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Inspirational perspectives and principles on the use of catalysts to create sustainability

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ABSTRACT

Most of the products on which our welfare state is based are composed of chemicals. The growth of the world's population, its ageing and the continuous improvement of welfare state aspirations augur an increase in the needs for all these everyday products in our lives. A high percentage of these chemicals are synthesised using catalysis. In this perspective paper, we highlight the importance of catalysis, which is at the heart of chemical processes, and therefore one of the tools for creating products that drive sustainability. We have compiled twelve methodological best practices in catalyst design and conception that can serve as inspiration for the creation and improvement of catalysts. We include some application examples to illustrate this.

1. Introduction

The idea of sustainability has been around for a long time but has gained considerable momentum in the last five years with the global campaign for the 17 Sustainable Development Goals (SDGs). Sustainability does not just mean living well and allowing our future generations to do the same. It is a profound concept that takes into account three basic pillars: the economy, the environment and society. These pillars have to be based on a level playing field, not only for future generations but also for today's generation. These pillars are underpinned by equality and are constantly evolving through the myriad disciplines of science, engineering, architecture, medicine, politics, the arts, humanities and culture to the fullest extent. By getting down to earth, every discipline can play a part in paving the way towards a sustainable society.

Chemistry and chemical engineering are at the basis of our daily lives, providing the main products that meet our demands and needs to maintain and improve our state of well-being.

The principles of green chemistry established a user-friendly framework for sustainable process design with a core in chemistry. In 1998 Paul Anastas and John Warner were able to distil from the best practices of chemistry, real and affordable practices that were already in application [1]. More than twenty years later, green chemistry is already a core discipline in most chemistry faculties and companies around the world, although a real push is still needed to make it a permanent reality.

Among the principles of green chemistry, one that incorporates considerable improvements in all the others is catalysis. Catalysis makes it possible to make materials react that did not previously do so, opening up the possibility of using renewable, safe or more readily available materials. It also makes it possible to reduce operating conditions in terms of pressure and temperature, with consequent energy savings.

Catalysis is at the heart of most chemical processes. Ninety-five per cent of chemicals in industry, which is equivalent to 80 per cent of their added value, are synthesised using catalysts. Of these, heterogeneous catalysis accounts for almost 80%, homogeneous catalysis for 15% and the rest is biocatalysis [2]. In many cases, the optimisation of these processes is so refined that it is very difficult to improve them further. In such circumstances we must find the breakthrough by approaching the heart, the catalyst.

In this perspective paper, we would like to recapitulate on twelve current trends that can be of great use for the definition of new out-of-the-box catalysts that intrinsically promote sustainability from within processes. With the help of these basis and a dash of creativity, we believe that existing catalysts can be improved, but also new, game-changing catalysts can be created.

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2. Basic principles for catalysis towards sustainability

2.1. Active metal

Use active metals that are accessible, stable and low-cost. Avoid the use of endangered, toxic or dangerous metals.

In most catalysts, metals are at the core of their catalytic activity and performance. Therefore, efforts to develop a more sustainable catalysis must consider the sustainability of active metals. The assessment of this characteristic can be focused on three main aspects: i) availability, ii) low cost, and iii) toxicity. In terms of availability and cost, there are major differences depending on the type of metals, being those called precious metals far less available and more expensive than those referred as base metals. Precious metals are in the second and third rows of the periodic table and those commonly used as transition-metal catalysts are Pt, Pd, Rh, Ru, Os, Ir, Au and Ag. They lack abundance in the Earth crustal, and that determines their high cost and fluctuations in price and supply. For example, in the period between 2018 and 2019, average palladium and rhodium prices were up 20% and 83% respectively, while the platinum price declined 11% compared to the same period last year [3]. The British Geological Society released a list of metals at risk of supply disruption where the platinum-group metals (ruthenium, rhodium, palladium, osmium, iridium, and platinum) are estimated to be at the highest risk [4]. In addition to the obvious economical and supply concerns related to precious metals, they also have environmental implications. Actually, mining and refinement of these materials require a large use of energy and emit large amounts of CO_2 [5]. Even though their high demand and scarcity, it is estimated that less than 1% of precious metals are recycled for reuse. This low percentage is due to the low economic viability of recycling processes, which often require large amounts of water and highly corrosive acids, while generating large amounts of waste.

