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Grand challenges for catalysis in the Science and Technology Roadmap on Catalysis for Europe: moving ahead for a sustainable future†

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This perspective discusses the general concepts that will guide future catalysis and related grand challenges based on the Science and Technology Roadmap on Catalysis for Europe prepared by the European Cluster on Catalysis. To address the changing scenarios in refinery and chemical production and move to a low-carbon sustainable future, the distinguishing elements of three grand challenges for catalysis are discussed here: 1) catalysis to address the evolving energy and chemical scenario, 2) catalysis for a cleaner and sustainable future, and 3) addressing catalysis complexity, the latter being organized into three sub-topics: advanced design of novel catalysts, understanding catalysts from the molecular to the material scale, and expanding catalysis concepts.

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Introduction

The main catalytic industrial processes currently in use were introduced in the twentieth century, mostly around the 1960s.[1,2] Key processes and the associated catalysts in refinery (reforming and hydroreforming, cracking catalysts, water gas shift, hydroisomerization and metathesis) and petrochemistry (propylene oxidation and ammoxidation, adiponitrile, propylene oxide, acetic acid, vinyl chloride, maleic anhydride) were

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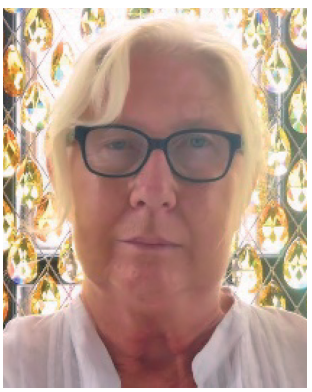

Siglinda Perathoner

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introduced. Although some developments have been presented slightly earlier (like hydrodesulphurization, Ziegler–Natta polymerization, Wacker ethylene oxidation and *p*-xylene oxidation) or later (methanol low pressure, vinyl acetate), it can be stated that the present structure of chemical production is largely sixty years old, with most of the catalysts in current use being essentially an evolution of those developed in those years. It can be highlighted that the transition to new refinery and petrochemistry (the latter based on light olefins as the main raw materials) has been concentrated in a relatively short period, around slightly more than a decade. Advances in understanding these catalysts have definitively improved their performances, but R&D of these directions has been progressively decreasing, being among those considered as "mature" technologies. New topics such as catalysis for biomass transformation have stimulated new developments in the last decade,[3–9] but the perception of the need to move to a new "disruptive" type of catalysts is increasing. Disruptive means catalysts based on new conceptual approaches and catalysis families to address the increasing societal demand for more sustainable production.[10,11]

Driven by competitiveness in a changing economic world with an increasing transition to renewable energy, chemical and refinery production are in a major transition phase to go beyond fossil fuels (as the main raw materials and energy source) and to increase sustainability.[12–17] It is worth noting that economic growth has shown cycles of about 60–70 years in the past, with a new cycle (synchronized also for the chemical industry) requiring the introduction of new technologies to address the change in use of raw materials and societal requirements.[2]

It is thus necessary to rethink chemical and refinery production methodologies, with a consequent need for new catalysis approaches. The future chemical production requires radically new types of catalysts and catalytic technologies. Develop a coherent approach to define the gaps and opportunities for catalysis to address this transition was the stimulus for the large and widespread effort to prepare a new "Science and Technology Roadmap on Catalysis for Europe".[18] The work was coordinated from the thematic European Cluster on Catalysis[19] launched in 2015 by the European Commission (Directorate General for Research & Innovation, Industrial Technologies) and gathered together more than 450 scientists, both from academia and industry, all over Europe. The roadmap can be downloaded from the Cluster on Catalysis website.[19]

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Three "grand challenges for catalysis" were identified in this roadmap: i) catalysis to address the evolving energy and chemical scenario; ii) catalysis for a cleaner and sustainable future; and iii) addressing catalysis complexity, the latter being organized into three sub-topics: a) advanced design of novel catalysts, b) understanding of catalysts from the molecular to the material scale, and c) expanding catalysis concepts. What emerges from this analysis is that the above-mentioned development areas require only in part to extend current catalysts uses and design (evolutionary development), for example in the area of biorefinery.[13] In fact, there are various areas requiring instead conceptually new types of catalysts and catalytic approaches, for example in solar-driven chemistry (*i.e.* chemistry driven by the use of renewable energy rather than thermal energy deriving from fossil fuels). This is the reason for the emphasis given in the roadmap on expanding catalysis concepts, in addition to the general need for a better understanding of catalysts from the molecular to the material scale.

This perspective paper, based on, but not limited to, the cited roadmap,[18] will discuss some of the characterizing aspects of these three grand challenges for catalysis. The aim is to present the general concepts that will guide future catalysis developments, with indications on trends and gaps in catalysis to accelerate progress in these fields. With respect to the roadmap, this perspective paper identifies a limited number of key aspects and provides the scientific background and literature to support them.

