pentagons show the positions of active B5 sites.

The observed reactivity is correlated with active B_5 sites which exist at Ru clusters. The optimum Ru particle sizes, which exhibit the maximum number of B_5 sites, have been calculated (Figure 16 A). It has been found that, for a given crystal morphology, they should be in the range of between 1 and 3 nm in diameter, as these ruthenium particles are considered to possess an irregular crystalline geometry allowing for the formation of B_5 sites in the intersection between the crystallographic planes.

It was found that the type of support has an influence on the shape and the electronic properties of the cluster and the active B_5 sites. Additionally, the numbers of active sites depend on the size of the ruthenium nanoparticle (Figure 16 B). Among a large group of nanoparticles with various structures and sizes that were examined, only those compatible with the structure of the carbon support stabilized on the surface.

9. Types of heterogeneous catalysts

Commonly, mediated and non-mediated heterogeneous catalysts may be classified according to their empirical formula as metals, their oxidants, salts and sulphides as well as solid acids. In Table 5 there is a specification of industrially important group of catalysts and reaction types, in which they are currently used.

Table 5. The classification of heterogeneous catalysts according to their chemical composition and examples of industrial processes in which they are used.

Catalyst group	Chemical compound/elements	Sample processes
Metallic	Ni	Fat hardening, steam conversion of methane
	Pt	Alkane dehydrogenation, aroma hydrogenation
	Pd	Alcohol hydrogenation
	Ag	Oxidising dehydrogenation/methanol dehydrogenation, ethylene oxidisation to ethylene oxide
Oxide	Cr	Alkane dehydration
	Fe	Ethylbenzene dehydrogenation, water gas reaction (HT-WGS)
	Mo	Oxidising ammonolysis, propylene oxidisation to acrolein and acrylic acid
	V	Sulphur dioxide oxidisation, ortho-xylene and naphthalene oxidisation to phthalic anhydride, benzene and butane/butene oxidising to maleic anhydride
Sulphide	Ni, Co, Mo, W	The process hydrorefining, benzene hydrogenation (of carbochemical origin) to cyclohexane
Solid acids	Aluminosilicates	Catalytic cracking, isomerisation, transalkylation and disproportionation of

	H_3PO_4/SiO_2	alkylaromas, alkylation of benzene with popylene. Ethylene hydration
Other	Pt-Re(supplements)-γAl_2O_3 H-ZSM-5 - Pt Ni-Mo-γAl_2O_3 $TiCl_4$ - $Al(C_2H5)_3$	Catalytic reforming Hydroisomerisation/xylene isomerisation Hydrocracking Polymerisation

Metal based catalysts are widely used in the processes of hydrogenation and dehydrogenation and in various types of hydrocarbon conversion processes, e.g. methanisation, steam conversion of methane into synthesis gas (syngas). Oxide catalysts have equally extensive industrial usage. For example, oxides of variable valency, e.g. copper, molybdenum, chromium, vanadium oxides, are used as catalysts in the processes of incomplete oxidation. In turn, irreducible oxides or reduced oxides with variable valency are used in reduction processes involving, e.g. alcohols, esters, acids, aldehydes etc. A group of sulphide catalysts finds usage in catalytic refining processes, e.g. hydrorefining (hydrodesulphurisation, hydrodenitrogenisation or hydrodemetalisation). Sulphide forms of catalysts are also used wherever the raw material is "sulphated". The importance of the last of the listed catalyst groups, i.e. solid acids, is also growing. Especially, amorphous and crystalline aluminosilicates are being widely used in the processes of isomerisation, alkylation and catalytic cracking.

In this work, the classification was additionally extended by a group of "other" catalysts, e.g. multifunctional catalysts that cannot be included in any of the previously mentioned groups. In the newer refinery and petrochemical solutions, multifunctional catalysts are often used as they possess several components in oxide and metallic forms that are necessary to obtain the desired catalytic effect. For example, in the processes of catalytic reforming, double action catalysts containing platinum on γ-Al_2O_3 have been used since early 1970s. The presence of metal provides the function of dehydrogenation/hydrogenation, while γ-Al_2O_3 is responsible for reactions requiring acid centres e.g. isomerisation and regrouping. In the newer reforming process solutions, catalytic systems of even higher complexity are being used, e.g. polymetallic, containing platinum, rhenium and other supplements such as: tin, gallium, lead, iridium applied on acidic media.

10. Preparation of heterogeneous catalysts

Figure 17 presents a diagram illustrating the most important methods used for preparation of heterogeneous catalysts divided into mediated and non-mediated (self-mediated) system preparation methods.

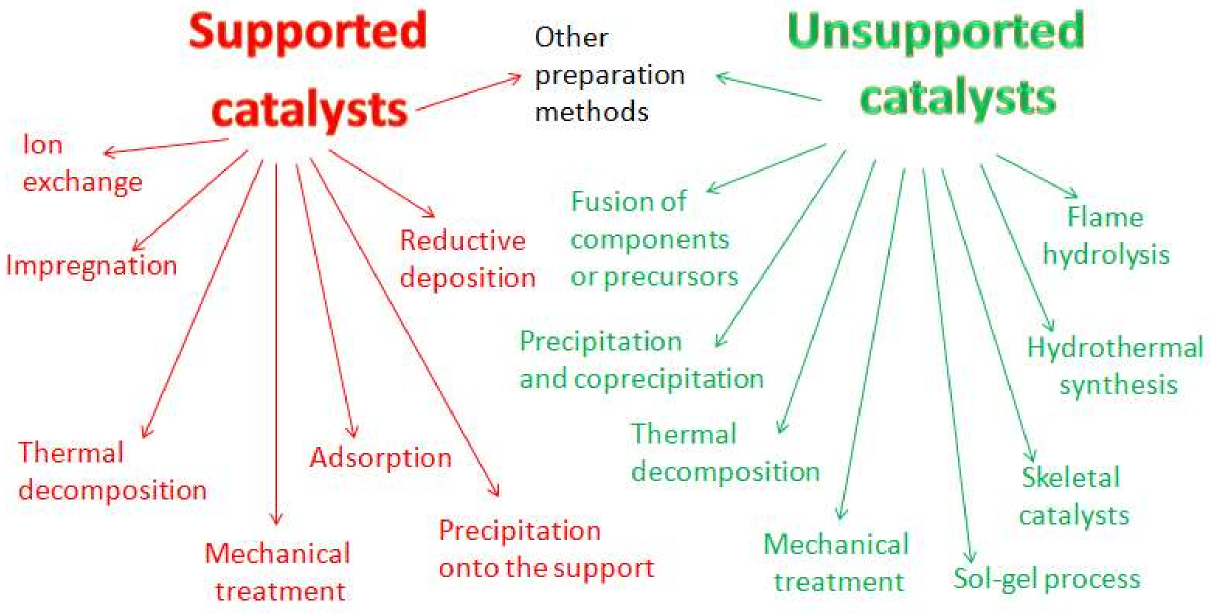


Fig. 17. Selected methods of heterogeneous catalyst preparation.

Not all methods are widely used. The ones that are more important from the practical point of view due to their universality and the number of applications is described below.

10.1. Preparation of mediated catalysts

Impregnation method It is one of the most universal methods of mediated catalysts preparation. This method is used to introduce:

- redox oxides, e.g.: Cr, V, Fe, Cu, Co, Mn, etc.
- acid-base oxides, e.g. Al, Ga, Mg, Na, etc.
- metals, e.g. Pt, Pd, Ag, etc.
- mixed compound components (metals, oxides, sulphides, phosphates, etc.).

