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MAJOR ADVANCES AND CHALLENGES IN HETEROGENEOUS CATALYSIS FOR ENVIRONMENTAL APPLICATIONS: A REVIEW

KATALIZA HETEROGENICZNA W ZASTOSOWANIACH ŚRODOWISKOWYCH: PRZEGLĄD POSTĘPÓW I WYZWAŃ

Abstract: Heterogeneous catalysis is one of the fastest developing branches of chemistry. Moreover, it is strongly connected to popular environment-related applications. Owing to the very fast changes in this field, for example, numerous discoveries in nanoscience and nanotechnologies, it is believed that an update of the literature on heterogeneous catalysis could be beneficial. This review not only covers the new developments of heterogeneous catalysis in environmental sciences but also touches its historical aspects. A short introduction to the mechanism of heterogeneous catalysis with a small section on advances in this field has also been elaborated. In the first part, recent innovations in the field of catalytic air, water, wastewater and soil treatment are presented, whereas in the second part, innovations in the use of heterogeneous catalysis for obtaining sustainable energy and chemicals are discussed. Catalytic processes are ubiquitous in all branches of chemistry and there are still many unsolved issues concerning them.

Keywords: heterogeneous catalysis, environmental chemistry, use of renewables, remediation, sustainable chemistry, sustainable energy

Introduction to heterogeneous catalysis and historical aspects

The 21st century has brought many challenges with one of the most important being the ubiquitous contamination of water (and wastewater), soil and air. This has given origin to environmental protection along with one of its forms: green chemistry [1, 2].

Green chemistry, also known as sustainable chemistry, is an area of chemistry and chemical engineering focusing on the designing of products and processes that minimize the use and generation of hazardous substances. This term emerged during the 1990s and according to Anastas and Warner [3] it has 12 postulates from which the ninth is catalysis, with the emphasis that it is *superior to stoichiometric reagents*. Catalytic reactants, as opposed to stoichiometric reactants, are not consumed in a reaction. Furthermore, they are a large part of chemistry itself, as can be observed in Figure 1.

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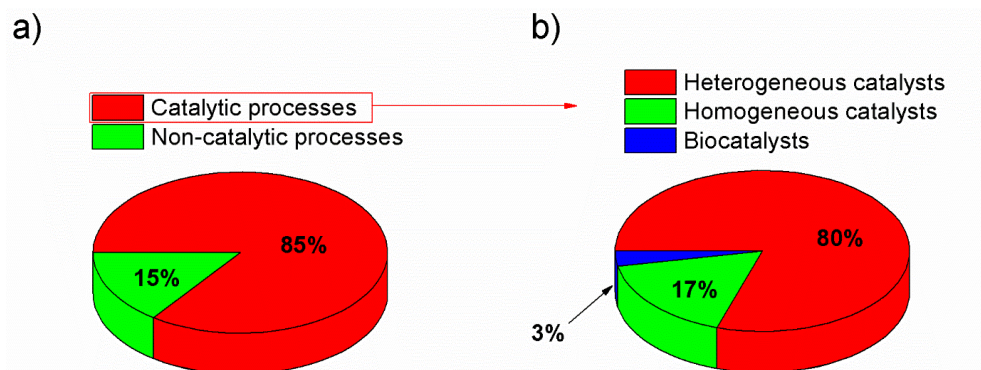[*] Corresponding author: stanislaw.waclawek@tul.cz

Fig. 1. Diagram presenting: a) the contribution of catalytic processes to the chemical industry and b) the contribution of heterogeneous catalysis in comparison to other catalytic processes [4]

Catalytic processes can be either homogeneous or heterogeneous (the contribution of biocatalysts and their developments were covered in the review paper [5]). Heterogeneous catalysis is a process that requires the use of a catalysis that is in a different phase than the reactant, i.e. the catalysis is usually in a solid phase and the reactant is in a gaseous or (less frequently) liquid phase [6]). Despite the many benefits, homogenous catalysis is often pH dependent (and sometimes less efficient and less environmentally-friendly [7, 8]) than the heterogeneous form [9-12], which can function in a wide pH spectrum [13]. In addition, as much as 80% of the catalytic processes concern heterogeneous catalysis, which makes this process a vibrant branch of chemistry [14, 15].

Heterogeneous catalysis was probably first observed by Berzelius and Mitscherlich [14], who determined that the reactions could be fastened by solids. The term *contact catalysis* was introduced at that time, and more than one hundred years had to pass for this term to become outdated. In 1895, the definition of catalysis as *the acceleration of chemical reactions by the presence of foreign substances, which are not consumed* was proposed by Ostwald [16]. He also determined that a chemical reaction occurs at a finite rate and that this rate can be used to determine the strength of bases and acids, for which he was awarded the 1909 Nobel Prize in Chemistry. Progress in catalysis is connected with Paul Sabatier, awarded the 1912 Nobel Prize for his work on the hydrogenation of ethylene and CO over Ni and Co catalysts. The true revolution in industrial catalysis occurred in 1918 when Haber synthesized ammonia from the nitrogen in air and hydrogen. Haber, along with Robert Le Rossignol, investigated the previously ignored high-pressure range. Le Rossignol and Haber discovered that at a temperature of 600°C and a pressure of approximately 20 MPa, an ammonia gain of approximately 18% can be acquired with osmium being used as a catalyst. Similarly to Archimedes, Haber had his eureka moment, after the first synthesis of ammonia, with the words "There's ammonia!" [17, 18].

Various catalysts were examined for ammonia synthesis in laboratory-scale recycling reactors designed by Bosch, which can be operated at high temperatures and pressure. The synthesis of ammonia was commercialized by BASF in 1913 and named the Haber-Bosch process [17]. Furthermore, iron catalysts for ammonia synthesis were also found by BASF to be very effective [19].