In this scenario, a current approach in the development of more sustainable active metals relies on the use of high crustal abundant metals referred as base metals. Titanium, vanadium, chromium, manganese, iron, cobalt, nickel, and copper, represent base metals with advantages over the use of platinum-group metals such as low cost, global availability and lower toxicity. Progress is being made in recent years to enhance the reactivity of base metals and overcome disadvantages like lower stability, selectivity and changing oxidation [5]. Despite base metal catalysts have been proved reliable for some reactions, further research is needed to confirm their feasibility in other reactions traditionally performed with precious metals, which will lead to substantial benefits for the future society and environment.

Regarding toxicity, base metals are often considered less toxic than precious metals with minimal safety concerns. However, the assessment of toxicity is complex. Actually, several works reported that widely considered heavy and toxic metals such as palladium, platinum, and gold compounds may not be so dangerous, while complexes of nickel and copper, generally assumed as green and sustainable options, may be significantly toxic (i.e., due to their solubility in water and biological fluids) [6]. A pioneer work recently reported a comprehensive comparison of the toxicity of 18 metals typically used in catalysis based on multicriteria analysis considering parameters such as the toxicity of pure metals and metal salts toward fish, *Daphnia magna*, and algae/plants, metal toxicity toward rats via ingestion, carcinogenicity, the endangerment degree of metals, the boiling point and energy for atom detachment [7]. Their conclusions were similar to those found in previous works [6] and showed ruthenium, molybdenum, platinum and manganese as the most favourable (less toxic) active metals, in contrast to nickel, cobalt, and palladium as the most toxic.

2.2. Designed in-silico

Design the catalyst using the best available in-silico techniques to optimise resources dedicated to testing and speed-up the development.

Heterogeneous catalysis exhibits an inherent design, invention difficulty and required effort as it combines atomic, microscopic, mesoscopic, and macroscopic scales. It involves thermodynamics, reaction, adsorption/desorption and mass transfer.

The observation of the reaction can be done by computational methods, but reaching chemical accuracy (error lower than 1 $kcal{\cdot}mol^{-1}$) is limited to few atoms. The calculation can be simplified by using Density Functional Theory (DFT), which allows the simulation of up to 100 atoms, at the cost of considerably reduced accuracy. Large areas cannot be simulated due to the high computational power required [8]. Furthermore, there are a number of grand challenges in the computational catalysis that still have to be solved, e.g. exponentially of rate of reaction with energy barrier, complexity of ligands in homogeneous catalysis, surface interactions with the active metal in heterogeneous catalysis or the difficulty of modelling electron and proton transfer steps in electro-catalysis [9].

Ab initio atomistic thermodynamics can be used together with DFT to investigate the influence of temperature, pressure or composition in the surface free energies.

The understanding of the reaction implies the prediction of reaction mechanism and reaction pathway, together with the kinetics. Microkinetic modelling can be done, for instance, by combining the Lattice-gas Hamiltonian (LGH) with Monte-Carlo (MC) simulations [10].

Machine Learning (ML) and Deep Learning (DL) techniques allow for the fast calculation of these atomistic properties, e.g. binding energy, using previous data from DFT of MC simulations.

Saxena et al. screened the catalytic options for ethanol decomposition and non- oxidative dehydrogenation reactions [11]. Single atom alloys and bimetallic alloys were analysed using ML, optimising the binding energies of oxygen and carbon starting from well-known properties. After selecting a proper alloy an ab initio microkinetic model was applied to estimate the performance (turn over frequency, TOF). The calculation took less than a second.

Kinetic experiments will in many cases be unavoidable, but the use of computational techniques can greatly reduce resources and time spent. The right combination of simulation prediction and experimental verification is the key to improvement in the medium and long term.

2.3. Scalable fabrication

New improved catalysts supports/structures and their manufacturing techniques are aimed to facilitate the performance of reactors at large/industrial scale.

Some examples of scalable-easy-manufacturing catalysts may be focused on the enhancement of design and fabrication of the catalyst at macro-level in order to optimise the mass/heat transfer and overall performance of the catalytic reactor system [12].

Moreover, the applicability of the catalyst is increased if it can be prepared in different formats, i.e. powder, pellets, foams, monoliths, etc.