Impregnation is carried out by applying a precursor from solvent solution (usually hydrous) on oxygen or carbon medium. The application stage may be performed using wet or dry method. In the wet method, the volume of the precursor solution used is higher than the volume of pores in the impregnated material. The solvent excess is removed by evaporation. In turn, in the dry method, the precursor is introduced in such solvent volume that only the medium pores are filled. The material after dry impregnation is moist but nor wet (vitreous). The solvent is removed in similar way as in the case of wet method. Usually, the dry method is more efficient in precursor introduction into the pores than the wet method. The media impregnated using either method are then transformed into oxide, sulphate or metallic forms by means of appropriate thermal and chemical processing. If it is necessary to synthesize the oxide forms it is usually achieved through high temperature processing in air or oxygen flow. Metallic forms of a catalyst are obtained by completing the preparation process with oxide form reduction, e.g. using hydrogen in high temperature Very often, the proper form of the catalyst is generated *in-situ* in the target reactor. A good example are the hydrorefining process catalysts, which are transformed from oxide forms into sulphate forms *in-situ* in the reactor through chemical processing by means of sulphur compounds introduced before the process.

Equilibrium adsorption method This method allows for controlling the degree of dyspepsia of the active ingredient on the medium surface to a much greater extent than the impregnation method.

It requires the knowledge of:

- isoelectric point of the surface (IEPS),
- forms of the applied ions in the specified conditions.

It consists in bringing the medium and the precursor dissolved in an aqueous solution into contact until the moment of saturation (point of equilibrium) under certain conditions of pH, temperature and initial concentration of the precursor in the solution. In this method, the solution volume is much higher than the volume of medium pores and the precursor concentration is low (usually $C_{mol} < 0.1$ mol/dm^3).

IEPS

In the aqueous solution of the precursor, the hydroxyl groups on the oxide medium surface retain equilibrium described in these equations:

$$N-OH_2^+ \rightleftarrows N-OH+H^+$$

$$N-OH \rightleftarrows N-O^- + H^+$$

Appropriate equilibrium constants for the above reactions are:

$$K_a=\frac{[N-OH]\cdot[H^+]}{[N-OH_2^+]} \qquad K_b=\frac{[N-O^-]\cdot[H^+]}{[N-OH]}$$

On the basis of the equilibrium constants and assuming that the it is possible to define the isoelectric point of any oxide medium surface (IEPS)

$$PI=\frac{pKa+pKb}{2}$$

The point is determined by pH value, in which the total charge of the medium surface is zero. Knowing this point is necessary for the selection of optimum pH in the equilibrium adsorption method. Below this IEP value the medium surface has positive charge and above it the charge is negative [55].

In Table 6, the IEPS values have been specified along with the associated capability of precursor cations and/or anions adsorption for a few important oxide mediums.

Table 6. Summary of isoelectric points for selected oxide media [56].

Support	IEPS	Adsorption
WO_3	0.5	Cations
SiO_2	1.0–2.0	
TiO_2	6.0	Cations or anions
ZrO_2 hydrous	6.7	
CeO_2 hydrous	6.8	
α-, γ-Al_2O_3	7.0–9.0	
Y_2O_3	8.9	Anions
Fe_2O_3	8.4–9.0	
ZnO	8.7–9.7	
La_2O_3	10.4	
MgO	12.1–12.7	

A large difference may be noticed in the values in the case of popular oxide mediums. For example, IEPS value for silica means that, in solutions with pH higher than IEPS, cation precursor adsorption is preferred, while in the case of MgO medium in pH range of 12.1-12.7 anion precursors will be adsorbed. The above indicates that it is important to select an appropriate precursor, which, depending on the solution pH and concentration, may occur in the form of compounds with variable charge and degree of polymerisation. After obtaining the equilibrium in certain conditions, the medium containing the adsorbed precursor is drained from the solution and then subjected to thermal and chemical processing analogical to the impregnated materials in order to obtain the final catalyst form.

Precipitation method in the presence of medium This method is usually used in production of highly active Ni/Al_2O_3 or Ni/SiO_2 catalysts. In this method, the precursor salt solution (usually metal) is brought into contact with the solid medium in the presence of a base. The hydrocarbons/carbonates generated *in-situ* are deposited on the medium surface. In the final stage, the drained catalyst with the applied precursor undergoes appropriate thermal processing in controlled atmosphere in order to obtain an active catalyst form.

The basic problem of this preparation method is uniform distribution of the active ingredient in the total medium volume (mainly in the pores of the medium). An important parameter is the precursor nucleation rate. Too slow hydrolysis and nucleation leads to uneven growth of precursor molecules on the medium surface. In turn, too fast growth of precursor molecules in the solution makes them unable to enter the pores of the medium, which results in non-homogeneous medium and precursor mixing. In order to avoid the problems described above, effective mixing of precursor solution with the medium is used as well as gradual addition of a base in the course of hydrolysis. In the latter case, the best effects are achieved using urea, which is heated to the temperature exceeding 60°C and undergoes slow degradation in the entire volume with equal speed according to reaction (1).

$(NH_2)_2CO + 3H_2O \rightarrow 2NH_4^+ + 2HO^- + CO_2$ (1)

Another advantage of urea is the fact that in the course of precipitation taking place in its presence, the solution pH is not altered because the rate of precipitation (HO^- ion consumption) is higher than the rate of their generation in reaction (1).

10.2. Preparation of non-mediated (self-mediated) catalysts

Mechanical mixing It is one of the most popular methods of industrial catalyst preparation owing to its simplicity and low waste production (Table 7). It consists in mechanical grinding or pressing of catalytically active ingredients or their precursors with promoters, structure stabilisers or/and blowing agents. In the final stage of the preparation, the obtained mixture is usually subjected to thermal processing. The basic advantage of this method is its simplicity and no need for using a solvent. The disadvantages are, inter alia, the lack of the possibility to precisely regulate the degree of the active ingredient dispersion, the lack of “close contact” between the precursor and the medium (at the preparation stage), which, in some cases, translates into worse catalytic effects compared to the analogues obtained using other methods.

Table 7. Non-mediated industrial catalysts obtained using the method of mechanical mixing (MM) and fusion (sinking together) (S) [55, 57].

Catalyst	**Preparation method**	**Usage**
Fe_2O_3(K,Cr,Ce,Mo)*	MM	EtB dehydrogenation
Fe_2O_3(K)	MM	F-T synthesis
$ZnO-Cr_2O_3$	MM	Carbonyl compound hydrogenation processes
Fe_3O_4(K,Al,Ca, Mg)	S	Ammonium synthesis
V_2O_5- $K_2S_2O_7$	S	Oxidising of SO_2 to SO_3 (H_2SO_4 synthesis)
Pt/Rh mesh	S	Ammonium oxidising to nitric oxide (HNO_3 synthesis)

[*] The elements in brackets are promoters.

Precipitation/co-precipitation method It is currently the most widely used method of industrial heterogeneous catalyst preparation (Table 8). In this method, the solutions containing the soluble precursor salts are mixed together in the presence of a base in order to obtain their co-precipitation in the form of hydroxide or/and carbonate mixture. The thermal processing method is identical to the method utilising a medium. Salts are usually preferred as precursors (nitrates, sulphates, carbonates or chlorides). Acetates and oxalates are used less frequently. The most often used bases are hydroxides, sodium, potassium or ammonium carbonates or bicarbonates. Co-precipitation of several metal cations results in a large degree of their dispersion and usually homogeneous mixture, which a significant advantage of this form of preparation.

Table 8. Commonly used catalysts and industrial media obtained using a method of co-precipitation/precipitation [57].