Factors shaping innovation in catalysis

Innovation in catalysis takes shape through push and pull factors. Push factors relate to the growing insight into the molecular basis of catalysis, which is spurred in particular by tremendous developments in *in situ*/*operando* characterization tools and computational chemistry methods.[20–25] Experimentally, progress stems also from major strides made by employing ever more realistic surface science models of heterogeneous catalysts.[26] In computational modelling of catalytic processes, there is an increased effort to describe the transformation over multiple length and time scales, *e.g.* to include transport phenomena together with the catalytic event. In addition, the understanding of the catalyst synthesis from a mechanistic perspective has been significantly progressed.[27–30] Together, these factors push the field of catalysis ahead from description to prediction. Whilst progress in these areas is impressive, it remains necessary to utilize the acquired insights to accelerate the discovery of novel catalysts to address new challenges arising from changing scenarios in society and the chemical industry.

To cope with these challenges, it is essential to foster and tighten the synergy between fundamental research and technological applications. A more rational approach to the development of new catalytic materials for chemical processes is in demand.[31–33] It should be knowledge based, but with a better identification of the key aspects which determine the reactivity. Important elements of such an approach are advanced synthetic approaches aimed at delivering materials with specific functional characteristics necessary to improve the catalytic performance,[34] preferably starting from cheap, earth-abundant and easily accessible raw building blocks.[35] The "catalysis by design" approach currently mostly refers to the use of as realistic as possible model systems, but its accomplishment is still hampered by a gap with aspects controlling reactivity under real conditions.[20,27,36–39] There are even some fundamental aspects, such as the turnover number, which need to be reconsidered, in particular regarding the relaxation time between the end of a catalytic cycle and the start of a new one. This time, typically not considered in mechanistic studies, instead often determines the overall turnover. A better understanding of the factors determining this relaxation time, and how to accelerate the process is thus key to increasing catalytic turnover,

There is a great need to also apply these methods to the synthesis of catalytic materials so that the concept of the ideal active site (particular in multifunctional catalysts) can be realised in the scalable production of catalysts.[40] *Vice versa*, it is highly desirable to understand the operation of technically relevant catalytic solids for which *in situ*/*operando* spectroscopy/microscopy is ideally suited, even if more effort is required to differentiate clearly between active and spectator or slowly transforming species.[41] Together, these approaches can lead to a real bottom-up approach to catalyst design by bridging the gap between theory and experiments under real (practical) conditions.[42–44] These goals can only be met by combining expertise in synthetic (organic and inorganic) chemistry in the context of materials science, theoretical modelling, physical chemistry and reaction engineering. Advances in understanding the reaction mechanism should be paralleled by progress in the science of catalyst preparation on the nanoscale level and in advanced microkinetics and reactor modelling.[21,45–51]

The pull factors are not only the need to increase energy efficiency and reduce waste in the chemical industry but also the growing need in industry to develop novel production routes for chemicals and fuels to increase competitiveness. Key elements to achieve these goals are catalyst design for multistep reactions,[52] *e.g.* to realize complex transformations in fewer steps (process intensification) and to exploit renewable energy sources in chemical production (solar-driven chemistry).[53] Another main driver is the change in the energy–chemistry nexus,[54] requiring one to reconsider the actual structure of the chemical production.

Industrial competitiveness is highly dependent on the identification of new reaction paths and the associated catalysts. Important aspects to accelerate the progress in this area deal with catalyst complexity: effective integration of homogeneous, heterogeneous and bio-catalysis[55] and implementations of new approaches for the design of multifunctional catalysts and for the advanced combination of catalysts and reactors in process intensification are among the main elements to explore. Among the emerging directions in catalyst design to move to the next-generation catalytic materials (Fig. 1), it is worth highlighting the following:

i) Understand cooperativity in catalysis, *e.g.* the role of the (supramolecular) environment around the active site and of surface ad-species (both reactive and spectator) and the synergy between main-group chemistry and transition metal chemistry leading to novel reactivity concepts, *e.g.* by unusual bonding modes.

ii) Develop heterogeneous catalysts prepared with atomic-scale precision, exploring in more detail the concept of single-atom catalysis; tailored design of the reaction environment, linking hierarchical design of catalysts on the nano- and mesoscopic scale to optimal reactor design on the macroscale including process intensification.

iii) Address the relaxation time for the catalyst active sites. This is the idle time necessary for a single active site to start a new catalytic cycle after having completed the former. This is often a key aspect determining the turnover.

iv) Develop novel approaches to break, in a specific substrate, strong bonds in place of the weaker ones, and novel possibilities to activate selectively small molecules such as O_2, N_2 and CH_4 under mild conditions. This would require developing conceptually novel catalysts.

v) Realize new strategies to force a sequence of transformations (in a specific order, *e.g.* vectorial reaction sequence) over a series of different active sites to move beyond the cascade reaction approaches.

vi) Design tailored catalysts, particularly for the new emerging areas of electro- and photo-catalysis. This involves, for example, the controlled synthesis of innovative nanocomposite catalysts and electrocatalysts by exploiting two-dimensional (2D) active layers (besides graphene). Besides graphene, chalcogenides, 2D oxides, monolayer catalysts and nanocarbons may be named as materials with interesting properties.

vii) Exploit novel possibilities given by integrated catalyst design. An example is tandem catalysis, which combines a homogeneous or heterogeneous catalyst and an enzymatic catalyst. Another example is the use of catalysis (in particular, photo- or electrocatalysis) to accelerate enzymatic reactions by substituting the use of cofactors in enzyme catalytic cycles.