To show the importance of this process, a comparison of between ammonia production using the Haber-Bosh process and other methods and population growth is presented in Figure 2.
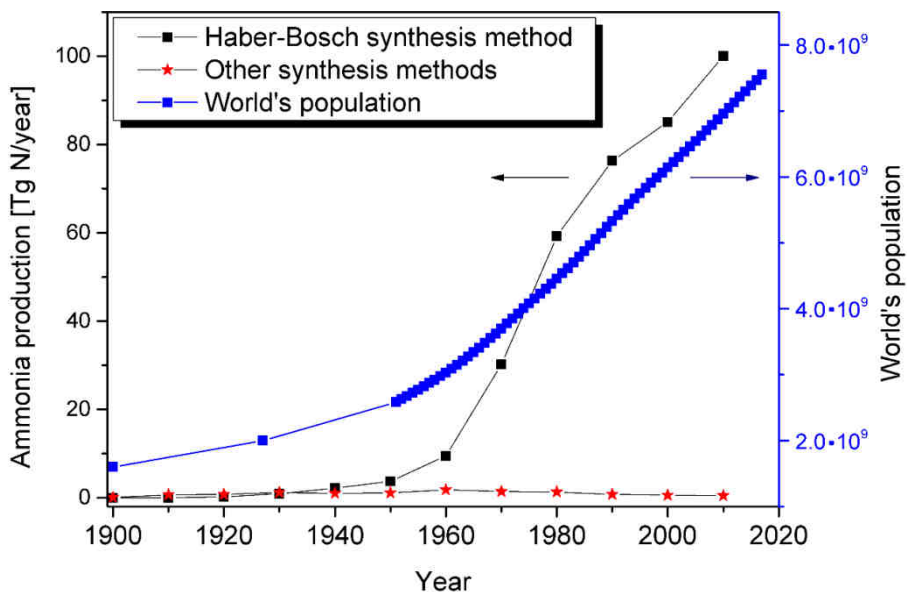

Fig. 2. World production of synthetic nitrogenous fertilisers (in teragrams per year) and the world's population growth [20, 21]

It is important to note that without invention of this catalytically driven process, there would be a global scarcity of food, which shows how much heterogeneous catalysis affects our daily life.

Although after its discovery, the world-wide production of ammonia grew fast, the exact mechanism of its synthesis was unknown for a long time, until Gerhard Ertl determined and improved this process by the introduction of promotors [22]. Furthermore, his work also focused on many other catalytic processes, e.g. catalytic oxidation of CO over platinum. For his overall impact on the investigation of chemical processes on solid surfaces he was awarded the 2007 Nobel Prize in Chemistry.

What is more, no less than 15 Nobel prizes have been awarded for studies on catalysis and many chemists around the world are repeatedly advancing the catalysts they have, and are motivated to discover new ones.

For more historical aspects concerning catalysis read [23] from a world-wide or [24] from a Chinese perspective.

Moreover, the beginning of the 21st century has brought a real outbreak in the form of using nano-materials in heterogeneous catalysis. Nano-materials have shaped constituents with at least one dimension less than one hundred nm. Due to a much higher specific surface area than macro materials, the effectiveness of nano-catalysis is much higher. The principles of nano-catalysis can be seen in Figure 3 [1]. It should be noted that the

supported catalyst particles in nano-meter dimensions were used way before the term nanotechnology was invented by R. Freeman [25].
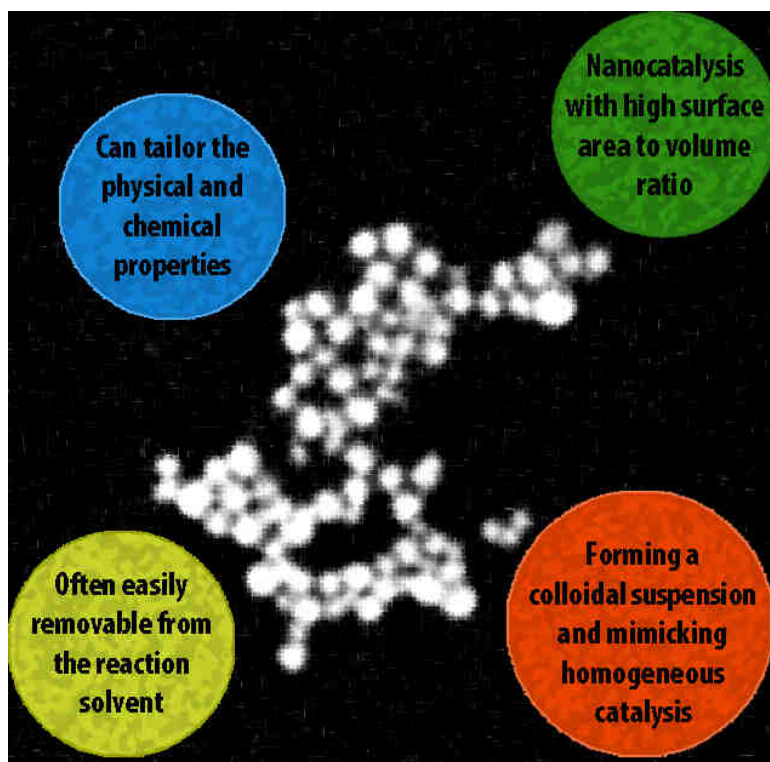

Fig. 3.   Nano-catalysis mechanisms. Based on [1]

Nano-technologies have offered useful and facile tactics for the arrangement of nano-crystals with distinct shapes, sizes and compositions. Also, nano-interfaces have proven to play a significant part in catalysis [26]. Accurate control of these nano-crystals delivers a vital basis for the investigations of structure-performance relations, which are essential for the creation of nano-crystals with enhanced catalytic performances for practical purposes [27]. The nano-effects in catalysis were also a subject of discussion in a recent review [28], which gave catalytic systems of carbon nanotubes, nano-metal oxides and 2D layered nano-catalysts as examples. Moreover, the essential ideas, the research procedures and some of the key scientific problems involved in nano-catalysis were summarized and analysed.

Going by the size-reduction path, supported single-atom catalysts has become a hot topic lately, due to the dispersion of isolated metal atoms on the surface of the support, which can exploit the atomic efficiency of noble metals, and the resultant single-atom catalysts frequently display extraordinary catalytic activity. However, precise synthesis of this material remains a large challenge [29, 30].

For example, graphene (or its unexfoliated form [31]) based materials were found to be a great supporting material for this purpose [29, 32-37]. This has enabled various

environmentally-friendly and useful applications in electrochemical energy storage/conversion and heterogeneous catalysis. A very recent review article [38] presented this broad topic in detail.

Some of the reviews of catalysis in environmental studies e.g. from 2001 by Baiker [39] and 2003 of Goodman [40] describe its largest advances at the time. Furthermore, in 2008, a review made by Newton [41] presented the impact of nanotechnology and its advances on heterogeneous catalysis. One of the largest reviews concerning heterogeneous catalysis was presented in 2012 by Fechete et al. [42]. Therein, the main catalytic findings and the key industrial catalytic processes over the last three hundred years, involving petroleum conversion for fuels and energy supply, emission control etc., were discussed. This review mainly concerned metal and metal oxide catalysts; however, in a recent review, carbon-based catalysts, often doped with heteroatoms [43], were described as being an efficient, low-cost alternative [44].

Although these numerous reviews present the wide knowledge of heterogeneous catalysts, only a few are up-to-date and deal with their environmental use [15, 45-51].