Catalyst or medium	**Material source**	**Catalytic usage**
Al_2O_3	Sodium aluminate, HNO_3	Medium, dehydration processes, Claus process
SiO_2	Sodium silicate (water glass), H_2SO_4	Medium
Fe_2O_3	$Fe(NO_3)_3$, NH_3 aq	EtB dehydrogenation
TiO_2	Iron titanate, titanyl sulphate, NaOH	Medium, Claus process, NOx reduction
CuO-ZnO-Al_2O_3	Cu, Zn and Al nitrate, Na_2CO_3	Methanol synthesis, WGS
Iron molybdate	$Fe(NO_3)_3$, $(NH_4)_2MoO_4$, NH_4OH	Methanol oxidising to formaldehyde
Vanadyl phosphate	Vanadyl sulphate, Na_2HPO_4	Butane oxidising to maleic anhydride
NiO-Al_2O_3	Ni and Al nitrate, Na_2CO_3	Aromatic hydrocarbon dehydrogenation
NiO-SiO_2	Nickel nitrate, sodium silicate, Na_2CO_3	

Sol-gel methods This method utilises a reaction between water and a substance dissolved in it, which leads to the generation of chemical compounds. The process is based on slow dehydration of the formerly prepared sol - a colloidal solution of molecules of a given material hydroxide which leads to the generation of a gelatinous substance called gel. The processes of hydrolysis and condensation take place simultaneously and their course depends on temperature, solution pH, volume of the solvent used and the type of catalyst. The sol-gel method is widely used not only in the preparation of catalysts but also media. Figure 18 presents the way of synthesis of widely used silica media.

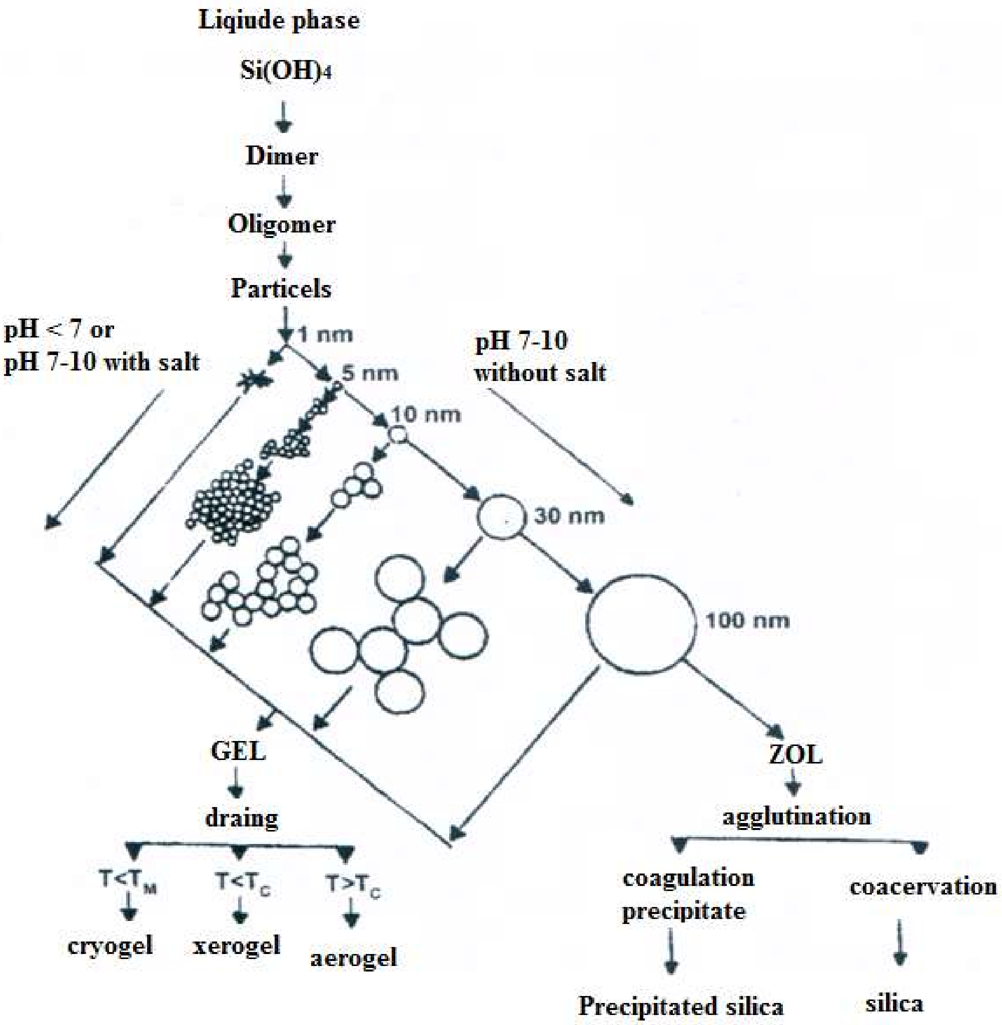


Figure 18. Silica synthesis methods, (T_M – sublimation temperature; Tc – critical temperature) [58].

Silica gel is a product of silicic acid condensation. Multiple condensation leads to the generation of three dimensional structures. In result of condensation, ever bigger molecules are generated, which show ever lower water-solubility – colloidal systems are formed (1–200 nm dispersed phase molecule size).

The generated colloidal systems known as hydrosoles may coagulate forming silicic acid gel ($xSiO_2yH_2O$), in which the SiO_2/H_2O proportion depends on the reaction parameters. Various conditions of hydrogel final processing allow for attaining silica materials of diverse desiccant properties. For example, cryogel is formed after the sublimation of a liquid substrate, aerogel is formed after the removal of the solvent in superficial conditions (above Tc) and xerogel is formed when hydrogel is dried below Tc.

10.3. Preparation and modification of zeolite catalysts

Zeolite-based catalysts find application in various refining and petrochemical processes and they are also used as selective sorbents.

Zeolite synthesis Hydrothermal method is a commonly used method in the production of a large family of crystalline aluminosilicates. In this method, the mixture of silicon and aluminium precursors with the addition of alkaline metals, water and, in some cases, organic compounds (so called structure forming templates) react generating crystalline aluminosilicates. The source of silicon is usually colloidal silica, water glass or alcoholates, and the source of aluminium are aluminium hydroxides and aluminates. Tetrapropylammonium or tetraethyloammonium bromide or hydroxides are used as structure forming template. Usually, the preparation is conducted in autoclaves in the temperature range of 80–170°C and pressure range of 0.5–1.0 MPa [25]. The time of synthesis is from 1 to 6 days. The product is filtered or centrifuged, rinsed, dried and calcined. The sodium form of zeolite is a product of hydrothermal synthesis subjected to ion exchange in order to obtain a proton form. Zeolite materials may also be subjected to other processes modifying their propertied, e.g. dealumination or isomorphic substitution.

Ion exchange Ions of lower valency such as Na^+, get exchanged with ions of higher charge, e.g. Cu^{2+}, according to equation:

$$2SNa^+ + Cu^{2+} \leftrightarrows SCu^{2+} + 2Na^+ \qquad (2)$$

where: S – means the solid phase surface.

This method is commonly used in modification of zeolites. Sodium cations are easily exchangeable for all other cations, also NH_4^+, from which H^+ is then obtained though thermal activation.

Isomorphic substitution This is used to describe network cation exchange for another cation. In zeolite materials or other aluminosilicates, silicon and/or aluminium ions may be substituted, e.g. with transitional metal ions (Ti, V, Cu) of variable valency or with other ions e.g. boron, gallium. In consequence of substitution with transitional metal ions, zeolites demonstrate redox properties and may generate free radicals [59].

Zeolite dealumination It consists in the removal of aluminium from oxyaluminium tetrahedrons from the zeolite material, which leads to the increase of molar Si/Al ratio. It causes the increase of zeolite acidity This process may be carried out without the participation of external silicon source (e.g. hydrothermal water treatment, chemical activity of acids, chelating agents or salts) as well as using an external silicon source (reaction with $SiCl_4$ steam, in $(NH_3)_2SiF_6$ solution).

11. Lab scale catalytic tests

In laboratory conditions, the measurements of catalytic properties are performed in micro scale, which means that the weight of the tested catalyst samples usually falls in the range of 0.1–1.0 g and substrate, e.g. gas, consumption in the range of 5–100 cm^3/min. The used devices (reactors, ovens, control and measurement instruments) also have small sizes proportional to the process requirements. In relation to the scale in which the laboratory tests are carried out, they are mainly aimed at:

- Screening of a group of catalytic materials – development of an active and selective catalyst formula.
- Research of reaction mechanism – especially when the research is supported by operando physico-chemical techniques.
- Research of performance stability – to a limited extent.