Although not exhaustive of the various possibilities, these emerging directions will likely be among the key factors shaping innovation in catalysts.[56]

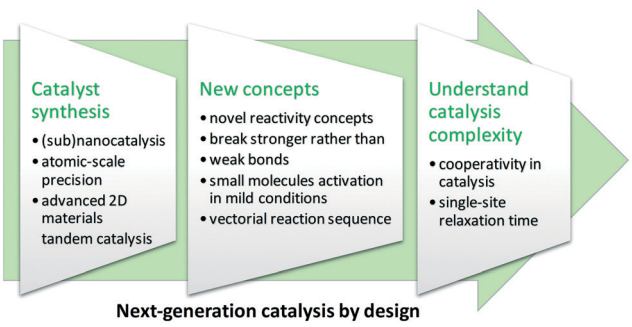

Fig. 1 Emerging directions in catalyst design to move to next-generation catalytic materials.

Grand challenges for catalysis

The transition to a sustainable and circular economy driven by chemistry based on renewable or recycled sources of energy and materials requires a new approach to catalysis based on a knowledge-driven approach and on actions facilitating the use of non-conventional approaches to catalysis development, fostering a revolutionary rather than evolutionary approach (Fig. 2).

History teaches us that new economic cycles[2] coincide with major modifications in key production processes, including those for chemistry. Such transitions are rather fast at the start of a new cycle, but it should be commented that Kramer and Haigh[57] remarked instead that there is no quick switch to low-carbon energy. However, this prediction (it can take 30 years to materialize, *i.e.* 1% of world energy mix) is based essentially on old predictions (2007 Shell Blueprints scenario), which do not account for the real economic dynamics and are already contradicted. Thus, there are different ideas about the time for transition, but one common agreement is the need to accelerate the transition. For this reason, the cited roadmap[18] emphasizes the need to intensify the generation of new ideas rather than promote incremental technology development and identify better mechanisms to intensify the full chain from fundamental research to innovations and applications.

On the other hand, the discipline of catalysis is characterized by two peculiar aspects. Firstly, it spans several orders of magnitude in terms of space (from the atomic sub-nanometric scale to the reactor level metric scale) and time domains (from the femto–picosecond level of elementary reaction steps to years of catalyst lifetime in industrial processes). Secondly, catalysis is an enabling technology in many different applications, well beyond only those of oil refineries and chemical productions.

As a consequence, the grand challenges for catalysis should take into account the complexity arising from its multiscale nature and from the quite broad range of applications.[58] However, it is necessary not only to look at the new emerging areas but to continue to support current areas of development.

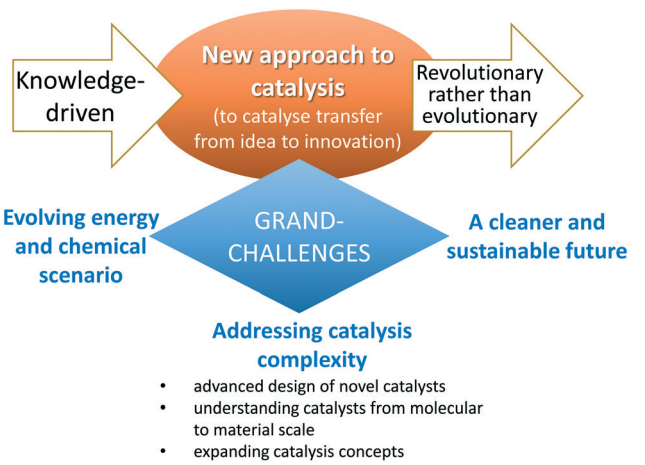

Fig. 2 The grand challenges for catalysis.

Two different types of grand challenges were thus identified:[18] (1) challenges related to specific applied objectives, such as energy or clean environment and (2) those connected to specific methodological aspects of catalysis. Two topics of the first type were identified (Fig. 2): i) catalysis to address the evolving energy and chemical scenario and ii) catalysis for a cleaner and sustainable future. A single topic of the second type was identified (addressing catalysis complexity), but organized into three sub-topics: i) advanced design of novel catalysts, ii) understanding catalysts from the molecular to the material scale, and iii) expanding catalysis concepts.

It is not possible to discuss here the details of these grand challenges and the related implementation and action plans widely described in the roadmap.[18] We discuss here only selected aspects, providing a glimpse into the main topics that will characterize the future of catalysis.