In the present review, the mechanism of heterogeneous catalysis as well as recent advances in its development are discussed. There is a continuous effort to unlock energy sources that are much more difficult to use than fossil fuels, but are more "green". Catalysis, for example, could make it more economically viable to split H_2O into hydrogen fuel (and oxygen), or could expose new methods for the use of raw resources e.g. CO_2 or biomass. Moreover, catalysis is used for the "green" remediation of water, air, and soil, with a considerable number of novel solutions regularly being published in the scientific literature. Furthermore, the future challenges in the area of heterogeneous catalysis have been addressed in this review.

The mechanism of heterogeneous nano-catalysis

As previously mentioned, catalysis is an influenced chemical reaction with the presence of a substance, which itself is not part of the reaction product. The chemical reactions always involve breaking bonds and the formation of new ones, as it can be seen in Figure 4, in order to go from a reacting molecule to a product, an energy barrier for breaking bonds has to be overcome and these energy barriers determine the reaction rate (Fig. 4) [14].

Catalysis is an alternative way of obtaining the immediate formation of a product, because of a lower energy barrier between the molecules and the catalysts. Therefore, catalysis research is mainly associated with identifying and characterizing the intermediates between the catalysts and the reacting molecules.

In heterogeneous catalysis, chemisorption (interaction between a particle on a solid surface and another phase) was found to be one of the most important processes. Chemisorption depresses the free energy of the closed system comprising the exposed, "clean" surface and atoms or molecules from another phase. This (potential energy level) can be measured via calorimetry or - less well defined - by a Clausius-Clapeyron analysis of isostere data [14]. The formation of new bonds may be associated with former bonds breaking through dissociation. The molecules can migrate across the surface and afterwards find another partner to form a new molecule, which can then be released back into the gas or liquid phase. Recent tactics for modelling sensations in heterogeneous catalysis on a molecular level were described in [53] (also see [54]). Modelling of porous structures and

their surfaces as well as adsorption and diffusion of reactants and products inside the pores by means of various Monte Carlo and Molecular Dynamics algorithms can be achieved, followed by quantum chemical approaches for computing reactions on the active sites. The active sites and their historical aspects were covered in a recent review [55]. Therein, a brief explanation of certain features of active centres, single-site heterogeneous catalysts, metal supported catalysts (e.g. nano-metal clusters), transition metal oxides, can be found. In another relatively recent review [56], the latest work on direct experimental detection of a molecular and atomic-level nature of adsorption sites, adsorption-desorption mechanisms of S^0-aromatic compounds, and surface chemical reactions upon regeneration of the "spent" sorbents for desulfurization of the liquid fuels, was presented. As it was mentioned in the review paper of [57], there is a need to project and prepare heterogeneous catalysts with sophisticated surface sites (e.g. [58]) in order to selectively promote reactions.
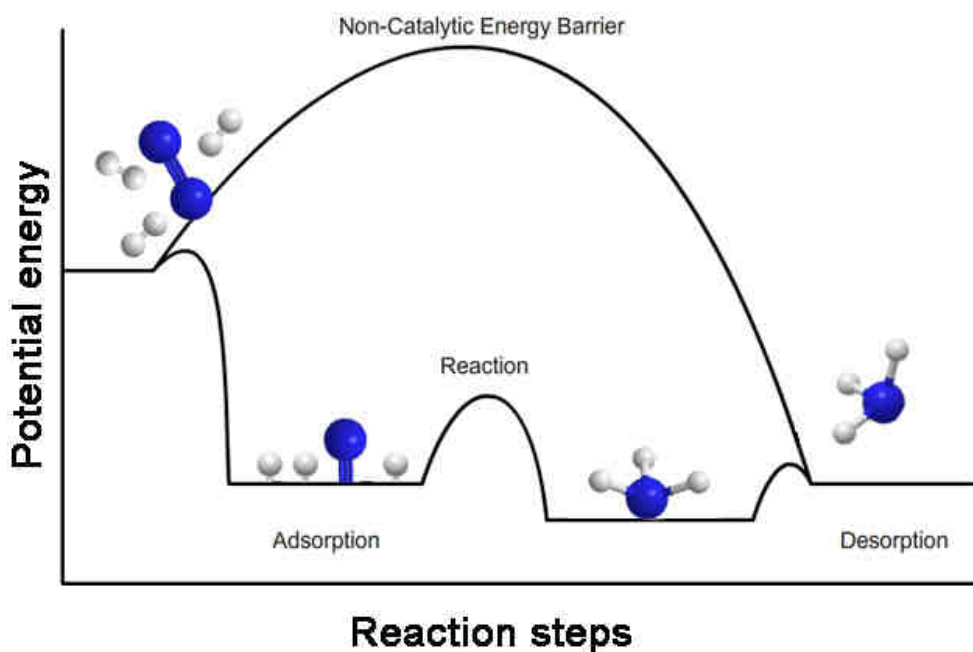

Fig. 4. Simplified diagram of the steps of a chemical reaction and overcoming the energy barrier, with and without heterogeneous catalyst (based on [52])

Selectivity is the next important issue in heterogeneous catalysis [57]. It is one of the most vital criteria for the creation of new catalytic processes. More selective catalysis can be both inexpensive and more "green", because it does not squander reactants, does not necessitate costly separation procedures, and produces less poisonous by-products [57]. Very often not only a single product is formed, but different products are also formed and the role of the catalyst is not so much linked exactly with the activity but the selectivity. If from A and B two different reaction products, C and D, can be formed, selectivity is the ratio of formation rate of product C (or D) over the total rate.

As it was mentioned in the works of Ertl [14, 22] for the Haber-Bosch process, the composition of catalysis is essentially Fe(II) or (III) oxide with small amounts of potassium, aluminium and calcium. Addition of these elements is very important, as they are the so-called 'promoters'. Without these promoters the catalyst would not be active enough. What is the role of these small amounts of promoters? They are embedded between the catalytically active sites of iron particles. The oxides of calcium form a framework, which prevents the catalyst from sintering at higher temperature [59] or even at moderate temperature [60]. The level of sintering is normally affected by the surface chemistry, demonstrating that besides the universally assumed Ostwald ripening, also other routes related with metal surface diffusion can be blamed for the nanoparticle size growth (for example: the synthesis method, the size and shape of the nanoparticles, catalysis dispersion on the support (the distance between the particles), or pre-treatment of the support and reaction environment). Additionally to the deterioration in metal dispersion, carbon supports can show chemical instability causing their partial destruction in the proximity of the nanoparticles both in oxidizing and reducing environments at high temperatures. Moreover, Kordas et al. [60] evaluated the possible events affecting metal sintering and damaging of the supports using transmission electron microscopy (TEM) analysis. Another study that presents visual examples of the sintering process of nano-scale systems (monitored *ex situ*, *in situ*, and under *operando* conditions) was published by Behafarid and Cuenya [61].

