

Catalysis for an Electrified Chemical Production[†]

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Abstract

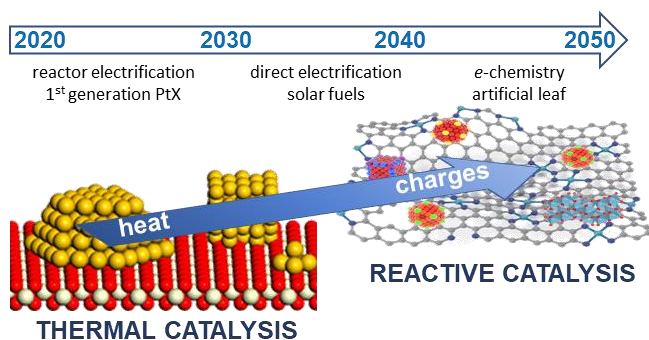
From a personal view, this perspective analyses the gaps and opportunities for catalysis to address the electrification of chemical production from a high-tech scenario. It is assumed that a significant substitution of fossil fuels is required to meet the net-zero emissions targets. This vision significantly impacts the future of catalysis and sustainable chemical production. We identified short (up to 2030), medium- (2030-2040) and long-term (2040-2050) objectives for catalysis. Novel catalytic routes of direct manufacturing chemicals and fuels using renewable energy should be developed. These are mainly based on photo-, electro- and plasma-catalysis, indicated shortly as "reactive" catalysis. Their common characteristic is that reactive species generated in these processes provide the energy to overcome the activation barriers. They differentiate from conventional heterogeneous catalysis, where the energy for the catalytic transformation is given by heat and thus indicated as "thermal" catalysts. The main priority in the short-term scenario is the design of novel "thermal" catalysts to exploit the new opportunities given by the electrification of chemical reactors. The innovation related to exploiting the novel possibilities offered by i) structured temperature gradients inside the reactor and ii) operations under fast dynamic temperature control. The medium-term challenge is direct electrification to produce chemicals and fuels, including energy vectors. Their development generates the bases for future carbon-neutral chemical production. Accelerating this innovative transformation requires identifying critical issues and focusing research on them. In the longer term, the necessity of artificial-leaf-type solutions is remarked. They should integrate all the necessary functionalities, including operations without a separate unit to capture/purify the reactants (such as N₂ or CO₂). These solutions will be an enabling tool for a distributed production of chemicals and fuels.

[†] This manuscript summarizes concepts and discussion emerged from the large EU initiative SUNERGY (fossil-free fuels and chemicals for a climate-neutral Europe; www.sunergy-initiative.eu).

Keywords

Catalysis roadmap, electrified production, electrocatalysis, net zero emissions, reactive catalysis

Graphical Abstract



Highlights

- catalysis scenario for carbon-neutral chemical production
- from "thermal" to "reactive" catalysis
- catalysis for electrified chemical reactors
- catalysis for direct electrified chemical synthesis
- catalysis to substitute the use of fossil fuels

1. Introduction

Electrification of chemical production, e.g., the use of electricity to drive chemical processes and minimise (avoid, preferably) the use of fossil fuels (FFs) to synthesise chemicals, is a grand challenge for innovation of the chemical industry and a necessity to meet the target of net-zero emissions (NZE) by the year 2050 [1]. *e*-Chemistry defines in a concise term the future carbon-neutral chemical production based on processes using directly renewable energy sources (RES) rather than FFs and alternative carbon sources to FFs [2,3]. Still, an extensive debate exists on whether this transformation is feasible, when it may be realised and even if needed.