The devices used in catalytic studies is composed of several modules. The most important ones are:

- Reagent flow regulators, e.g. mass flow regulators for gas and infusion pumps for liquid flow regulation,
- mixer/evaporator, the purpose of which is to obtain raw material mixtures of desired content and flow intensity,
- reactive module, i.e. a reactor, in which the reaction takes place, equipped in a heating module (furnace or controlled waterbath) and a system of reactor pressure and temperature control,
- separator (e.g. gas-liquid) and dust filter,
- analytical station facilitating analysis of mixture content after or during the process.

Laboratory tests of heterogeneous catalysts in microreactors are conducted using the continuous or pulse method. Flow microreactors used for testing processes conducted in gas phase are made of steel (surface-passivated) or quartz. In the case of pressure processes in wide range of temperatures, steel reactors are usually used, while in the case of processes performed at pressures close to atmospheric pressure, quartz reactors usually perform well, and in relatively low temperatures, glass reactors offer good performance. In the case of liquid phase processes in the presence of heterogeneous catalysts, a glass reactor is usually used with a jacket through which the heating medium flows (water, silicone oil, etc.) Examples of a few commonly used solutions for continuous method reactions in gas or liquid phase are presented in Figure 19.

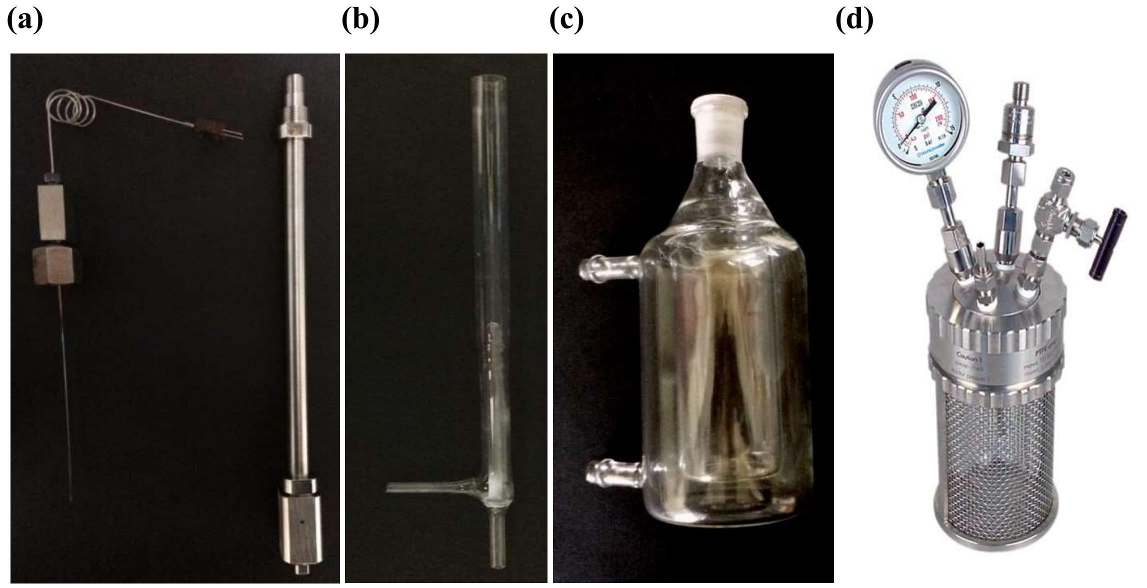


Figure 19. Steel (a) and quartz (b) pipe type flow reactor for processes performed in gas phase and glass reactors with a heating jacket for pressure-free (c) and pressure (d) processes conducted in liquid phase.

Certainly, apart from the above-mentioned reactors, a series of other solutions and structures are used in research laboratories. They differ in construction, catalyst position, process method and reagent dosage. The choice of a particular solution usually results from the aim of the performed catalytic experiments.

There is a wide variability also in the design and method of supplying heat to microreactors. In the case of steel and quartz flow reactors for gas phase processes performed in wide range of temperatures (~50–1,000°C) pipe ovens of various designs are used, while, in the case of controlled reaction, waterbath is usually applied (Figure 20).

Currently there are complex devices available on the market for the measurement of catalytic properties in processes performed in gas phase, liquid phase and mixed phase (steam-gas etc.) They are usually modular devices facilitating configuration of the number of reagents (gas and liquid), flow ranges, pressure and reaction temperature according to the user's requirements.

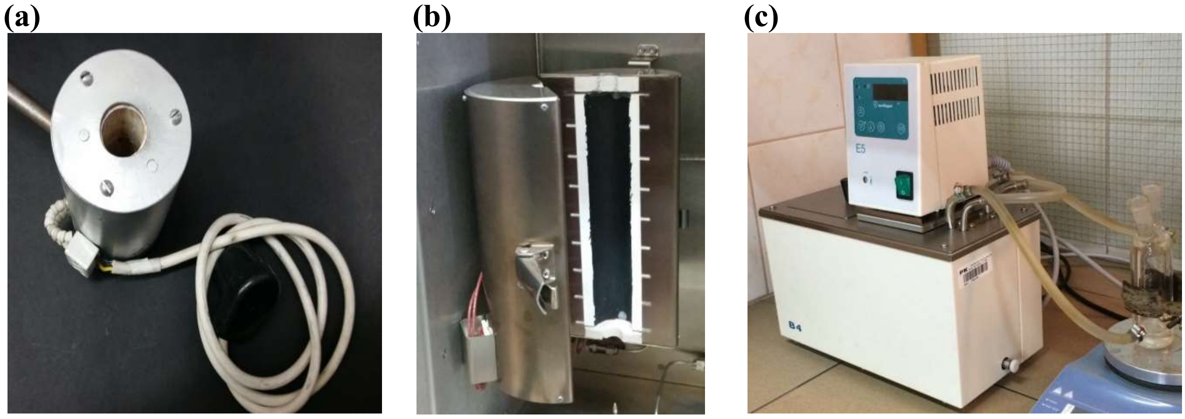


Figure 20. Simple (a) and laterally opened (b) pipe furnace for processes conducted in gas phase and waterbath (c) used for reactor heating, e.g. jacketed glass reactors for processes carried out in liquid phase.

Novel device solutions studied in recent years are catalytic and flow (microfluidic) microdevices with capabilities and potential usages that grow proportionally to the development of incremental material production technology (3D printing methods, new material development, etc.) [59–62].

The main advantages of such devices are:
– simplicity of reaction conditions control in microscale,
– possibility of very good reagent mixing,
– efficient mass and energy exchange,
– easy configuration thanks to modular design,
– possibility of scale increase by serial combination of the modules.

These devices may be adapted, e.g. to preliminary catalyst selection for processes performed in liquid phase, synthesis of biologically active compounds or reactive components in multi-stage microscale synthesis. The most currently proposed solutions involve the application of integrated printed catalytic devices, in which multi-stage synthesis is conducted in one catalytic device containing two different catalysts and a column for the final product purification (Fig.21).

Using catalytic microdevices is not limited to mere laboratory scale research. They have been successfully used in pharmacy, e.g. in production (naproxcinod, H1 or NK1 antagonists) [62].