3D printing allows for a very specific and tailored design for mass transfer and low pressure drop. Special attention has to be taken to the binders used [13].

2.4. Fast induction and in-situ activation

Fast induction periods are desired, saving time and materials. In-situ activation eases the handling and activity.

Fast induction rates allow catalysts to reach their optimum activity (highest conversion and selectivity) in short period times since they are activated, which benefit the performance of the reaction and increase the productivity, saving time and materials.

In-situ activation also eases catalyst handling and activity. Thus, a specific catalyst design/preparation aimed at shortening the induction period of the catalyst or improving the activation procedure (i.e. reducing time/energy consumption, or eventually, improving the catalysts performance or stability) may have a significant impact on the

overall performance and time life of a catalyst, thus improving its properties as a more stable and efficient material, and thus its sustainability in terms of cost and environment impact [14]. One example is improvements in the design of catalysts for methane dehydro-aromatisation (MDA) reaction, in which a specific mixed of metals (Fe, Pt) to dope the active phase is able to promote a rapid formation of the active sites and, in addition, to withstand sintering/agglomeration, thus, improving the stability and optimal performance of the catalyst and also inhibiting the accumulation of coke on the external surface of the catalyst during the reaction [15,16].

2.5. Stability

Design for stability, to avoid poisoning, degradability and leaching.

Despite catalysts are not consumed during reaction, their stability is limited and tend to deactivate with prolonged reaction times. Catalyst deactivation leads to a significant decrease in process yield and selectivity with production of undesirable components. Therefore, decreasing or avoiding deactivation is essential to improve sustainability in catalysis and thus reducing the need to replace spent catalysts with consumption of new materials, energy and water. At the same time, improved stability may enhance the efficiency of the chemical process saving operation cost and decreasing the production of pollutants and undesired by-products.

In order to design stable catalysts, it is paramount to understand their specific deactivation reasons. The most common ones are summarised below along with some strategies applied to overcome them.

i) Poisoning by components in reagents or reaction intermediates. A typical example of poisoning occurs during hydrocarbon processing where sulphur is present in some reagent molecules (mercaptans, thiophenes…). Sulphur is strongly chemisorbed over metallic surface of catalyst (and may form stable metal sulphides) and disables its catalytic activity. CO is another well-known poison for catalysts. This is a critical issue in fuel cells fed with hydrogen produced from hydrocarbons. Small presence of CO in the hydrogen feed (over 20 ppm) leads to quick deactivation of Pt catalyst in the anode of the cell since it is adsorbed over the Pt surface forming stable Pt-C bonds. Another typical example of poison is coke. It is an undesirable by-product produced during hydrocarbon processing at high temperatures. It does not form chemical compounds with metals or supports. However, it grows over the catalyst surface and blocks the access of reagents to the catalytic active sites.

ii) Sintering, described as a compaction and densification of active metals or supports, frequently occurs when a catalyst is subjected to high temperatures. In supported catalysts, high temperatures leads to a nucleation of the dispersed metallic particles and their aggregation in the form of larger crystals with subsequent loss of active sites exposed to reagents. The consequence of this process is a decrease of the catalytic activity. Catalytic supports also suffer from this compaction process and collapse of their porous texture. The outcome is a reduction of the surface area of the catalyst, diminishing the active sites exposed to reagents. Similar compaction effects take place in bulk catalysts lowering their catalytic activity.

iii) Loss of catalyst components in the reaction media. These phenomena occur in liquid phase catalysis (eg. the lixiviation of Ca from catalysts during synthesis of biodiesel) but also in gas phase reactions, when metal particles of certain elements volatise under high temperatures (eg. RuO_2 is oxidised and forms gaseous RuO_3 and RuO_4 molecules). Another example under this section is the dealumination of zeolites used as catalysts or catalytic supports when subjected to harsh hydrothermal conditions.

Different strategies have been applied to improve the stability of catalysts and overcome or reduce their deactivation. For example, the addition of lanthanides (usually La or Ce oxides) to catalytic supports promote the formation of carbonate and hydroxyl intermediates during reaction which contribute to the gasification of coke produced from hydrocarbons processing [17].