The truth is that catalyst deactivation (mainly by sintering) is ultimately inevitable, and its recycling should also be a subject of research. Several methods of catalyst recycling and redispersion were the subject of a study [62]. Another, even more recent report [63] presented current efforts in the field of recyclable catalysis, and also collected and discussed the results of recycling studies performed with a wide range of heterogeneous catalysts developed in recent years. The report also provides a thorough analysis of the available data and a discussion of issues related to recyclability in general (the literature was covered until 2017).

In order to gain further knowledge about heterogeneous catalysis there is the need to develop methods by which investigation of the catalysts under more realistic (operating) conditions would be possible. In recent years, much effort has been made to perform experiments in practical reaction environments, and to observe the dynamics of catalysis with high (spatial, temporal and energy) resolution. For instance, Lundgren et al. [64], have shown the strengths and weaknesses of the experimental techniques (i.e. near ambient pressure x-ray photo emission spectroscopy, planar laser-induced fluorescence, and high energy surface x-ray diffraction) for testing the catalytic CO oxidation over a Pd(100) single crystal surface. Electron microscopy and its derivatives have significantly influenced the characterization of heterogeneous catalysts, in particular supported metal catalysts, and can provide nano- or atomic-scale evidence on the morphology, structure, composition, and electronic state of the area of interest. Therefore, further development of electron microscopy is one of the most important steps to gain further knowledge about heterogeneous catalysis [65]. For example, Tao et al. [66] presented the scheme and functioning of a home-built high-pressure and high-temperature reactor equipped with a high-resolution scanning tunneling microscope (HR-STM) for studying catalytic materials. In this scheme, the STM body, sample, and tip are placed in a small high-pressure reactor ($\sim$19 cm^3) situated within an ultrahigh vacuum (UHV) chamber. Tests performed on two samples both in a vacuum and under in high pressure demonstrated

the ability of *in situ* examinations of heterogeneous catalysis and surface chemistry at an atomic resolution and at a wide pressure range, from UHV to a pressure higher than 1 atm. Other researchers [67] focused on the main advantages of both low energy electron microscopy (LEEM) and photoemission electron microscopy (PEEM) for understanding structural and chemical alterations on the surface of model catalysts in real time and under well-defined environments when chemical reactions take place. The LEEM/PEEM method to model approaches in catalysis is possibly important due to many aspects, e.g. this method usually offers the opportunity to do tests and follow processes in real time and under *in situ* and *in operando* conditions. Furthermore, numerous processes are happening throughout the catalysis of a chemical reaction, i.e. adsorption, dissociation, diffusion, recombination, bond formation, and so on. Moreover, as described by [68] *in situ* environmental transmission electron microscopy (ETEM) can be used to study nano-structures in parallel with conversion and selectivity measurements.

Also, improvements in Raman [69] and infrared spectroscopy [70] should be considered as important for gaining further knowledge about catalysts. For example, tip-enhanced Raman spectroscopy combines plasmon-enhanced Raman spectroscopy with scanning probe microscopy to simultaneously provide a chemical fingerprint and morphological information for the sample at a nano-meter spatial resolution. Whereas, *in situ* attenuated total reflection infrared spectroscopy can explore processes happening at solid/liquid(/gas) interfaces that are occurring in heterogeneous catalysis and electrochemistry. A recent and interesting review deals in detail with infrared spectroscopic techniques for the characterization of catalytic systems [71].

A more detailed mechanism of heterogeneous catalysis (as well as the basics of nano-catalysis) has been described in many research works; therefore, for more information not mentioned in this article e.g. conservation and transformation of energy, see [1, 14], electrocatalysis [72], photocatalysis [73] and photoelectrocatalysis [74, 75].

Innovations in the use of nano-catalysis in the environment

As previously mentioned, the use of catalysts in the environment is of enormous importance. Although heterogeneous nano-catalysis is nowadays ubiquitous in almost all environmental sciences, several areas are dynamically developing, i.e. catalysis for clean air (including automotive exhaust catalysis), water (wastewater) and soil, and use of renewables. Recent developments in these topics are addressed below.

Catalysis for clean air, water, wastewater and soil

Air (including automotive exhaust catalysis)

Research in the field of catalytic air cleaning started with automotive exhaust catalysis, which has led to greater advances in heterogeneous catalysis investigation, starting in the 1960s, systematically through commercialization in the mid-1970s, and still on-going today. The purpose of car exhaust catalysts is to remove pollutants, which consist mainly of carbon monoxide, small fractions of nitric oxides, and hydrocarbons (Table 1).

A reaction to progressively rigorous emission standards is the tendency to create increasingly complex catalysts. These aim to reduce the complexity and cost of the catalyst without losing performance [76, 77].

Catalytic removal of toxic substances

Toxic substance	Source	Removal
Hydrocarbons (VOCs)	Chemical / petroleum industry, Solvents, Car exhausts	Oxidative
Carbon monoxide	Car exhausts	Oxidative
Sulphur dioxide	Power plants, Heating	Reductive / Oxidative
Nitric oxides	Car exhausts, Power plants	Reductive

Many of these catalysts work by using a device that is a porous support medium of oxide, a so-called "wash code", under which small particles of precious materials like platinum, palladium or rhodium are deposited and exposed to molecules from the gas phase that are interacting with the surface. Carbon monoxide molecules are absorbed through the carbon atom, like in carbonyl compounds, and oxygen molecules are then dissociated, leading to the oxygen atoms being chemisorbed. Chemisorbed carbon oxide molecules migrate and meet each other, react and form a new substance, which can then be released back to the gas phase.

The platinum-group metals are broadly used as catalysts for the abatement of automotive exhaust pollutants. The scarcity of the platinum-group metals and the growing demand from an ever-expanding automotive sector have led to scientists improving the effectiveness of the use of the platinum-group metals. Orthodox catalysts typically consist of platinum-group metal nanoparticles dispersed on high surface area oxide supports. An appealing strategy for reducing metal loading is the use of single atoms as catalytic active sites, which represents a highly atom-efficient alternative to the use of nanoparticles (as discussed in "Introduction to heterogeneous catalysis and historical aspects"). The chemical conditions that facilitate the stabilization of the notoriously oxophobic precious metals in oxide environments were also reviewed in a recent work [78].

Recently, Ganzler et al. [79] proposed an universal idea to adjust noble metal dispersion (size, structure), for example, during the operation of an exhaust gas catalyst. The dynamic structural behaviour of platinum nanoparticles on the ceria surface under reducing/oxidizing conditions was evaluated at moderate temperatures ($< 500°C$) and exploited to enhance the catalytic activity of Pt/CeO_2-based exhaust gas catalysts. Indeed, ceria has been used for a long time in catalytic converters for the abatement of air pollutants from vehicle exhaust systems i.e. ceria can gather oxygen from poisonous nitrogen oxide, creating harmless N_2.