We have recently discussed these aspects [4], showing that this is feasible and necessary to achieve NZE targets. The recent war in Ukraine has further shown how the market of FFs is heavily

interdependent and controlled by factors not linked to a competitive market. Crude oil is predicted to rise to over 150 US\$ per barrel in 2023 (Trading Economics global macro models), with enormous consequences on the chemical production system. Thus, reducing the dependence on production from FFs is a strategic and economic necessity out of the need to meet climate change (CC) targets. However, the fast acceleration of environmental disasters associated with CCs further stimulates the societal pressure to control greenhouse gas (GHG) emissions. A combination of aspects, as typically occurs in deep transitions [5], is thus accelerating the change in chemical production from a system nearly exclusively based on FFs to a new model. The analysis of deep transitions [6] evidence how they require new prediction models. Conventional techno-economic does not correctly estimate when and if new technologies critical for the transition can be implemented. A more extended debate, out of the scope of this manuscript, would be necessary to discuss all these aspects and the different opinions, indicating that FFs will remain the backbone of chemical production in the future.

On the other hand, a decade ago, the transition to chemical production beyond FFs was considered a full unrealistic hypothesis. We early introduced this possibility [7]. Now important consulting companies such as McKinsey [1] and International Renewable Energy Agency (IRENA) [8] or the Nova Institute [9] indicate this as a required path. Cefic, the European Chemical Industry Council, actively shares this vision [10]. An Institute dedicated to these aspects was created in the Netherlands [Delft e-Refinery Institute]. A significant European initiative [SUNERGY, www.sunergy-initiative.eu] involves more than 300 stakeholders, including several companies, around this vision.

Thus, there are converging indications in considering this as a crucial element of the future of chemical production. While differences are present in priorities and technologies, a shared aspect is that this transformation requires innovative catalysis.

Photo-, electro- and plasma-catalysis trio is a crucial technology to realise this transition toward directly electrified chemical production (*e-chemistry*) [11,12]. The term "reactive" catalysis is used to lump together photo-, electro- and plasma-catalysis and differentiate it from conventional heterogeneous catalysis. The latter was defined as "thermal" catalysis because the heat provides the energy for the process. Even if some catalytic processes occur at room temperature, the thermal energy still allows for overcoming the transition barrier. In "reactive" catalysis, the energy for the process derives from highly reactive species generated through the use of RES. These species can be holes and/or electrons generated by light-harvesting in semiconductor materials or by application of an electric potential to an electrode (electro- and photo-catalysis) or can be radicals, vibrationally excited species, etc., generated by direct activation of the reactants by non-thermal plasma generated through RES (plasma-catalysis) [13-15]. These reactive species determine the pathways of

transformation differently from the conventional (thermal) catalysis case, where the path is determined by the energy to overcome the activation barrier (of the rate-limiting step) after typically the chemisorption of the reactant(s). Jaramillo et al. [16] used similar terminology to differentiate the two types of catalysis.

Even if this distinction and terminology may create some perplexity, we consider functional to clarify concisely that photo-, electro- and plasma-catalysis (reactive catalysis) are different from conventional heterogeneous catalysis (thermal catalysis). It is thus a functional definition helping to clarify the challenge facing catalysis to realise the next carbon-neutral chemical production. Traditional heterogeneous catalysis will have a role in this future scenario. Still, the focus here is on identifying gaps and the need to accelerate the catalytic routes for the direct use of RES.

An essential element is that different design aspects are necessary for adequately developing "reactive" catalysts [13-15], although this aspect was not well recognised in the literature. Even if significant progress has been realised in understanding and designing "thermal" catalysts, the use of the same methodologies and conceptual approaches to "reactive" catalysts shows limits, as demonstrated for direct electrocatalytic synthesis of NH₃ from N₂ and H₂O [17]. This observation suggests rethinking the catalysis fundamentals [13,15], as discussed later.

The electrification of chemical production requires technologies still using traditional heterogeneous catalysts but with the aid of renewable energy to produce the thermal energy (heat) necessary for the reaction. This includes cases where electrical heating of the reactors is used to lower the carbon footprint of the process. Or when radiations such as microwaves or others are instead used to generate (in-situ) the thermal energy for the reaction. We earlier showed [3] that the different ways to supply thermal energy (in the case of conventional versus electrified reactors) influence transport phenomena, thus determining different mass- and temperature profiles. Consequently, an optimal catalyst design could differ in shape, porosity, properties and composition. Several EU projects are currently exploring this question.