Sulphur traps are also used to preferentially adsorb it and avoid the contamination of the active metal sites. The Ellingham diagram of metal sulphides is an interesting tool to choose the right components of these traps since it shows free energy of formation of different sulphides at different temperatures. A recent example is the use of Mn oxides as sulphur traps in emission control catalysts [18].

In order to avoid sintering of alumina supports, manufacturers have engineered optimised formulations by forming highly thermally stable aluminates (e.g. $LaAlO_3$) in the surface of alumina. Despite the reduction of the surface area of the novel support, the stability of its porous texture under high temperature is greatly improved.

Zeolite catalysts used in fluid catalytic cracking processes usually suffer from dealumination by steam at high temperatures. A strategy to address this issue is by engineering the zeolites with the addition of rare-earth elements and phosphorus [19].

2.6. Biomimetic

Catalysts designed by nature are very effective, work at ambient conditions and are very specific by using molecular recognition (self-assembly).

John Warner, one of the early founders of Green Chemistry, illustrates very well how the basis of modern chemistry is based on collision reactions. The probability of collision is increased by increasing pressure and temperature [20]. At the same time, he points out that this model differs greatly from nature, where there is no single collision reaction. In nature, molecules approach, recognise, "snuggle" each other and then react at ambient pressure and temperature.

Moreover, Janine Benyus opened a simple way to design inspired by nature. Biomimicry takes nature as a model, as a mentor and as a measure. Catalysts exist in nature, it is the only way to create efficient and effective reactions at room temperature and atmospheric pressure.

Directly designing an enzyme is still a long way off, but mimicking them is now possible. There are several possible options for creating biomimetic metal organic framework (MOF) catalysts as explained by Chen and Chuan [21]:

- Using metals as biomimetic active sites.
- Encapsulation to prevent self-aggregation and increase shelf life.
- Newly created support or framework based on a similar biomimetic structure.
- Incorporation of biomimetic parts via organic linkers
- Post-synthesis modification

The traditional chemistry of preparing imines from aldehydes, ketones, amines, nitriles and others is well known. But of all the possible methods, reference was rarely made to how nature does it. Specifically, copper amine oxidases (CuAOs) are responsible for these processes of controlling the metabolism of amines of different types. Bioinspired by CuAOs, quinone-based catalysts have been developed [22].

2.7. Circular by process design or origin of the resource

The catalyst should be designed to be circular in the support, active metal and additives.

A catalyst based on the circular economy can be developed based on different approaches, which typically take into account the entire catalyst value chain, from the origin and resources of the materials the catalyst is made of, to the after-life of the catalyst, and key impact/sustainability parameters such as the carbon footprint of the manufacturing process. Different approaches may be considered to qualify a catalyst as sustainable based on the circularity of a catalyst, as

outlined below:

I. Circular by origin of the raw materials/resources:

Presently, most of the catalytic materials are sourced from finite geological deposits. By recovering catalyst from waste and reclamation of active metals from spent catalyst, the dependence on natural resources that are unsustainable will be reduced, likewise the quantity of materials going to landfill. A circular economy perspective, considering the E-waste management along with the recovery of noble metals from spent catalysts, can be considered as a new concept of catalyst cradle-to-cradle process and, eventually, a promising sustainable source for catalytic materials manufacturing [23–26]. An example of this emerging circular value chain is the recovery of the valuable metals from industrial and post-consuming products such as electronic waste materials (E-waste). According to the Global E-waste Monitor 2020 [27], E-waste is the world's fastest growing waste stream and the amount is estimated to increase to 52.2 million metric tonnes by 2021 and the trend could be going up to reach the amount will reach 74 million Mt. in 2030. The increasing generation and accumulation of E-waste is clearly pointing to a critical environmental challenge which needs to be addressed in the immediate future. Thus, the design of renewable catalyst made from waste materials or a catalyst based on recycled materials is an alternative clearly more sustainable, especially when it is aimed at precious metals which are more difficult, expensive -and environment-costly- to extract (e.g. Au, Pt, Pd, Ru, etc.) [28, 29]. In addition, the recovery of valuable minerals from industrial effluents treatment and leaching process in mining exploitations are potential applications than can be develop as potential case exploitations based or circular-by process/design [30,31]. To that end, several strategies have been reported for metals recovery from E-waste and industrial streams, although there is still a long way to go to find environmentally friendly and efficient protocols in this regard [30,32]. In combination with Section 2.1, when the use of noble metals is required (as substitution is not possible), finding sustainable recycling methods and strategies will be the key to success.