Catalysis to address the evolving energy and chemical scenario

The future scenario for refinery and chemical production considers the progressive substitution of fossil fuels with raw materials derived from biomass and CO_2, even if fossil fuels will still play a relevant role as feedstock for at least the next two to three decades, and even with a progressive shift to cleaner fossil fuels, *e.g.* natural gas.[10,12,59] A common objection is that fossil fuel resources are abundant enough to still maintain the competitiveness of their use and thus that there is no real need for their substitution. However, this is a rather simplistic consideration. Societal and economic drives (related to the increasing costs for climate changes) and geopolitical motivations (related to the concentration of fossil fuel resources in a few countries) are progressively shifting the use of fossil fuels to renewable energy sources (also with changes in the use of oil fractions produced by refineries) and in parallel promoting the politics of saving energy. These aspects, rather than just the amount of available fossil fuel resources, will drive the cost dynamics of fossil-fuel-derived products, making them progressively less competitive with respect to alternative sources. In regions lacking fossil fuel resources, this transition may be forecast to occur within one to two decades. It is thus imperative for competitiveness, especially in these regions (like Europe), to develop chemical and energy vector production based on alternative raw materials and especially the use of renewable energy. Nowadays, the carbon footprint of chemical production is often, over 70–80%, associated with the use of fossil fuels to supply the energy to drive the process (including separation) and many process steps to arrive at the final product from raw fossil fuels. It is important that the forthcoming "new chemistry" integrates as much as possible with the actual structure of production to minimize the costs associated with the transition.

Additionally, fossil fuel-based production processes still need to be further improved to maintain a high level of innovation and to secure competiveness. However, redesigning industrial chemical production, including refinery, from the perspective of using renewable energy and alternative C sources, is the grand challenge facing catalysis.

Converting biomass as one of the alternative raw materials represents a challenging endeavour, since this feedstock is much more complex than traditional fossil feedstock. In this framework, the main challenges for catalysis relate to the following:

1. Selectivity, *e.g.* how to convert complex biomass to preferably a limited number of target (platform) molecules – either drop-in (e.g. which can be directly inserted in the actual production chain) or new molecules (e.g. which substitute those actual in use) – in as few steps as possible, in order to limit separations.

2. Stability, *i.e.* how to achieve a catalyst that can handle "poisons" present in the biomass and that survives the conditions needed to convert biomass or fossil sources of lower grade.

For biofuels, the optimal integration within current refineries requires (in the short term) development of catalytic technologies to produce hybrid bio- and fossil fuels, for example by co-refining biomass pyrolysis oil in a conventional oil refinery.[60,61] Co-processing requires improving current catalysts for fluid catalytic cracking (FCC), hydrocracking and hydrotreating and developing novel, low-cost solutions for H_2 production. While in the short term this is a possible solution to meet international renewable energy targets, the effective contribution to the mitigation of CO_2 global emission provided by life cycle analysis (LCA) by considering all the production cycles for biofuel is still limited.[62,63] It is thus necessary, in the long term, to develop solutions and related catalysts more effective in reducing greenhouse gas (GHG) emissions. Integration of solar fuels, biogas and third-generation algal fuels in refinery are envisaged as possible technical solutions.[59]

For chemical production from biomass sources, the main challenge is to reduce the costs of separation and find new solutions to overcome the gap between the complexity of biomass and the high-purity required for chemicals. Development of catalysts able to selectively convert specific molecules within a complex mixture and which may be eventually directly integrated within separation solutions (membranes, for example) is one of the most relevant endeavours. Reduction of process steps, use of renewable energy and energy efficiency are among the key targets, which imply exploring novel catalytic solutions. Tandem electrocatalytic reactors are one of the examples in this direction,[64] but require developing novel specific electrocatalysts.

The conversion of carbon dioxide into solar fuels or solar chemicals brings its own challenges,[65–70] since the starting molecule is simple and relatively stable. Developing more complex molecules involving C–C bond formation during CO_2 conversion is the challenge, which may result in breakthrough possibilities.[71–73] CO_2 may be converted, for example, directly to acetic acid during CO_2–H_2O co-electrolysis.[73] The actual acetic acid production involves a multistep process: production of syngas, its conversion to methanol followed by carbonylation to acetic acid. The energy efficiency of the overall process is in the 10–20% range but can be

increased to over 80% in the direct electrocatalytic reduction of CO_2 by considering the use of renewable energy and process intensification, in addition to the use of CO_2 as the feedstock. Bringing the process to industrial use entails improving productivity, faradaic efficiency and stability, and in turn developing novel catalytic solutions which meet these requirements. This requires in turn a better understanding of the process occurring at the surface of the electrocatalyst, enabled by an integrated approach of surface-sensitive physical–analytical methods with traditional electrochemical techniques.[74] However, a gap between these studies and practical electrocatalysts still exists. Theoretical modelling has also made relevant advances,[75–77] but some critical issues are still open, for example, how to integrate the effects induced by application of a voltage to the electrocatalysts in the presence of an electrolyte, with related effects of surface-induced reconstructions, modification in the adspecies (type, concentration), mobility of charged species, *etc.* This understanding would extend the use of electrocatalysis to novel areas, but it would also require developing novel electrode concepts, such as 3D-like electrodes to intensify the process and reduce the costs.[78,79] Recognising the interconnectedness between living nature and technologically relevant electrocatalytic reactions, for example oxygen reduction and evolution catalysed by cytochrome C oxidases and photosystem II, respectively, and hydrogen oxidation and evolution catalysed by hydrogenases, is also necessary.[80] Electro-organic synthesis processes[81] have not been able to establish themselves on a larger scale, except in a few cases (adiponitrile synthesis, in particular), but have a large potential for application, when new catalytic materials and electrodes will be developed.[82,83] Metal-free doped nanocarbons and two-dimensional nanosheets as advanced novel electrocatalysts in energy generation and conversion offer great possibilities in this direction.[84–86]