Electrification of the chemical production thus creates opportunities for innovation and development of new catalysts and clues to reconsider the fundamentals of catalysis for a more effective design. Analysing these aspects is compulsory to accelerate the transition to carbon-neutral and sustainable production.

1.1 Timing for the transition to an electrified chemical production

It is increasing the agreement on transforming chemical processes to achieve an ultra-low carbon footprint in line with the expectation of NZE targets. This target would require developing solutions

beyond the actual nearly exclusive use of FFs for chemical production. Still, debate exists on when this transition could be realised and the degree of substitution of FFs by RESs that should be realised. Many scientists believe that transition may occur after the year 2050, and conventional chemical processes and catalysis (based on FFs) will still dominate in the following decades. Some scientists believe that the extensive current attention on "reactive" catalysis (photo-, electro-, and plasma-catalysis dominate publications on catalysis in recent years) is not justified. The future of catalysis will be just the use of more advanced tools for the precise synthesis and mechanistic understanding of traditional "thermal" catalysts or better computational tools for simulation, data mining and catalyst intelligence [18-26]. Even in the area of "reactive" catalysis, the approaches for the rational design of the catalysts are essentially the same as those for "thermal" catalysis [27-34].

The thesis we will instead introduce in this perspective view is that

- (i) phasing out of the introduction of new plants based on FFs use (e.g., based on the current technologies) will be faster than expected and already be operative from around the year 2035;
- (ii) the realisation of political goals such as NZE by the year 2050 requires accelerating the development of the 2nd (and 3rd) generation technologies for the direct use of RES (thus, primarily based on photo-, electro- and plasma-catalysis), bypassing intermediate solutions such as the development and commercial introduction of power-to-X (PtX) solutions, which will delay, if not inhibit the effort for the necessary next-generation technologies;
- (iii) catalysis science and technology must be transformed to develop the new catalysts required to meet the above indications faster.

We do not have the claim to prove undoubtedly these statements, and this is not the scope. This special issue aims to present personal viewpoints to allow the reader to make his/her vision of the future of catalysis by comparing different indications, some of them likely indicating different targets. Indeed, the resources dedicated to a specific topic, and thus the stakeholder (and financial agencies) support to promote a specific direction, will be crucial in prioritising research efforts. Thus, a strong community and, at the same time, convincing elements are necessary to push a path to the alternatives. As commented later and in other papers [3,4,13,15], when deep transitions involving a complete societal, economic and technological transformation occur, the use of conventional assessment criteria does not allow correct predictions. History teaches that companies with too conservative approaches often lost their role during these transformations. Gas and oil in the following decades will still play a role. However, the sign of an irreversible transformation is when new industrial investments consider alternatives beyond FFs. We suggest that we are already close to this situation. Companies need to develop their new business just in time during this deep transformation.

However, there is an induction time before a novel technology can be implemented. It is thus mandatory for all companies and society to correctly predict the changes and look in time at the new technologies for the future. Thus, even if we are aware that traditional catalysis and the use of FFs will still be necessary for the following decades, our message is that the priority is to accelerate the development of technologies based on new catalysis beyond FFs. However, this requires effort to go beyond current approaches to photo-, electro- and plasma-catalysis. This manuscript aims to clarify this concept and indicates targets and gaps to overcome. If this is realised, "reactive" catalysis will play an industrial relevant role even in the decade from around 2035-2040. The future of catalysis lies thus in accepting this challenge which requires, in our opinion, adopting new conceptual approaches rather than improving the current ones.

A high-tech scenario vision is the basis of our discussion on the future of catalysis. We will not discuss here all the pros/cons and the different opinions on this, but rather introduce elements of reflection, in addition to those earlier commented [3,4,13,15], to focus then discussion on the identification of key aspects necessary for catalysis to realise the transition to sustainable production and economy.