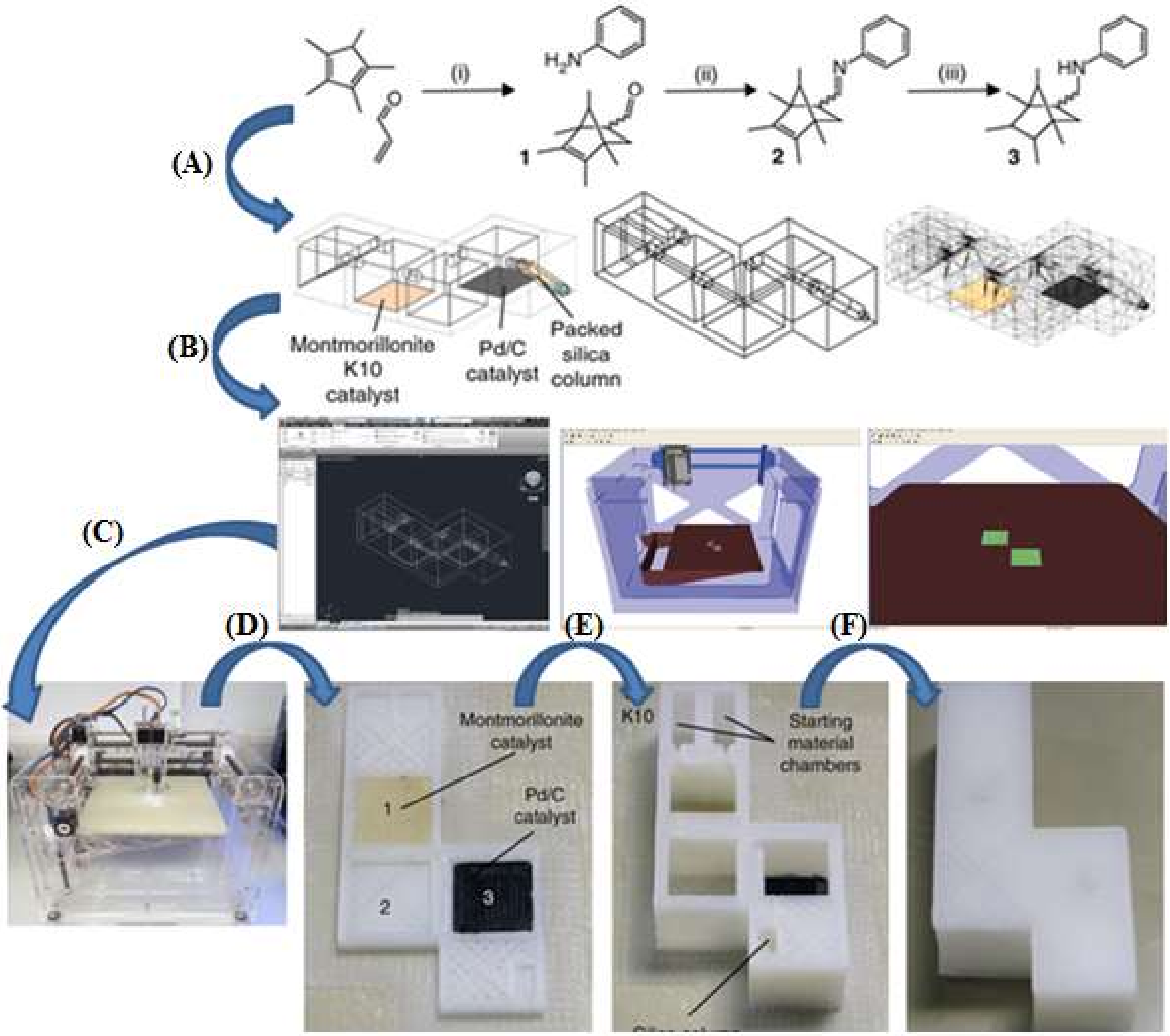


Figure 21. A device printed using FDM technique equipped in two catalytic reactors and a silica column for reaction product purification. (a) reaction design, (b) multi-functional device design, (c) CAD model preparation, conversion in printer software, (d) device printing with introduction of catalysts and silica gel in the final stage (according to [60]).

Quantitative and qualitative analysis of the composition of the post-reaction mixture is carried out using gas or liquid chromatographs, and in simpler cases (less complicated reagent mixtures) using FTIR analysers or mass detectors. The measurements may be performed during the reaction (*on-line*). For this purpose, the measuring devices must be equipped in dispensers facilitating direct dosing of the mixture leaving the reactors. They can also be performed periodically, e.g. by collecting a defined sample volume (usually liquid) in the intended intervals using a syringe. In the case of processes performed in gas phase, in order to correct the differences in volumes injected onto the analytical device (e.g. chromatograph) and reaction contraction (change in the number of moles), a standard is introduced into the raw material mixture, usually in the form of inert gas (argon or nitrogen) with a defined retention time not overlapping with the reagents'. On the basis of the obtained results of the quantitative analysis, information can be obtained regarding the catalytic properties such as: proper activity, reaction rate, performance and selectivity towards the product(s), the degree of substrate conversion or work stability.

12. Catalyst deactivation

Catalyst deactivation is one of the essential problems in the industrial implementation of catalytic processes. The catalysts should work for as long as possible. Different processes are responsible for slight or dramatic catalyst deactivation. In this sense, the deactivation could be classified depending on the type of process as [63, 64]: chemical (poisoning, vapour formation, vapour/solid–solid reactions), thermal (thermal degradation), physical (sintering), mechanical (fouling, attrition, crushing).

Poisoning is the most important deactivation type and is defined as a strong chemisorption of species on the active sites, which succeeds in blocking catalytic reaction. Two different types of poisoning may be distinguished: selective and nonselective (Figure 22).

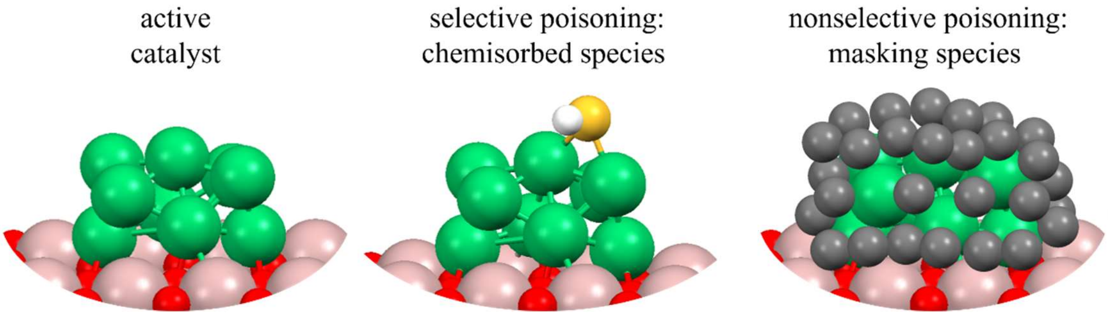


Figure 22. Examples of selective and nonselective poisoning: Ni/Al_2O_3 catalyst poisoned by sulfur (middle) and carbon (right) species.

Selective poisoning: A chemical poison agent chemisorbs directly at the active sites or support rendering the catalyst partially or fully inactive (Figure 22, middle). Mainly the chemisorption of such poisons is permanent and resistant to the catalyst regeneration process. Examples of such poisons are: i) metals such as Pb, Cd, Hg, which react with Pt catalysts and form inactive alloys, ii) sulfur present in biomass during the methanation process over a Ni/Al_2O_3 catalyst result in permanent sulfur adsorbates at both the active phase and support [65]. After the regeneration process the catalyst is deactivated after a short time. Usually, catalyst poisoning is undesirable and increases the costs of the catalytic process. However, poisoning of catalysts may be used to improve the selectivity of reactions. Poisoning may allow for selective intermediates to be isolated and final products with a desirable stereochemistry to be achieved. One example is Lindlar's catalyst, where Pd is poisoned with Pb to allow for the reduction of an alkyne to the corresponding alkene and prevent the reduction of the alkene to the corresponding alkane.

Nonselective poisoning: This type of deactivation process includes both, fouling and masking of active catalyst particles (Figure 22, right). The deposition of the fouling species over the catalyst surface, both at the active phase and the support, succeeds in masking the active sites and pores of the catalyst. One example is carbon deposition over an Ni/Al_2O_3 catalyst during the methanation process [66]. The active Ni-nanoparticles are covered by carbon. However, this process is rather based on physical interactions and reversible. Carbon deposits are removed during catalyst regeneration and the catalyst returns to its previous activity level, except in the situation where the active nanoparticles are lifted by carbon whiskers and lost during the regeneration process.

Other types of deactivation are also important and should always be taken into consideration.

Vapour formation is defined as a gas reaction with the catalyst surface, which results in the production of volatile species.