Solar fuel/chemical production is a potential strategy to reduce the negative impact of increasing atmospheric CO_2 and contribute to the storage of excess renewable energy. In the short term, reducing the H_2 production cost through better catalyst design in electrolysers is a critical factor,[87] but in the long term, the direct use of renewable energy without intermediate H_2 formation to convert CO_2 into solar fuels and chemicals should be exploited.[88] This requires, among other aspects, developing new classes of electrocatalysts, which can also operate in synergy with photo-active materials and catalysts. Together with catalytic technology for chemical production from CO_2, integrated in the long term in artificial leaf-type devices, these processes will lead to the realisation of a more carbon-neutral chemical industry in the decades to come.

In general, among the further needs in R&D on photo- and electro-catalysis, the following aspects can be highlighted:

- to develop new types of electrocatalysts able to lower the necessary cell voltage and energy consumption.

- to prepare advanced and more stable photo- and electrocatalysts (and cell materials) for higher temperature flow-reactor cells; for example, operation at high temperature and pressure in tandem cells.

- to extend the use of photo- and electro-catalysis to a broader range of processes, which requires developing innovative and highly productive electrodes (for example, 3D-type) able to intensify the processes and reduce the costs.

- to develop electro- and photo-catalysts for selective conversion of low-value feedstock (*e.g.* biomass, glycerol, *etc.*) to high-value chemicals.

- to design and develop novel oxygen-reduction electrocatalysts for energy conversion and storage applications.

- to substitute or significantly reduce dependency on critical raw materials (CRMs) such as platinum-group metals (PGMs).

This short survey, summarized in Fig. 3, remarks how conceptually new types of catalysts and approaches are needed to address the evolving energy and chemical scenario. The following main bullet points may be indicated to address the evolving energy and chemical scenario:

- new or more efficient use of raw materials (from new uses of natural gas to biomass and CO_2, including non-conventional hydrocarbons and hybrid bio- and fossil products);

- more efficient and intensive integration of renewable energy with catalysis;

- realise energy-saving processes through catalysis;

- increase process efficiency through highly selective catalysis, low energy-intensive operations, complex and variable feedstocks, multi-functional smart catalysis, increasing and gradual encroachment of enzymatic catalysis/synthetic biology in areas traditionally seen as belonging to heterogeneous catalysis;

- process intensification in fine chemicals/pharmaceuticals by catalysis and integration of catalysis with other technologies (*e.g.* membrane technologies) to reduce the number of process steps;

- molecular catalysis in energy processes; new catalytic technologies for energy storage and conversion (including fuel cells, H_2 production, compression and storage);

- new manufacturing methods for catalysts: pursuing atomic control of materials and properties, and efficient scaling-up;

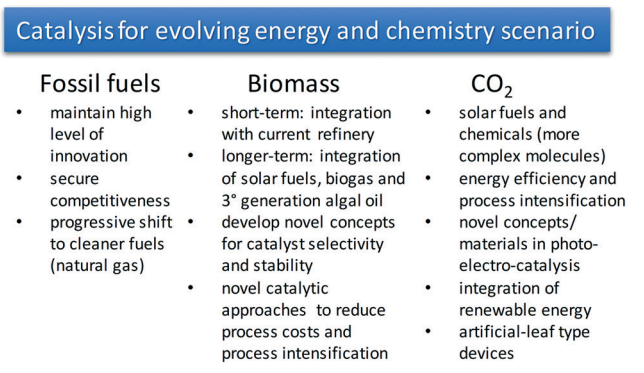

Fig. 3 A schematic summary of the main aspects related to the grand challenge of catalysis for the evolving energy and chemistry scenario.

- cost of catalysts *vs.* performance as key driver for improvement: many factors affect performance in real applications which are not always understood, especially in how they impact each other, from support variability to feedstock variation;

- substitution or minimisation of CRMs in catalyst preparation, particularly in emerging areas (biomass conversion, photocatalysis, photoelectrocatalytic (PEC) water splitting, green/blue hydrogen production) and industrial processes; design and set-up of robust chemo-, regio- and stereoselective heterogeneous catalysts;- design and set-up of catalysts for graphene science.