1.2 A concise scenario for catalysis to move to an electrified chemical production

The high-tech scenario at the basis of our discussion on the future of catalysis is based on the idea that within 15 years, the new plants for chemical production will no longer be based on current thermocatalytic processes. It is worth noting that the recent war has demonstrated the importance of overcoming geopolitical limitations related to the large monopoly of FFs production and distribution. Thus, acceleration is present in the technologies that can avoid the strong dependence on FFs. Even if chemical production accounts for less than 10% of the use of FFs, the impact is more significant i) being one of the hard-to-abate sectors, ii) due to the energy-chemistry strong nexus, and iii) its significant impact on our style of life.

Considering that the use of FFs can be decreased in sectors such as mobility without affecting the cost of FFs is an economic error. The cost of FFs is firmly bound to the related economic system, and thus a decrease in the income from one use will reflect a substantial increase in the cost of FFs for the remaining uses. Thus, there is a strategic need to substitute the dependence on FFs, accelerating the development of the necessary technologies. The deep transition occurring [5,6] cannot involve only some areas, mobility, for example, without substantial implications on the other areas, such as chemistry. For this reason, solutions under debate, such as the so-called crude oil-to-chemicals (COTC) processes [35], e.g., the direct production of olefins from crude oil rather than from refinery or natural gas fractions, do not represent, in our opinion, the right solution for sustainability and the changing economy.

Therefore, our thesis is that the future of catalysis lies in its capability to reply to the request to accelerate the development of technologies to substitute the use of FFs for chemical production, both in terms of energy and carbon source. There is a progressive alignment of many stakeholders on this thesis, even if others neglect or minimise this need.

At the same time, however, short-term solutions for the electrification of chemical production still require using conventional thermal catalysis but reinventing them to exploit novel possibilities. This viewpoint will thus analyse with a personal perspective the needs and gaps for catalysis to address the challenge of electrification chemical production in the short- and medium term, with some indications for a long-term vision where the current centralised methods of producing chemicals will be substituted from a fully distributed system.

2. A high-tech scenario and implications for future catalysis

For the EU, the new climate law approved on 12 May 2021 sets NZE as a binding target for 2050. However, the current greenhouse gas (GHG) emissions trend is still far from reaching this objective. This is illustrated in Figure 1 based on the data and estimations reported in the McKinsey reports on the NZE transition [1,36]. This Figure evidences the EU will need to reduce net GHG emissions much faster to meet 2030 and 2050 climate targets. The reduction rate should be increased by a factor between 3 and 4 to reach the target. Among the five sectors indicated in this report (power, transportation, building, industry and agriculture), the industry sector is the hardest to abate and has higher decarbonisation costs, estimated at around 100-120 €/tCO_{2e} in the cited reports.

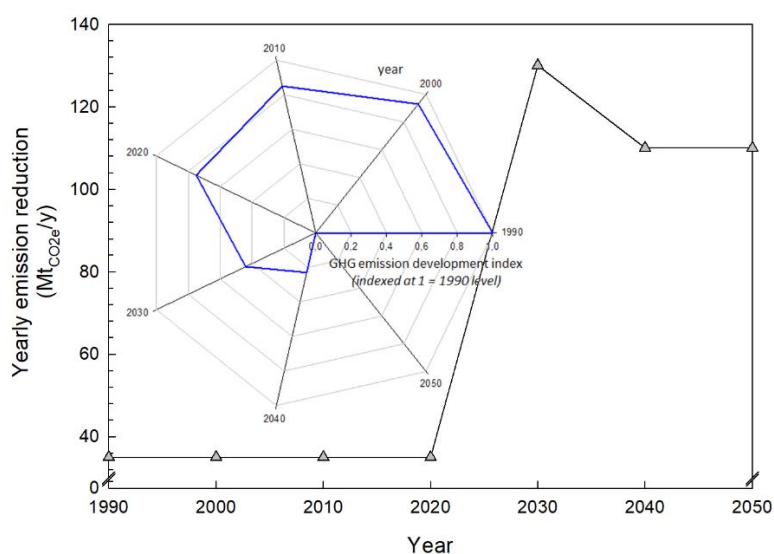


Figure 1 Trend for reducing GHG emissions in Europe to meet the NZE target in 2050. Main graph: yearly emission reduction (in MtCO_{2e}) to reach the NZE objective. Inset radar graph: change of the GHG emission development index to 1990. Based on the indications in McKinsey reports on the NZE transition [1,36].