Carbon monoxide removal

However, NO_x is not the only contaminant that can be abated by ceria. It can use the stored oxygen on its surface to convert lethal carbon monoxide into less-harmful carbon dioxide [80].

The very recent papers of [64] and [81] discussed the mechanisms of CO catalytic removal using Pd and Pt alloys, respectively. Lundgren et al. [64] argued that the surface structure of PdO(101) has a significant influence on the catalyst activity, due to the presence of coordinatively unsaturated sites of Pd atoms, similar to under coordinated Ru and Ir atoms found in $RuO_2(110)$ and $IrO_2(110)$, respectively. Whereas Zhao et al. [81]

focused on the impact of surface and subsurface Pt neighbours on the binding strength of CO on Pt. This mechanism was further examined by Caporali et al. [82] who tested CO and propene oxidation over a Pd/Al$_2$O$_3$ catalyst. They also used isotopically labelled ^{18}O$_2$ to analyse the reaction mechanism and found that in the presence of water, most of the oxidation is due to the water and not dioxygen. On the other hand, Jeon et al. examined another mechanism of CO oxidation concerning a spontaneous alteration in the oxidation states of Pd/WO$_3$ towards an active phase during catalytic cycles of CO oxidation [83]. They revealed that the facile oxygen transfer among Pd and WO$_3$ layers not only accelerates the spontaneous changes into the active form, but also acts as a promotional role in CO oxidation over the Pd layer.

One example of an extraordinary catalyst is nano-gold (nAu), which was found to be very different in comparison to its bulk counterpart, i.e. the former is a superb catalyst, whilst the latter is exceptionally inert. nAu is often utilized as a catalyst for CO and VOC oxidation and researchers are continuously working on the mechanism [84, 85]. It should be mentioned that nAu and nano-platinum have different properties in the process of catalytic oxidation. For instance, it was found that nAu particles smaller than 5 nm are more active in comparison to other noble-metal catalysts, whilst Pt particles of the same size are less catalytically active [86].

NO$_x$ removal

There have been many reviews on the catalytic reduction of another major contaminant emerging from car exhaust system, namely nitrogen oxide (NO$_x$). Piumetti et al. [87] list several treatment technologies for NO$_x$ formed in diesel engine cars i.e. direct catalytic decomposition, catalytic reduction, NO$_x$ traps, plasma-assisted abatement and NO$_x$ reduction combined with soot combustion. As stated therein, the concurrent removal of soot and NO$_x$ by the use of multifunctional catalysts, is one of the most interesting tasks for the automotive industry.

Similarly to the oxidation of CO, the reduction mechanism of NO$_x$ is also a common subject of discussion. For example, the reduction of nitric oxide (NO) by water on Cu(110) in a well-defined environment was examined by Shiotari et al. [88]. They gained an essential insight into the catalytic reduction of NO under ambient conditions. According to them, N-O bond weakening can be caused by water induced partial filling of the unfilled 2 pi* orbital of NO. Reaction of the complex with another water molecule induces further destabilising of the N-O bond, leading to bond rupture. It was revealed that hydrogen-bond pairing induces back-donation and thus plays a vital role in N-O bond cleavage.

Oxidation of NO$_x$ at ambient temperatures was also reported as a promising way of regulating NO emissions, since NO$_2$ in the presence of water can be further removed as HNO$_3$. Due to their large surface area, high porosity, and relative chemical inertness, carbon-based materials are very appealing in de-nitrification (De-NO$_x$) as catalysts or catalyst supports [89].

In addition, TiO$_2$ can be used for photocatalytic abatement of NO$_x$ pollutants in the air [90]. For example, in a very recent research article [90] it was found that TiO$_2$ coatings are suitable for use on construction materials (concrete, plaster). Furthermore, photocatalytic coatings maintain high effectivity over several years. It should be added that researchers from the Technical University of Liberec have also contributed to NO$_x$ removal with the use of TiO$_2$ [91, 92].

Another possible treatment of NO was found by Hu et al. [93], who fabricated multi metal catalysis on carbon nanofibers under visible-light irradiation. Photocurrent tests and electrochemical impedance spectroscopy also demonstrated that the catalyst had a high efficiency of interfacial charge separation, which is critical for improving the photocatalytic activity. Moreover, the membrane of the photocatalyst was stable and recyclable after multiple runs [93].

Volatile organic compounds (VOC) removal

Other air pollutants that can be catalytically abated are volatile organic compounds (VOCs) [94]. For instance, formaldehyde is the most common VOC released from households and is related to many health risks, including sick building syndrome. Photocatalytic materials were also proven to be effective for degradation of these contaminants [95]. After UV irradiation with a TiO_2 filter for 2 hours, the removal efficiency of gaseous formaldehyde increases to approximately 90%. Contributions to the removal of gaseous formaldehyde by oxidation decomposition include natural dissipation (12%), photodegradation (30%), and photocatalytic treatment (58%). The removal of formaldehyde and other gaseous pollutants i.e. methanol, acetone, benzene, toluene, naphthalene, and ethyl acetate was covered in a review paper concerning mesoporous silica and supported catalysts materials [96]. The correlation between the surface environment, pore structure, and the morphology of mesoporous silica materials and adsorption of VOC molecules was also assessed therein.

The review of Silva et al. [97] described heterogeneously catalysed oxidation of VOCs with the use of bio-recovered chromium from wastewaters. Using this method, it is possible to simultaneously recover potentially toxic metals and utilize them as an efficient and valuable catalysts in environmental applications.

Desulphurization

Various metal oxides, e.g. MnO_2, Cr_2O_3, Fe_2O_3, CuO, CoO, NiO [98], SnO_2-ZrO_2 [99] or WO_x [100], can be used in the desulphurization of gases and oils. Moreover, various catalyst-supporters including γ-Al_2O_3, permutite, silica gel, and activated carbon were evaluated and tested as a means of enhancing catalytic activity of metal oxides [98]. It was described therein that γ-Al_2O_3 doped with MnO_2 can serve as a removal-effective sorbent for adsorption and oxidation of SO_2.

Sulphur recovery in these processes can also be achieved as reported by [99], who also proposed the removal pathway, i.e. elemental sulphur is created by the direct conversion of SO_2, so the created sulphur is partially transformed into H_2S with the hydrogenation, and the Claus reaction proceeds through the acidic sites.