Vapour/solid–solid reactions involves the reaction of the catalyst active phase with fluid, support or promoters, which results in the deactivation of the catalyst.

Sintering is an important type of loss in catalyst activity [67], especially for high temperature catalytic processes (e.g. exhaust gas treatment, catalytic combustion, methanation or steam reforming). Two mechanisms of nanoparticle sintering are the most probable: particle migration and coalescence (the mobility of particles which are mobile due to a Brownian-like motion on the support surface) and Ostwald ripening (migration of adatoms or mobile species, based on the differences in free energy and local adatom concentrations on the support surface).

Deactivation by thermal degradation is, like sintering, an essential problem for high temperature catalytic processes mentioned above and includes the loss of the surface area of active phase or support.

Fouling is defined as the physical decomposition of fluid species inside pores or over the surface of a catalyst.

Attrition/crushing means a loss of the active phase of a catalyst by mechanical-induced processes. Such deactivation may be observed e.g. in fluid reactors.

13. Catalytic process optimization steps

Catalytic process design requires several important development steps and interactions between catalyst design and process optimization [68-70]. The time necessary to obtain an industrial catalytic process from an initial idea is around 10-15 years. The whole optimization procedure typically consists of three major stages: laboratory primary and secondary screening as well as process scale-up to the half-technical and industrial level (Figure 23, [70]). Primary screening starts with an idea for a new process, via screening for a potentially effective catalyst and its synthesis (powder, in gram-scale) up to the first reaction tests using a catalytic micro-reactor system. The secondary screening of this stage includes the detailed characterization of catalysts using e.g. modern spectroscopic and microscopic tools, understanding the reaction mechanism and kinetics as well as long term stability tests. As a final step, the most promising catalysts are scaled up –catalyst synthesis is optimized (shaped catalysts, in the kilogram/ton scale), the optimal reactor system for the industrial process is chosen and pilot and plant tests are conducted. After pilot and plant testing, the final decision for the implementation of the catalytic process is formed, including, among other factors, the costs of the catalyst and the profitability of production.

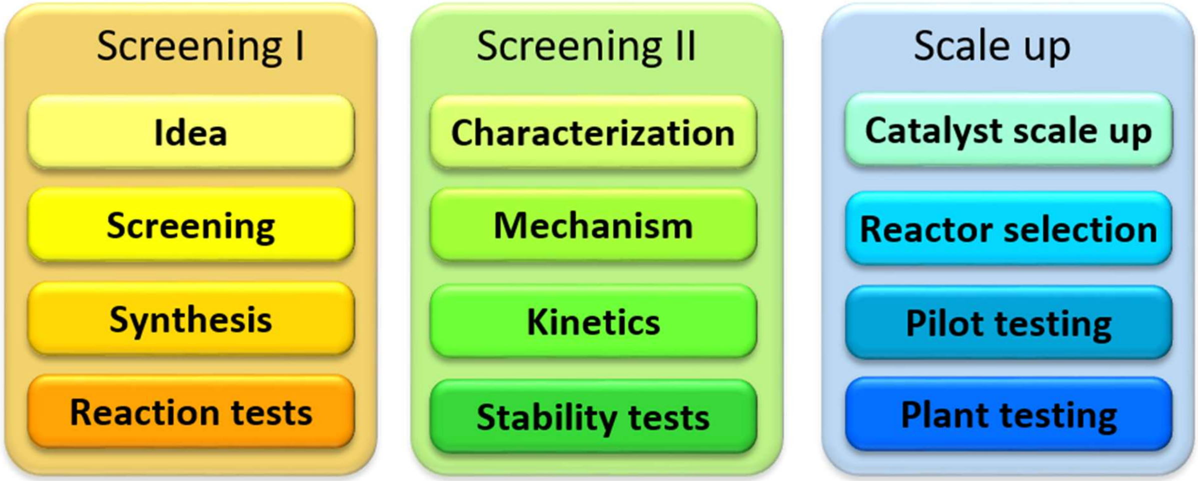


Figure 23. Typical sequence of activities in a catalytic process development.

Catalyst design is based on the establishment of synthesis-property-function relationships [71]. These relationships are mainly derived from powdered catalysts in the secondary screening stage. Operation in industrial reactors requires (i) adapting lab-preparation protocols for multi-ton manufacture and (ii) shaping of the catalyst powder into practical shapes. In addition, other considerations at the reactor level such as mass and heat-transfer phenomena and fluid-dynamics may also come into play. Consequently, a critical aspect which arises is whether the synthesis-property-function relationships obtained with powders can be directly extrapolated to real catalysts. Given the relatively low success rate of catalysts from the laboratory scale making it to the final plant stage, this is unlikely to be the case. The catalysts designed with an optimal performance for a certain process requires the consideration of a combination of chemical, physical and mechanical properties. This "triangular concept" has been suggested for catalyst design by Bartholomew [72], as illustrated in Figure 24.

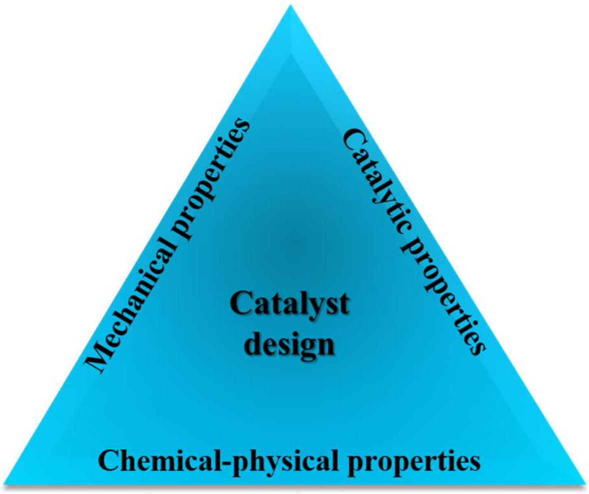


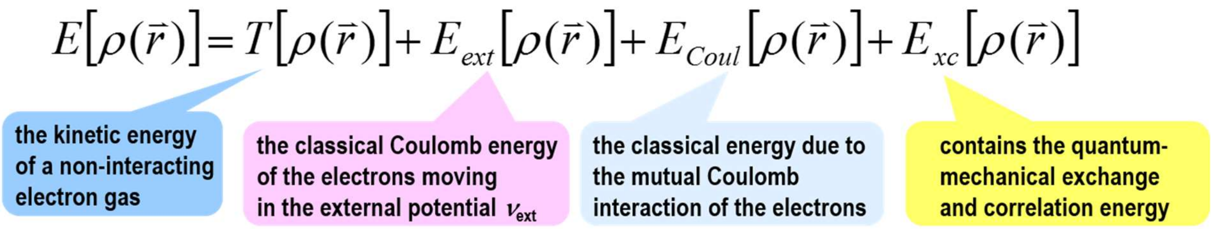
Figure 24. Concept of the triangle of catalyst design, adapted from [73].

The triangular includes the most important functionalization properties for catalysts: i) mechanical (attrition, strength), ii) chemical-physical (porosity, surface area, acidity, composition, density), iii) catalytic (stability, activity, selectivity). In addition, the chemical-physical properties of the active phase, specifically the formulation shape, size and crystallinity of the nanoparticles are significant factors to be optimized during catalyst design.

14. Theoretical modeling of catalytic reaction

One of the long-term targets of research in heterogeneous catalysis is to gain an understanding of the investigated processes on a molecular level in order to discover general catalysis principles and/or to develop better catalysts based on a rational design. For a given reaction, both commercial catalysts and home-made model catalysts with identical or at least a similar composition need to be studied, following the surface processes and modifications applying a complementary combination of surface science analytical techniques under *in situ* or *quasi in situ* conditions [74]. However, a comprehensive view of the processes occurring on the catalyst surface may only be obtained by combining these experimental results with the modelling of the reaction mechanism using, for example, the *ab initio* density functional theory (DFT) method [75,76].