The R&D outputs in the above areas in the next one to two decades will be relevant. A more detailed analysis was given in the cited roadmap,[18] but it is useful to cite some of them:

- development of integrated flexible processes and catalysts enabling rapid response to changes in both raw material and energy inputs, as well as type/volume of production. This will allow for the design of easily adaptable refinery complexes that can handle a greater variety of feedstocks and follow market demands more closely;

- realization of improved catalytic processes for the direct use of natural gas and light alkanes to produce chemicals or transportable fuels;

- understand and control the reaction mechanisms and the catalyst functions such as hydrogenation and acid/base functions for operation in water; this will in turn support the development of stable and selective catalysts;

- understand and control the catalyst selectivity, both chemoselectivity and regioselectivity for over-functionalised feedstock, as this will lead to fewer by-products and thus a more efficient process in general;

- integrate the catalysis with separation technology in order to mitigate the challenges presented by high dilution, feed contaminants/heterogeneity or abundant by-products;- integrate different forms of catalysis (hetero-, homo-, bio-enzymatic, electrophoto-) to arrive at more efficient product formation (in terms of atom and energy economy);

- scalable electrolyser technology based on cheap and abundant catalytic metals to convert renewable electricity into hydrogen;

- integration of solar energy and CO_2 use in chemical and fuel production;

- development of a world-scale system to trade solar fuels and chemicals, and thus the associated renewable energy, as currently made using fossil raw materials.

Catalysis for a cleaner and sustainable future

Catalysis is a key enabling technology for a cleaner and sustainable future, and it is thus necessary to intensify research in these areas. Two main directions can be identified (Fig. 4):

- Catalysis for eco-technologies, from air to water and waste, to address stationary to mobile sources; this area includes the aspects of photocatalysis related to depollution. This area entails, for instance: (a) environmental heterogeneous catalysis: catalytic combustion/oxidation of VOC and Cl-VOC, removal of organochlorinated compounds and abatement of combustion emissions and (b) development of novel (photo)catalysts and (photo)catalytic technologies for water and air depollution and for sterilisation in health and hygiene applications.

- Catalysis to improve sustainability of chemical processes, in terms of atom economy (the aspects related to energy economy are included in the previous section) and improved processes to produce the main intermediates and chemical products/monomers; this area includes (a) the effort to move towards 100% selectivity; (b) catalysts in novel process design for resource and energy efficiency; (c) novel catalytic processes to reduce eco-impact or risk of fine and specialty chemical production (including asymmetric catalysis, organo-catalysis and enzymatic process, tandem process); (d) catalysis for novel polymers; one of the examples in this context is the synthesis of industrial relevant polycyclic carbonates, for which effective catalysts are still lacking.

Realizing these objectives requires an integrated effort between catalyst and process design/engineering, the two aspects being intertwined and not sequential. For this reason, a challenge is also to proceed towards a new eco-conception based on an integrated LCA and evaluation of the sustainability in catalysts and processes.

Although these areas of development are clearly very relevant for sustainability and societal impact, they represent in large part the evolution of the already on-going catalysis. Thus, for conciseness of this perspective, they are not discussed further here.

Addressing catalysis complexity

Innovation in catalysis impact and in addressing the societal challenges requires a knowledge-based approach and fostering capabilities in four main areas:[23,27,37–39,40,42,89–107]

- develop novel routes for precise synthesis of catalysts;

- improve the integrated understanding and modelling of catalysts from the molecular to the material scale, including catalyst dynamics under catalytic operations;

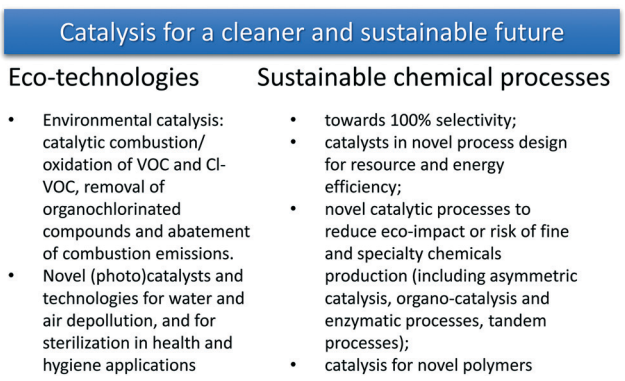

Fig. 4 A schematic summary of the main aspects related to the grand challenge of catalysis for a cleaner and sustainable future.

- expand process and reactor concepts and related tailored catalyst design;

- link the advanced design to catalyst scale-up and manufacturing at low costs and preferably without CRMs.

The future development of new and improved catalytic materials and processes will require a methodological shift towards rational design based on fundamental knowledge. The integration of new spectroscopy and microscopy tools along with predictive modelling strategies will allow designing and synthesizing novel catalysts for targeted reactivity of new molecules and materials. A scientific approach to scaling-up and practical manufacturing of these catalysts is a further step to more cost-effective and sustainable catalytic processes. Improved fundamental knowledge of catalysts, including their processes, will enable, among other advances, the replacement of noble, scarce, and toxic elements by more abundant and environmentally safe metals for catalysis.

Important contributions to the resolution of the complexity of catalysts will be provided by studies on model catalysts, like thin films[108] or well-defined single sites,[109] of the catalytically active material. Such model catalysts allow for the application of a variety of surface science methods that have no access to real catalysts present as particles[110–113] and are essential for the validation of theoretical methods before predictive contribution becomes possible.