Not only gases but other matrices can be catalytically desulfurized [101]. One example was presented by He et al. [100] who reported a synthesis of an amphiphilic tungsten oxide catalyst with oxygen vacancies for sulphur removal from fuel oil (with 100% efficiency) and a 15 times recycling performance without a significant decrease in activity.

Water / Wastewater / Soil

Since the 1970s, titanium dioxide (TiO_2), and to a lesser extent zinc oxide (ZnO), has continued to gain interest in the research and industry communities due to its high photocatalytic activity, good chemical stability, non- or low-toxicity, inexpensiveness, and

more or less long term photostability [102]. In 1972, Fujishima and Honda [103] demonstrated its potential to split H_2O into hydrogen and oxygen in a photoelectrochemical cell. From there on, there have been numerous review papers concerning TiO_2 remediation of water, wastewater, soil and air, with probably the best-known being written by Pelaez et al. [102].

Recently, Pellegrino et al. [104] also studied the influence of aggregation on TiO_2 nanoparticle photocatalytic activity. They found that the phenol degradation rate at low photocatalyst loading depends intensely on the photocatalyst aggregate size, where the absorbed fraction significantly varies with size. The effect is primarily due to the low penetration depth of the radiation inside the aggregates, limiting the volume fraction of the aggregates that is irradiated and, therefore, photocatalytically active. Not only the size but also the shape of the aggregate is important according to two very recent studies [105-107] as it can significantly influence the photocatalytic degradation of organic pollutants. TiO_2 particles were reported in the shape of nano-wires, belts, rods, sheets [105, 106], and mesoporous [107] among others.

Moreover, TiO_2 particles can be coupled with a variety of other materials, e.g. membranes/nanofibres [108, 109], graphitic nitride g-C_3N_4 [110] (similar work has been carried out with ZnO [111]), and graphene oxide [106] to serve as a composite for photoanode with a double synergistic effect or for the photocatalytic degradation of pollutants.

Recently, Zhou et al. [112] found an optimal ratio between (001) and (101) planes of anatase TiO_2, which can suppress the recombination of photoexcited electron-hole pairs. The results indicated that the removal efficiency was different and the percentage of (001) was 32% exhibiting the best photocatalytic activity.

Various contaminants can be eliminated using photocatalysis, e.g. nitrates [113], pharmaceuticals [114], bisphenols [108], BTEX [115], thiols, thiophene, rhodamine B [116], herbicides [117], or organic dyes [118].

The latest reports have revealed that plasmonic nanostructures can be exploited to drive direct photocatalysis with visible photons, where the nanostructures act as the light absorber and the catalytic active site [119-124]. It has been found that they can have a higher photocatalytic degradation efficiency than non-plasmonic nanostructures.

Several other metals can be used for the remediation of water/wastewater, e.g. gold [125, 126], silver [127], platinum and its alloys [128], or carbonaceous materials [129]; however, their cost probably will not enable their large-scale exploitation.

Heterogeneous catalytic conversion of pollutants can also be established with large variety of peroxides [13, 130-133] and iron in various valence states [134-137]. In the case of peroxides, the main aim of the catalytic activation is to weaken the O-O bond of the oxidizing agent [13, 138]. This can lead to the formation of more reactive radicals, for example $^{\bullet}OH$, $SO_4^{\bullet-}$ [139-141]. Metal-based activation of persulfates is still the dominant catalytic procedure [13, 142]; however, carbo-heterogeneous catalysts for persulfates have recently become very popular [143-145], although this topic still remains controversial [146]. Several oxidants can also be heterogeneously activated by subsurface minerals [147], which makes their application for e.g. groundwater remediation more facile.

Heterogeneous catalytic removal of pollutants from water with the use of nano zero-valent iron (nZVI) was studied in detail by many authors [148-153]. nZVI has been applied at many contaminated sites (*in situ*) where it not only adsorbs and reduces contaminants but also enhances bioremediation [154, 155]. Both *in situ* applied oxidants

(ISCO) and reductants like nZVI are interesting examples of how heterogeneous catalysis can improve groundwater quality.

Use of renewables

As mentioned above, heterogeneous catalysis is extensively used in the conversion of dangerous pollutants into products of lower toxicity. However, this is not the only way catalysis can positively influence the cleanness of the environment [156]. Concepts of catalysis for sustainable energy conversion, such as electro-catalytic water splitting for the production of the climate neutral energy carrier hydrogen as well as syngas $(CO + CO_2 + H_2)$ conversion for the synthesis of high-energy fuels from CO_2, can serve as only few examples. In the latter parts of this manuscript it was decided to focus on three important and fast developing branches, i.e. photoelectrochemical production of hydrogen, carbon dioxide conversion to valuable products, and biomass conversion to valuable products.

Photoelectrochemical production of hydrogen

Photoelectrochemical (PEC) water splitting under sunlight irradiation has received much attention for the creation of renewable hydrogen from water on a large scale. There are many questions that still remain unanswered concerning the improvement of energy conversion efficiency, utilization of longer-wavelength photons, enhancement of the reaction efficiency at any given wavelength and increase in the lifetime of the semiconductor [157, 158].

Similarly to other applications of heterogeneous catalysis, platinum has also been widely used as the co-catalyst for the evolution reaction of hydrogen, but also similarly to other applications, the high cost and its scarcity may limit the large-scale commercial application of the solar-to-fuels technique. Moreover, decreasing the amount of platinum in fuel-cell catalysts could help bring hydrogen-powered automobiles to the mass market. Researchers are pursuing several attack lines in order to shrink the platinum content, e.g. using it more efficiently, replacing some or all of it with palladium [159] (which performs similarly and is somewhat less expensive), substituting either of those precious metals with cheaper metals such as Ni or Co, and foregoing metals altogether. Commercial catalysts tend to consist of thin layers of platinum nanoparticles deposited on a carbon film, although researchers are also testing substitute substrates. For instance, Li et al. [160] used copper oxide as co-catalyst immobilized on anatase TiO_2. The hydrogen evolution efficiency from the copper oxide co-catalyst was comparable to those of systems containing the platinum co-catalysts [160]. Also, engineered Ta_2O_5 nano-rods were synthesized for a visible-light driven hydrogen generation process [161]. It was found that the self-doped Ta_2O_5 nano-rods displayed excellent visible light absorption and efficient visible-light photocatalytic activity for hydrogen production, and the formation of Ta^{4+} species effectively narrowed the band gap of Ta_2O_5. Furthermore, a possible visible-light photocatalysis mechanism of the self-doped Ta_2O_5 nano-rods for hydrogen production was also proposed. It was recognized that the coupling of graphene quantum dots (GQDs) with semiconductor photocatalysts endows the resulting nanocomposites with enhanced photocatalytic performances; however, the essential roles of GQDs have not been clearly revealed yet. Lei et al. [162] synthesized coupled CdS/GQDs nano-hybrids for highly effectual photocatalytic hydrogen generation. It was revealed that GQDs mainly played the role of an electron acceptor instead of a photosensitizer in enhancing the photocatalytic H_2

evolution performances of CdS/GQDs nano-hybrids. Wang et al. [163] determined that 2-D C/TiO$_2$ heterogeneous hybrid is an interesting potential substitute for noble metals in the hydrogen evolution process. Very recently, Kwak et al. [164] found that the catalytic activity of the bimetallic (molecule-like) nano-cluster, PtAu$_{24}$(SC$_6$H$_{13}$)$_{18}$, for hydrogen production is significantly higher than the benchmarking platinum catalyst. The molecule-like bimetallic nanocluster represents a class of catalysts that bridges homogeneous and heterogeneous catalysis and may provide a platform for the discovery of finely optimized catalysts.