DFT method. The principles of the method were created by Kohn, Hohenberg, Sham and Mermin in the 1960s [77-79]. In the DFT method, the wave function of the N-electron system (defined in the 4N-dimensions: spatial coordinates and electrons spin) is replaced by the electron density, $\rho(r)$, defined in 3-dimensional physical space. The method, is based on two main Hohenberg-Kohn theorems: First, the ground state properties of the multi-electron material may be defined as a function of the electron density. Second, the theorem defines an energy function for the multi-electron system. Figure 25 shows the definition of multi-electron system total energy as a function of $\rho(r)$. The correct ground state electron density minimizes this energy function.



$$E[\rho(\vec{r})] = T[\rho(\vec{r})] + E_{ext}[\rho(\vec{r})] + E_{Coul}[\rho(\vec{r})] + E_{xc}[\rho(\vec{r})]$$

Figure 25. Energy definition in DFT method.

The exact form of electron exchange and correlation E_{xc} function is unknown. In the simplest variant, LDA (*Local Density Approximation*) and LSDA (*Local Spin Density Approximation*), the E_{xc} is a function of local electron density [80,81]. In a more sophisticated definition, GGA (Generalized Gradient Approximation), E_{xc} is extended to include the gradient of electron density [82,83]. Higher level hybrid functions (e.g. B3LYP) include the mixing of correlative-exchange energy with exchange Hartree-Fock energy and gradient corrections [84]. The advantage of the DFT method is the simplicity of the calculation algorithm resulting from the approximate integration of both the exchange and the correlative effects [85]. This allows for the calculation of very large systems, such as catalysts and biological systems, which is not possible using the standard Hartree-Fock method. It is worth emphasizing that DFT produces results comparable to post-HF calculations, Configuration Interaction (CI) or Couple Cluster (CC).

Geometrical model. In DFT studies, two models are used for the geometrical representation of the surface cluster and periodic model (see Table 9 and Figure 26) [86,87]. The cluster model is based on the assumption of the local nature of interactions between the molecule and the active centre located on the surface and neglects long-range interactions. The part of the surface with an active centre is excluded. The long-range interactions are included by taking into account the influence of the ionic environment (cluster in the electrostatic field [88-89] or the saturation of broken bonds by hydrogen atoms [86]. The second method is the periodic model [87]. It is the standard solid state physics model based on the general formalism of the band theory and the periodicity of the crystal lattice. A comparison of the advantages (+) and disadvantages (-) of both models is described in Table 9.

Table 9. Comparison of models used for the geometrical representation of the surfaces.

Cluster model	Periodic model
electronic structure of cluster with different size & symmetry saturated by H atoms: R(O-H)=0.97Å O-H bonds || broken O-M bonds all electrons included in calculations	unit cells with different size, symmetry & number of layers large surface-surface separation (e.g. 100Å) different number of K-points semi-core pseudopotentials
+ localized interaction	+ periodic arrangement of all atoms
+ finite section of surface	+ 3D system
+ detailed geometry & local charge	- catalytic material describing a very large supercell
- problem: embedding	- problem: artificially strong

- limitation: physical/chemical parameters depend on size & geometry of cluster	- coupling adsorbate/molecules, only high coverages, cell size balance needed

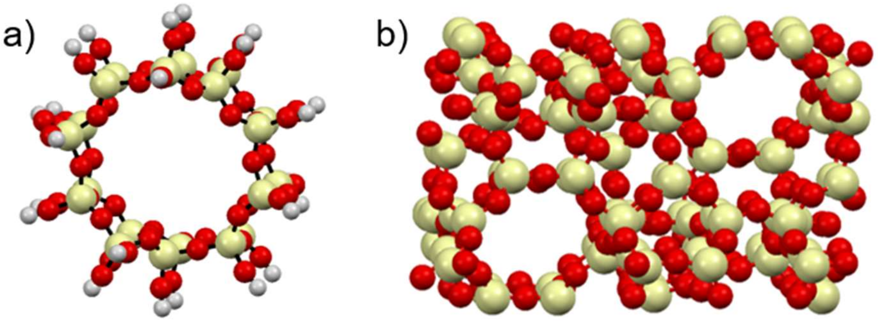


Figure 26. Geometric representation of the catalytic system using the DFT method: a) cluster, b) periodic cell.

Theoretical modeling of the catalytic reaction requires several steps (Figure 27), which must succeed in order to find a reaction mechanism at the catalyst surface.

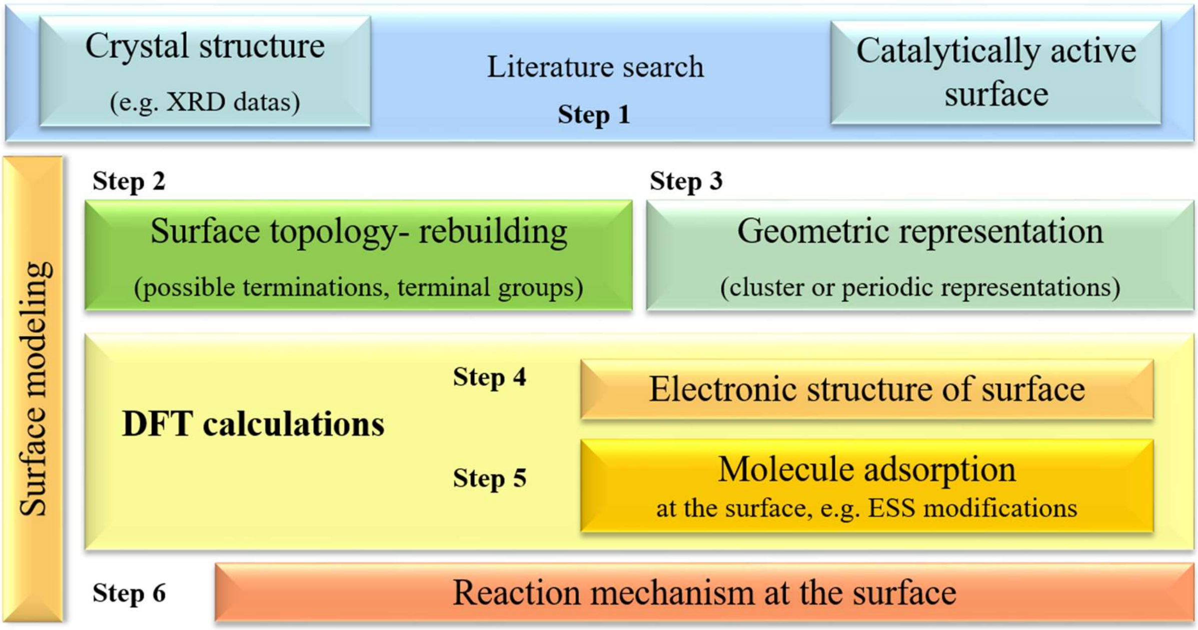


Figure 27. Necessary steps of surface reaction modeling using the DFT method.

Useful Electronic Structure Parameters

atomic charge distribution - charging of atoms, information concerning ionic binding;

bond order analysis - information concerning a covalent contribution to the total bond;

charge density differences - direct information concerning bond formation; quantifies the charge rearrangement due to bond formation;

electrostatic potential - local charging and binding at the surface; quantifies the electronic and nuclear electrostatic interaction with an external point charge;

energetic distribution of the occupied and empty electron states;

electron densities - description of bonding in ground and transition states;
electrostatic potential maps – information concerning the distribution/delocalization of charge;
total density of states (D0S) and atom projected density of states (PDOS) *–comparable with* the valence energy region ⇒ UPS;
reactivity indices (Fukui functions) - type of attack: nucleophilic, electrophilic, radical;
vibrational frequencies – comparison with IR / Raman frequencies to localize adsorbed species
ionization potential of core electrons – to develop theoretical NEXAFS, XAS, XES, RIXS spectra

After many years of DFT investigations, the level of theoretical insight into electronic structures, geometries, stabilities and adsorption properties of model catalysts is now reaching a level that allows for the investigation of more complex catalytically active systems. An important goal for the near future would be to build a bridge between the applied industrial catalysts and model systems at an atomic level by using a combination of experimental and theoretical methods. The methodology for the investigation of catalytic systems in such a way requires in particular, the examination of (i) metal-support interface investigations and modeling, (ii) modeling of reaction mechanisms through a comparison of theoretical and experimental spectra, (iii) the mechanism of catalyst deactivation by a combination of experimental and theoretical spectra. Several challenges still remain on the long road to a complete understanding of real-world catalysts: (i) a more detailed explanation of imperfections, e.g. defects, steps, and their effects on the reactivity of catalysts, (ii) a more detailed description of complex systems, where different materials are either used for the support or the supported phase, and (iii) the improvement of the models used to obtain the theoretical spectra of complex systems.