II. Circular by the manufacturing and performance process design:

Catalysts that use green/clean technologies for their fabrication involve the utilisation of fewer natural resources, reducing pollution and waste, recycling and/or reusing materials, and producing moderate emissions in their processes. All these inputs lead the manufacturing process to consume less energy and resources making the fabrication of the catalyst itself more sustainable and cost-competitive than other conventional processes [28]. The green technologies most frequently encountered are the recycling of waste, waste water treatment and renewable energy, for instance, the application on new hierarchical-titanium dioxide catalysts, which include active microporous zeolites and mesoporous matrix for diffusion, allows for innovative green applications such as the synthesis of fuels from catalytic cracking of waste plastics [33].

III. Circular by the end-use or application of the catalyst:

A catalyst may be also considered sustainable if it has been designed for special applications focused on climate change mitigation, e.g. through the production of carbon-negative products and fuels (CO_2-to-chemicals processes), elimination of pollution from industrial/human activity in the world, etc. [34,35]. Additionally, the catalysts for automobile emission control are based on precious metals such as platinum, palladium, and rhodium. At present, more than 15 international companies are producing about 100 fundamental types of solid catalysts. Catalysts play an essential role in industry not only in economic terms but also in reducing pollution of the environment [36].

2.8. User of renewable resources

Active catalysts with renewable materials may help in the transformation of our oil-based society into a bio-based society.

Active catalysts with renewable materials can help transform our petroleum-based society into a bio-based society, for example by producing chemical building blocks derived from CO_2, such as C1 molecules (methane, methanol, formaldehyde) or different C2-C4 molecules ranging from ethylene/olefins materials to other long-chain hydrocarbons, or even offering an alternative to the current production of products from crops or other bio-based materials (e.g. agricultural residues such as terpenes, fatty acids and lipids can be used as bio-based platform chemicals for the preparation of biopolymers). For example, agricultural residues such as terpenes, fatty acids and lipids can be used as bio-based chemicals for the preparation of biopolymers [37,38].

In addition, active catalysts towards biomass and natural products contribute to the decarbonisation of industry and the economy to boost the transformation of our oil-based society into a bio-based society. There are several examples of new catalysts specifically designed for the transformation of biomass into biofuels and renewable chemicals. These catalysts will play an important role in integrated biorefineries and bio-based industries in the future [39]. As an example, one of the most promising heterogeneous catalytic processes in biomass being studied is the production of furfural. Furfural is a C5 building block that can be converted into a large number of value-added chemicals and bio-chemicals, as well as producing advanced synthetic fuels [40].

2.9. Aligned with SGDs

The product may help in the advance of society towards sustainability. The target of the main product should be aligned with one or several of the SDGs.

Humanity faces major challenges that affect billions of lives. In the last 50 years the world's population has doubled from 3.8 billion to 7.8 billion people. The foundations of sustainability were outlined in the report World Commission on Environment and Development in 1987 [41]. Far from focusing only on the classical definition that refers to the first line of the report, the term sustainability is very deep and difficult to understand and to define clearly. It is linked to the welfare state with its needs, aspirations and the individual interpretation of each of them [42]. These ideas have been translated over the years into various joint global actions, such as the millennium goals. However, it was not until 2015 with the establishment of the 17 Sustainable Development Goals (SDGs) that there has been a real take-off and a global understanding, not only by creators, but also by companies, media and public opinion [43]. So much so that clear references to the different goals can now be found in practically all products, processes and organisations.

From a simplistic point of view, the welfare state, its needs, are satisfied through products (understanding product in a global way). The increase in population comes with an increase in the number of needs and therefore an increase in the consumption of products. The inherent aspiration to improve the welfare state of each individual also increases it.

Chemistry and chemical engineering are at the foundation of the creation of various commodities: food, medicines, construction, transport, communications, packaging, clothing and others. Catalysis and catalysts have not only accelerated the kinetics of reactions at the molecular level, they have served to accelerate the development of the welfare society by giving universal access to all these products. Catalysis has helped to reduce the consumption of raw materials and energy and to avoid more toxic or dangerous production routes, for example.