Further information about the cost-effectiveness, present technological concerns, drawbacks related to low conversion effectiveness, new ways of creating renewable hydrogen, the bio-mimicking method delivered by artificial leaves, and nano-scale engineered processes for advances in the efficient and cost-effective creation of fuels from water and CO$_2$ can be found in a recent review paper [165].

It should be noted that there are many, still-developing methods involving heterogeneous catalysis for "green" hydrogen production, e.g. steam methane reforming, the water-gas shift reaction and other [166-177].

Carbon dioxide conversion to valuable products

Methanol demand is constantly growing in chemical and energy industries. It can be commercially produced from synthesis gas (syngas; CO + CO$_2$ + H$_2$) using CuO/ZnO/Al$_2$O$_3$ catalysts. It is worth noting that recently Smith and his colleagues [178] developed a solution-processing method for the mineral malachite to arrange a new class of copper/zinc oxide materials, called zincian georgeite, that could be more effective as a catalyst for methanol synthesis and for hydrogen production. Nowadays, a great deal of effort is being put into the development of technologies for the production of fuels from carbon dioxide (CO$_2$) due to its negative effects on the global environment from its role in climate change and ocean acidification [2]. Over the years, some valuable works on CO$_2$ hydrogenation to methanol have been reported in the literature. CuO/ZnO/Al$_2$O$_3$ catalysts, which enable methanol production from syngas, show poor activity for CO$_2$ hydrogenation at low temperature (T < 250°C) [179]. Therefore, there is a search for suitable catalysis for this process. One example was proposed by Porosoff et al. [180] who demonstrated the feasibility of using the non-precious metal material molybdenum carbide as an active and selective catalyst for CO$_2$ conversion by H$_2$. García-Trenco et al. [181] found that a Pd/In catalyst shows an improved methanol selectivity over the whole temperature range studied (190-270°C), reaching > 80% selectivity at 270°C, compared to only 45% for the reference Cu/ZnO/Al$_2$O$_3$ catalyst. What is more, very recently, Wu et al. [182] used supported gold catalysts at low temperature for efficient hydrogenation of CO$_2$ to methanol. In their study, Au/ZrO$_2$ with Au particles (1.6 nm) had unprecedented high catalytic activity and excellent selectivity for the reaction, and methanol could be obtained even at 140°C, which is obviously lower than previously reported. Recently, Sun et al. [183] identified AuFe as the best metal alloy amongst twenty metals for CO$_2$ reduction at a low overpotential. Such AuFe alloys display exceptional CO$_2$ reduction performance. It was determined that nearly a 100-fold increase in mass activity toward CO$_2$ reduction can be achieved with an AuFe nano-alloy in comparison to bare Au nanoparticles. In another study by Bahruji et al. [184], Pd/ZnO prepared using the sol-immobilised method showed higher a conversion of CO$_2$ towards methanol than the classic impregnation method. They also stated that maintaining a small particle size is important for high methanol selectivity.

The mechanism of this process was researched by Wu and Yang [185], who found that the combination of formate and formic acid hydrogenation steps can be treated as the "effective rate-determining step". Therefore, the formation of methanol is mainly controlled by the surface coverage of formate and hydrogen at a steady state, as well as by the effective free energy barriers.

Photocatalytic conversion of CO_2 to CO was also a subject of research conducted by Truong et al. [186] and Aguirre et al. [187]. The latter created Cu_2O/TiO_2 heterostructures for CO_2 reduction through a direct Z-scheme, while Truong et al. created rutile TiO_2 nano-crystals with exposed (331) facets for enhanced photocatalytic CO_2 reduction activity.

Heterogeneous catalysis in the process of CO_2 methanation is also of significant importance and recent work [188] presented the possibility of lowering the energy spent / energy stored to 0.41-0.43, which is lower than the conversion of CO_2 to methanol process (0.45) (within their experimental conditions). Various catalyses have been used recently for CO_2 methanation e.g. Co/ZrO_2 and Co/Al_2O_3 [189], Ni_3Fe catalyst supported on gamma-Al_2O_3 [190], K_2CO_3/Al_2O_3 (transformation of CO_2 into methane with conversion > 99%) [191].

Biomass conversion to valuable products

Apart from CO_2, biomass is the only carbon-containing, abundant and renewable source of energy. Due to this fact, the increased use of biomass as a feedstock for the chemical industry is very attractive at first glance. However, utilizing it in an economical way is still an important challenge [192]. Between the various technologies, catalysis is expected to be a key tool for chemical transformations of biomass-based starting materials, which will contribute to a broader recognition of renewables [50]. Generally, there are three main conversion platforms to selectively convert biomass into more valuable products (i.e. pyrolysis, gasification, and biochemical).

Yamaguchi et al. [193] performed gasification of non-recyclable paper waste such as shredded documents and paper sludge. The order of the catalytic activity of metals for the gasification was found to be Ru > Rh > Pt/Pd. A charcoal-supported ruthenium catalyst (Ru/C) was found to be the most effective for the gasification of paper and cellulose. Production of hydrogen from polyethylene glycol contaminated wastewaters by supercritical water gasification with Ni/ZrO_2 heterogeneous catalysis was the subject of a paper by Yan et al. [194]. Gasification of sewage sludge and the possibility to use the created gas as a fuel was also evaluated [195-197].

However, fast pyrolysis was found to be the most efficient way of biomass transformation [192]. Ruddy et al. [198] reviewed the latest developments in heterogeneous catalysts for hydrodeoxygenation of biomass pyrolysis products. Applications of transition metal sulphide catalysts for deoxygenation processes were shown and related to the performances of noble metal and metal carbide, nitride, and phosphide catalysts. Agblevor et al. [199] tested red mud as a catalyst to substitute zeolites in a fluidized-bed reactor to pyrolyze biomass to make crude oil. The team processed the bio crude oil using a traditional catalytic hydrotreating process to make a gasoline-type fuel and tested it on a lawn mower, among other things.