15. Examples of catalytic processes

The choice of technology used in the process depends on many factors, which can be reduced to common denominators of cost effectiveness and environmental performance. The catalytic processes, which constitute over 90% of the currently used chemical processes, are required to utilise catalysts, which apart from high activity and selectivity, should also be characterised with easy separation and regeneration as well as low price and lack of toxicity. A very important issue, which has already been indicated, is the catalyst performance stability, which determines the manner of the process conduction. Even in the case of obtaining a single type of product, the technologies can differ considerably, as exemplified by the process of propane dehydrogenation to propene. In practice, the four most commonly used technologies are Catofin (CB&I Lummus), Oleflex (UOP), STAR (Uhde) and FBD (Snamprogetti-Yarsintez) [90–91]. These technologies differ by the type of catalysts used, the way of catalyst regeneration and heat supply as well as reactor design. The process parameters, performance and the catalyst used are presented in Table 10. In turn, reactor configuration diagrams are presented in Figure 28.

Table 10. Conditions and performance obtained in industrial processes propane dehydrogenation to propene [25, 91].

Process	Oleflex	Catofin	STAR[a]	FBD
Reactors	Adiabatic moving beads	Parallel adiabatic fixed beds	Isothermal tubular reactors	Fluidized reactor
Catalyst	Pt-Sn/Al_2O_3	CrO_x/Al_2O_3	Pt-Sn/(Mg/Ca/Zn)Al_2O_3	CrO_x/Al_2O_3
Catalyst live (years)	1–3	1–2	1–2	Not available
Temperature (°C)	547–617	587–647	477–617	547–597
Pressure (bar)	1–3	0.1–0.7	3–8	1.1–1.5
Conversion of propane (%)	25	48–65	30–40	40
Selectivity to propene (%)	89–91	82–87	80–90	89

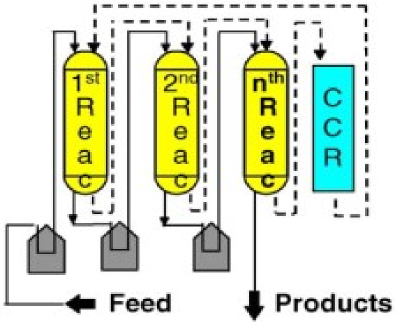
[a] without oxydehydrogenation reactor.

Oleflex process. It is executed in a similar way to catalytic reforming from the same company. The process is carried out in a battery of adiabatic flow reactors with a moving Pt-Sn/Al_2O_3 catalyst bed, which gradually moves from the first to the last reactor in the course of dehydrogenation process. Heat is supplied mainly through the heating of reaction mixture between subsequent reactors (stages) in a multi-sectional furnace. Partial hydrogen recycling to the reactor prevents rapid coking. The deposit is removed from the surface of deactivated catalyst (in the last reactor) under air flow in the regenerator. At the regeneration stage, the catalyst is also heated and then gives out the heat in the dehydrogenation process. The regenerated catalyst is then returned to the first reactor.

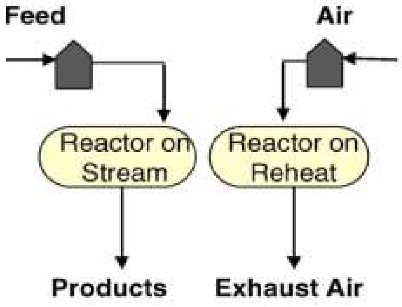
Catofin process. This process utilises a battery of reactors operating periodically in dehydrogenation/regeneration cycles. The applied catalyst, CrO_x/Al_2O_3 (supplemented with potassium ions), is located in a static bed in adiabatic reactors. Usually 5–8 reactors are operated in 12-minute cycles. In the course of each cycle, the catalyst bed goes through the stages of dehydrogenation/purification/regeneration/purification. The heat for the endothermic reaction is supplied at the stage of catalyst regeneration. In the course of carbon deposit burning, the heat is stored by the catalyst and then gradually released at the dehydrogenation stage.

STAR process (steam active reforming). It is a solution, which in many aspects resembles the process of steam conversion of methane to syngas. The dehydrogenation process is carried out in the presence of Pt-Sn/Zn-Al_2O_3 catalyst agglomerated by a mixture of calcium and magnesium aluminates, which play the role of filler and binder. The catalyst is located in pipes placed inside the furnace. The heat necessary for the reaction to take place comes mainly from burning of liquid or gas fuel in the inter-pipe space. The problem of deactivation is dealt with in a similar way as in steam conversion, in which the raw material is diluted with steam that plays the role of carbon deposit gasification factor. In this solution, the time between regenerations is extended to 7 hours.

Oleflex



Catofin



STAR

FBD

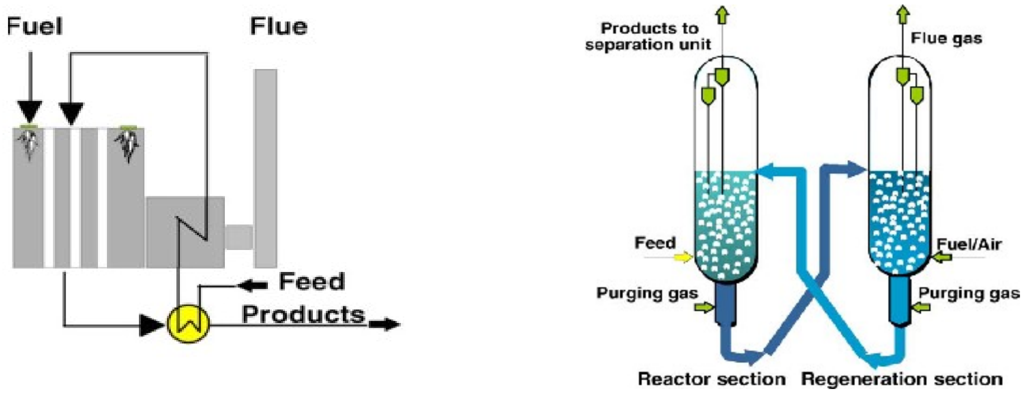


Figure 28. The most important technologies of propane dehydrogenation to propene [19].

In newer solutions that are not presented in Figure 28, Uhde company additionally implemented a hydrogen oxygenation reactor after the dehydration reactor in order to increase the propane equilibrium reaction. The reaction of partial hydrogen oxygenation provides additional heat for the stage of propane dehydrogenation.

FBD (fluidized bed dehydrogenation) process. In the last of the presented solutions, the dehydrogenation process and catalyst regeneration is carried out using fluidized bed. In terms of the technological concept, the process resembles early solutions used in the fluid catalytic cracking (FCC) process. In the propane fluidized dehydrogenation reactor, the process is conducted in the presence of CrO_x/Al_2O_3 catalyst. The product and the reacted raw material are separated from the catalyst on a battery of cyclones. The deactivated catalyst is regenerated with air in a regenerator, from which it is returned to the propane dehydrogenation reactor after removal of deposits and reoxygenation. The heat necessary for reaction is supplied by the regenerated catalyst, which, in the course of regeneration (burning of carbon deposit), is heated to the temperature of > 650°C. During the reaction, the catalyst gives out heat and cools down to the temperature of < 560°C.

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