Sometimes when we are in our labs trying to create a new catalyst or improving one of its processes we lose perspective, we look too close by zooming in. We are very focused on reducing the temperature by 1 °C or the pressure by 1 bar or the amount of catalyst by 1 mg to make it more sustainable. But we have not stopped to think about what this really

means.

Zooming out will help us understand why our actions in developing a catalyst contribute to improved global sustainability. And more importantly it will give us extra motivation for continuous improvement.

Johnson Matthey has developed this idea in its GRI report in which it analyses some of the global needs and explains its strategy at the product development level (catalysts) to contribute globally [3]. For example, they estimate that the demand for hydrogen will increase tenfold in the coming years and present a portfolio of catalytic technologies for its generation. They are also looking at scaling up fuel cell processes for electricity production by hydrogen conversion.

2.10. Low impact subproducts

Catalysts should be designed to avoid subproducts or to minimise their environmental and economic impact.

Avoiding the formation of undesirable side products prevents the waste of chemicals, minimises the need of purification steps, affects the energy consumption of subsequent separation processes and makes the processes more environmentally friendly [13]. Actually, catalyst selectivity directly determines the atomic economy of the catalytic process.

Therefore, the smart design of heterogeneous catalysts should improve their selectivity by avoiding the formation of subproducts and/or minimising their environmental and economic impact.

Unfortunately, enhancement of selectivity is typically achieved at the expense of overall activity [45]. High catalyst selectivity is achieved by applying strategies of coupling, decoupling or confinement of adsorption sites and active sites to tune the diffusion barrier and activation energy barrier in different routes. For instance, undesirable sites on the surface of heterogeneous catalysts are often blocked via pre-treatments with specific chemicals. This is the case of hydrocarbon reforming catalysts, which are exposed to small amounts of H_2S before introducing the crude oil feeds. Sulphur selectively blocks the surface sites for hydrocarbon hydrogenolysis, affecting those for skeletal isomerization to a much lesser extent [46]. Another example is the hydrogenolysis of glycerol to 1,2 – propanodiol (1,2 – PDO) [47]. Ru/C catalysts are poorly selective towards the target 1,2 – PDO achieving a 12% selectivity whereas the main product obtained is ethylene glycol. However, when the same catalyst is sulfonated (Ru-S/C) the selectivity to 1,2 – PDO greatly increases to 79%. A similar strategy has been reported for the selective hydrogenation of benzene to cyclohexene over Ru-Zn catalysts as a synthetic route to obtain nylon. A critical step in this reaction is the undesired formation of cyclohexane which is a more stable product than cyclohexene. Hydrophilic modification of the Ru-based catalyst is the most effective way to improve cyclohexene selectivity [48]. The stagnant water layer formed over the catalyst support is enriched in benzene whereas cyclohexene (the first hydrogenation product) quickly desorbs from it. This process enables the further progress of this reaction and avoids additional hydrogenation of cyclohexene to cyclohexane since the diffusion gradient drives the migration of the former into the aqueous phase.

2.11. Open data and artificial intelligence

Sharing catalytic data and manufacturing techniques together with artificial intelligence (AI) may boost for new sustainable catalysts and applications.

The availability of catalytic open data from design, characterisation, operational variables (pressure, temperature, flowrate, etc.), performance KPIs (e.g. conversion, selectivity, etc.) and kinetics will help in the improvement and design of future catalysts and catalytic processes. The use of artificial intelligence relies on the availability of enough data and high-quality data.

A number of databases are now available related to material properties, crystal structures, inorganic materials, surface reaction energetics and DFT calculations, 2D materials, chemical reactions on catalytic surfaces and others [49]. Training a proper ML algorithm with such data instantly (e.g. 788 reaction data set), activation energies can be estimated with 90% accuracy almost [50].

One recent example can be found in the web-based catalytic platform Catalyst Acquisition by Data Science (CADS) providing management and analysis of data and prediction of properties [51].

2.12. Operando and in-situ tracking

Measuring the real instantaneous performance of the catalyst at relevant reaction conditions will enable a better optimisation of the catalysts, their processes, and better future designs.