Direct (single step), non-syngas based catalytic routes of methane conversion to value added products are also cost-effective and were reviewed in a recent paper [200]. On the other hand, scientists from Surrey [201] developed $Ni-Sn/Al_2O_3$ catalysts that can be

effectively utilised to produce flexible syngas streams from CO_2/CH_4 mixtures, and can be applied as an efficient route for CO_2 utilisation.

Heterogeneous catalysis for esterification and transesterification for the clean synthesis of biodiesel was discussed in several review papers [202-205] (also from the Chinese perspective [206]). In one of the examples, the transesterification reaction of rapeseed oil with methanol, in the presence of homogeneous and heterogeneous catalysis (Mg containing MCM-41, Mg-Al hydrotalcite and K^+ impregnated zirconia), for the creation of biodiesel fuel was studied [207]. In short, a homogeneous catalyst considerably hastened the transesterification reaction compared to the heterogeneous catalysts; however, the use of homogeneous base catalysts necessitates neutralization and separation from the reaction mixture, running to a series of environmental liabilities related to the use of high amounts of solvents and energy.

Biomass can also serve as a precursor for catalytic synthesis of liquid alkanes. Gu et al. [208] described a general strategy for the synthesis of high-quality lubricant alkanes from renewable biomass.

Conclusions and further challenges

As mentioned above, heterogeneous catalysis is applied in various branches of science but mostly in chemistry. For example, the activation of various kind of species can be obtained using various catalysts. Moreover, heterogeneous catalysis is very important for all aspects of environmental chemistry.

Heterogeneous catalysis is a discipline involving all the different aspects of chemistry, inorganic and analytical chemistry in order to characterize the catalysts and their forms (Fig. 5). Largely discussed here, surface science is a part of physical chemistry, the identification of the elementary steps to form kinetic loss and determine the damage of this reaction is a part of physical chemistry as well. As a last step, industrial chemistry needs to combine all of these things together to understand the solid handling, chemical reaction, energy engineering, and heat and mass transfer of these catalytic processes.

Nowadays, about 130 Tg of ammonia are used in fertilizers per year and about 2% of the total energy consumption arises from this industry. If it would be possible to find a process that works with lower energy costs, this would have enormous consequences, although this remains a challenge.

The next challenge would be to improve spectroscopic and microscopic methods to provide surface structural data as well as gas phase concentrations in a spatially and time-resolved manner. With help from theoretical scientists who can run sophisticated modelling (with such rapid development of computers) it would be possible to determine how all sorts of variables affect performance, i.e. from chemical composition, size and shape of metal nanoparticles, to the detailed architecture of support structures. Such partnerships between chemists and physicists should one day make it possible to wisely design superior catalysts for inexpensive fuel-cell vehicles, among other things.

Furthermore, ecological transport systems demand not only carbon neutrality during driving but also through the manufacturing and supply of fuel. Further development in heterogeneous catalysis will definitely result in an enhanced design of catalytic processes, which could be harmonious with the demands of our changing automotive and energy sectors.
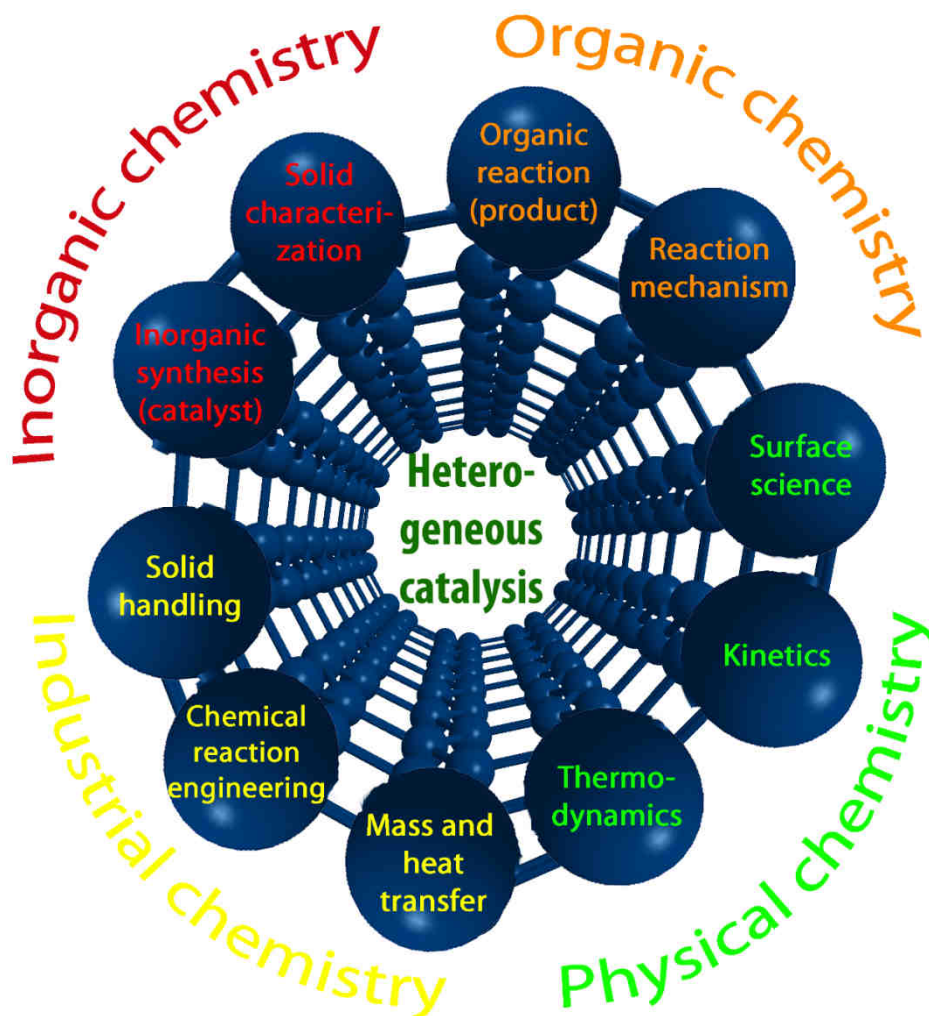
Fig. 5. Use of heterogeneous catalysis in various chemistry sectors

Lastly, it must be stated that the education and training of young scientists should focus more on "green" chemistry (including the chemistry of heterogeneous catalysis). In the future, it is important to change this state and to attract more chemists to this branch of chemistry for, as it is stated in [2], "the benefit of our children and their future".

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