The identification of catalyst descriptors and structure–reactivity relations with model catalyst studies will foster fundamental understanding as well as advanced design concepts.[114]

Addressing catalysis complexity also pushes forward the need to reach a higher level in the development of synthetic multifunctional catalyst (multi-reactor) systems.[115–117] Two complementary approaches can be identified. The first aims at improving the efficiency by which chemicals are produced by integrating modular catalytic systems and catalytic nanoreactors[118–121] in a plug-and-play fashion within a flow system.

The second approach aims at the integration of multiple catalysts in a single environment[53,122–126] in which catalytic processes influence each other through multiple feedback loops, with the ultimate aim of synthesizing life *de novo* and producing a synthetic cell.

Both approaches rely on the concept of molecular complexity, in which control over different length and time scales is crucial. Modularity can be also pursued through structured catalysts,[127–129] allowing generation of modular reactors and providing similar conditions such as packed beds with the advantage of a low pressure drop. The next step, however, is to structure the catalysts at the nano and even active-site level, forcing the reaction transformation over a predetermined sequence. Nanoscaling of catalysts and reactors[130–132] is required to further downscale (by orders of magnitude) the control level which is actually present in micro-reactors, which has already downsized the control level used in current structured catalysts and reactors.[133] This approach will also require developing novel advanced methods of preparation. Currently the most common method to produce structured catalysts is extrusion, but casting and additive manufacturing methods are in progress. Additive manufacturing[134] is an advanced technique that has the potentiality to tailor the catalysts to simultaneously optimize mass, heat and momentum transfer for each specific reaction. An effort is necessary to move to nano-scale additive manufacturing.

A further main challenge to be addressed (on knowledge bases) is catalyst and process compatibility. A catalyst is usually only effective under its own set of special experimental conditions and usually has limited tolerance for other chemical species in the system. On the other hand, it is often not considered how the feed composition may change the surface nature of the catalyst itself, or selective doping may be used to tailor the surface reactivity in complex reaction networks.[135] The use of complex feedstocks, reaction cascades or one-pot syntheses requires the rational design of targeted catalytic functionalities that should not interfere with other functionalities.[4,136–138] Catalysts that can selectively convert a single functionality into complex, multi-functionalised molecules would be desirable.

Based on this background, three main areas were identified to address the challenge of catalyst complexity (Fig. 5):

- advanced design of novel catalysts

- understanding catalysts from the molecular to the material scale

- expanding catalysis concepts

The discussion of each of these aspects goes beyond the scope of this perspective, and thus only some aspects will be discussed here to give a glimpse of the critical challenges for catalysis future. More aspects can be found in the cited roadmap.[18]

In catalyst design, new approaches to assemble different building blocks in a tailored manner and develop a specific structure with control of the characteristics from the molecular and nanosize level to the macroscopic one necessary for industrial operations have to be developed.[118,139–143] This will also allow overcoming the traditional separation between homogeneous, heterogeneous and bio-catalysis.[144,145] In parallel, it is necessary to enable new synthesis procedures for structuring these catalytic materials over multiple orders of magnitude in scale. Other promising approaches for chemocatalysis are aimed at the development of nanostructured catalysts from defined molecular, in particular organometallic, catalyst precursor compounds, the use of preformed metal (hydr)oxide colloid/carrier systems (*e.g.* PVP-stabilised, supported PdO_xH_y particles), nanostructured carbon-based materials and conductive polymers (*e.g.* polyaniline).

Selective design of the catalyst surface/morphology with a large number of atoms with coordinatively unsaturated sites and control on defects delivers highly active catalysts and can open up new reaction paths.[146–148]

Another major challenge results from differences in the rates at which catalysts lose their activity, usually through poisoning or leaching. A workable integrated multi-catalyst system will therefore provide the opportunity for independent catalyst-activity management.

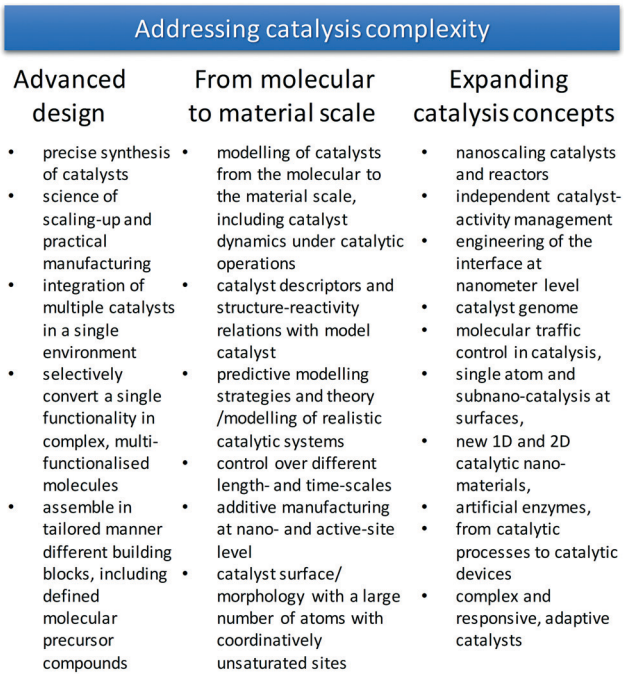

Fig. 5 A schematic summary of the main aspects related to the grand challenge of addressing catalysis complexity.