The knowledge of structural characteristics of the catalyst, e.g. surface structure, and the main kinetic performance parameters in terms of conversion, reactivity, selectivity and yield are key for a good catalyst design.

In situ characterisation has been carried out during the last 60–70 years and provides valuable information of the catalyst in its working place, but under a controlled atmosphere. Operando goes far beyond, measuring simultaneously the catalyst characteristics and the product scheme. Under such approach the catalyst structure is observed under real or almost-real conditions of pressure, temperature, flow, reagent concentrations, etc. which enables the connection between structure and performance to a higher level. Almost any type of catalyst can be analysed using operando, supported or unsupported, metal or metal oxides and of many types, such as mesoporous silica, zeolites, polyoxometalates, bulk mixed oxides, sulphides or even sorbents in a vast number of reaction applications [52].

Operando is difficult to master. According to the data obtained from a Scopus database search (i.e. “in situ+catalysis” vs. “operando+catalysis” or “in situ spectroscopy + catalysis” vs. “operando spectroscopy + catatalysis”) year after year more groups around the world are joining in, with chemistry (34%), chemical engineering (27%) and materials science (11%) being the areas that use it the most. At the same time, in situ analysis continues to grow and provide valuable information. Considering scientific publications, "in situ" is still between 4 and 9 times higher in volume than "operando" in 2020 depending on whether the word "spectroscopy" is added to the search. The in situ technique is more widely used, as it is understandable that not all groups involved in catalyst characterisation study the kinetics and specific reactions in such detail.

The current man-made climate change is strongly related to human activities and in particular to CO_2 emissions. Major R&D efforts are being made in CO_2 capture in several ways. Chemical CO_2 capture can be achieved by non-reducing strategies (carbonates, ureas, carbamates, carboxylic acids, etc.) and by reductive strategies (H_2, CO, methanol, formic acid, etc.) [53]. Reductive strategies are complicated, as they require large amounts of energy and/or more drastic conditions, so the room for improvement is large. As an example, Yang et al. demonstrated the effectiveness of single-atom heterogeneous catalysis in electrochemical CO_2 reduction [54]. They identified the catalytic activity of single-Ni-atom, i.e. monovalent Ni(I), for the CO_2 reduction using operando X-ray absorption and photoelectron spectroscopy. Operando analysis allows a better understanding of the principles of catalysis and thus the possibility of better catalyst design. Cheng et al. carried out a similar research based on the deposition of the single-atom-Ni and other metals on nitrogen-doped carbon nanotubes [55].

In many cases, the terms in situ and operando are used interchangeably, as Grey and Tarascon pointed out [56]. They present a comprehensive analysis of in situ/operating techniques used in electrochemistry for the design and analysis of more sustainable batteries. In particular, how to improve charge and discharge cycles. Reducing the amount of active metal required or improving the number of cycles are clear examples.

3. Conclusions

The world is accelerating and more and more products are being used every day. Chemistry and chemical engineering are at the basis of the creation and production of these products that contribute to the welfare society. Certainly, catalysis is one of the technologies that can drive the development and creation of new products. At the atomic-molecular level, catalysis is able to reduce the energy barrier and even eliminate it, making the miracle possible.

We have analyzed the best and most innovative practices in catalyst design considering sustainable chemistry, with the basis on the principles of green chemistry and green engineering. As a result of that we have compiled 12 basic principles that may inspire the improvement or creation of new catalysts considering the active metals, the products created and renewable resources used, scalability, stability, fast-induction and circularity. We also focus on computer science for possible in silico design and everything related to data and artificial intelligence. Importance is given to biomimicry, getting inspiration from nature's designs and operando techniques to unveil the real catalyst in action. Finally, the purpose of all this should be based on grand challenges such as the Sustainable Development Goals.

We can certainly say that catalysis is an exponential technology (following Peter Diamandis' thinking). Mathematically, because it is based on Arrhenius' law, but practically because it affects more than a billion people every day.

CRediT authorship contribution statement

Juan García-Serna: Conceptualization, Methodology, Visualization (graphical abstract), Writing – original draft, Writing – review & editing and Supervision. **Raúl Piñero-Hernanz**: Writing – original draft, Writing – review & editing. **Desirée Durán-Martín**: Writing – original draft, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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