When combining chemical processes side by side or within a single system (as in the bio-inspired approach), catalysis is essential as it allows independent control over the rates at which the various reactions occur. Such control is crucial if the various reactions are to be efficiently integrated. Without catalysis, such control is largely lacking and one would be dependent on the rate constants of the various reactions. That, in turn, would severely restrict the ability to engineer well-integrated complex chemical systems. For example, a cell would not be able to function in the absence of ways to regulate independently (through catalytic processes) the rates at which the various chemical reactions inside the cell occur. Thus, by developing, within a biomimetic approach, integrated catalytic systems, we will open up new opportunities, ranging from a more cost-efficient production of chemicals to functional complex artificial systems.

An improved fundamental understanding of catalysts and of catalytic reactions would unlock many new opportunities for the application of catalysis and lead to new catalytic routes and to new molecules.[149–152] These advances are a key to shift towards a more sustainable and economically valuable catalysis, from academic research to industrial application levels. A prerequisite for tackling the challenges defined above is the further development of sophisticated characterisation tools. A step forward will derive from theory and modelling of realistic catalytic systems, requiring one to obtain physical insights from studying realistic systems or model systems under practical (*in situ* and *operando*) conditions. Understanding complex systems will tremendously speed up progress in all fields of catalysis.

Engineering of the interface between different components of heterogeneous catalysts at nanometer level can radically alter their performances, and the control of the contact points on the surface over various length and time scales will allow the design of new complex materials. In this regard, the fundamental understanding of the effect of crystal shape, habitus and face, and the development of new synthetic approaches and of novel characterisation tools capable of mapping chemistry at the surface, are needed to unlock several unexpected properties and functionalities. For heterogeneous catalysts, atomic-scale precision should be combined with the 3D meso- and macroscale location of components to create realistic, robust and stable new catalysts.

In parallel to the development of a more precise control of catalyst architecture, efforts are necessary towards developing new classes of catalysts as well as new ways to use catalysis. Among the areas relevant to expand catalysis concepts, the following may be cited:

- catalytic nanoreactor design,[121,124,153,154]
- catalyst genome,[155]
- molecular traffic control in catalysis,[156,157]
- single atom and subnano-catalysis at surfaces,[158–161]
- multifunctional molecular catalysis design,[102,109,162,163]
- new 1D and 2D catalytic nano-materials,[164–169] and advanced nanostructured electrocatalysts[170,171]
- artificial enzymes,[172–175]
- from catalytic processes to catalytic devices,[69,176,177]
- complex and responsive, adaptive catalysts,[178]
- electrocatalysts for next-generation energy-saving processes.[179,180]

The forecast of R&D outputs in the general fundamental and methodology area in the next one to two decades will be the following:

- computational methods that account for the complexity of chemical/catalytic processes on various time scales and length scales (multiscale modelling);
- mechanistic insight by combining spectroscopy with computational methods;
- a transient view of catalysis that accounts for out-of-equilibrium processes instead of the current steady-state view;
- precise control of morphology, composition and defect structure, leading to influencing optical, electronic and catalytic properties on multiple scales;
- a toolbox to translate chemical descriptors of catalysis and catalysts into predictors and to design rules for new molecules and synthetic methods;
- the science-based development of highly stable catalytic molecules and materials with self-repair and self-assembling properties;
- control and efficient generation of highly reactive (hypovalent) catalytic intermediates;
- precise control of selectivity in synthesis and catalysis, including regulation mechanisms to accommodate changes in reaction conditions (*e.g.* as observed in natural photosynthesis);

- targeted activation of specific catalytic sites and the control of reaction speeds and mechanisms, allowing for a cost-effective utilization of catalyst materials and an efficient replacement of noble metals by cheaper and more abundant materials;

- novel synthetic methods for ligand preparation as well as predictive modelling for achieving sophistication in ligand engineering in order to develop ligands with the desired chemo-, stereo- and regioselectivity and high values of TOF and TON;

- new homogenous (organo)catalysts for photoredox catalysis, molecular redox catalysis and challenging group-transfer reactions;

- chemoselective catalysts that can selectively convert a single functionality in complex, multifunctionalised molecules.

Conclusions

This short *excursus* about future directions and challenges for catalysis evidences well how catalysis will play a key role for a transformative society, energy and chemistry. Three main challenges for catalysis were shortly discussed here to address these challenges, based (but not limited to) on the wider discussion which we reported in the Science and Technology Roadmap on Catalysis[18] prepared in the frame of the activities of the thematic European Cluster on Catalysis.[19]

We aspire that this paper may contribute to highlighting the main factors shaping innovation in catalysis. In addition, we hope to have evidenced how R&D on catalysis is a critical enabling factor for the changing scenario in chemistry and energy. These aspects will accelerate the transition to a more sustainable society.

We expect also that researchers may use this perspective paper to identify the more relevant areas on which to focus their R&D, and that companies and financial agencies may use it to recognize better the directions and impact of innovation in this field for future chemistry and energy.

Conflicts of interest

There are no conflicts of interest to declare.

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