The message from Figure 1 is that a drastic acceleration in introducing decarbonisation technologies is necessary, with the most challenging area being the industry sector. In this area, the refinery, chemical, and other energy-intensive industries [37] need energy in a constant supply and in large amounts. Thus, the direct coupling with RES, even considering some storage options, presents intrinsic limitations. A consensus is that suitable energy vectors are necessary to overcome this gap. These energy vectors should be easy to transport and stock yearly. For this reason, H₂ shows limits and extensive attention is given to producing liquid hydrogen vectors.

2.1 From *e*-fuels to solar fuels

e-Fuels is a popular term to define fuels (the equivalent of those produced from FFs) produced using RES. The state-of-the-art, implemented at the pilot stage and in some demo units, is a multi-step process:

- (i) CO₂ is captured from industrial emissions, concentrated and eventually purified;
- (ii) green H₂ is produced, typically by electrolysis (alkaline electrolyzers are the most mature technology, but attention is currently given to PEM-type electrolyzers; solid-oxide electrolyzers still present various technological challenges);
- (iii) CO₂ and H₂ are then co-fed to a thermocatalytic unit, where the final *e*-fuel is produced in one or more steps.

There are some alternatives in this process scheme, such as using CO₂-H₂O co-electrolysis. However, the multi-step character is still present, as well as the inefficiencies deriving from the coupling of technologies having different dynamics of operations and requirements. The "eFuel Alliance" (www.efuel-alliance.eu), having the mission to lobby and promote the field, indicates costs between 1.6 and 2.0 €/l in 2025, supposed to decrease to 0.7-1.33 €/l for gasoline in 2050 (higher costs for diesel). These estimations are somewhat optimistic, and on average, the cost of *e*-fuels is currently higher than 2€/l, with estimations indicating that it cannot decrease below around 1.5€/l even in 2050. These costs are too high to consider the practical impact of *e*-fuels on GHG reduction. These economic perspectives suggest that *e*-fuels are not a promising route, although more extensive discussions that include other aspects would be necessary. These additional aspects were earlier discussed [15] with the conclusion that passing to the next-generation technologies, overcoming the intrinsic limitations of PtX multi-step (1st generation) technologies, is better.

The cost and energy efficiency analysis of PtX technologies [38] reveals that a) the capture/concentration of CO₂ and b) the production of the high-energy H₂ molecule are the two critical elements. In the direct electrocatalytic technologies to produce solar fuels (we will call *solar*

fuels those produced directly in electrocatalytic technologies, to differentiate from 1st generation *e*-fuels), the hydrogen equivalent (H^+/e^-) rather than the H_2 molecule are produced and used to reduce CO_2 (or N_2 if the target fuel is ammonia). Thus,

- i) the energy losses related to producing the H_2 molecule and then activating it,
- ii) the thermodynamic equilibrium barriers present in CO_2/H_2 reactions,
- iii) the energy losses in having multiple steps operating in different operative conditions,
- iv) the capital costs for multiple unit operations

result significantly reduced. In addition, the electrocatalytic reactors may be (potentially) designed to operate with gas-diffusion electrodes (GDE) containing functionalities allowing them to work with diluted CO_2 concentration stream. Even if the status of the research is still at low development (Technology Readiness Level – TRL lower than 3), solar fuels may be produced indicatively at costs below 1 €/l making them effectively compete with FFs and *e*-fuels [15]. These tentative estimations highly depend on the capability to design practical devices and electrocatalysts which meet expectations and can be industrially implemented.

There is a high risk of making estimations based on technologies that are still not available and mature at the right TRL level. For this reason, it is typically argued that the only practical solution is based on current PtX technologies (*e*-fuels), which are already at high TRL. However, investing in technologies

- i) with limitations (in GHG reduction, costs, energy efficiency, use of resources and integration with the territory) that cannot likely be overcome (thus leading to high production costs)
- ii) which cannot become operative before the year 2025-2030,

likely will delay reaching the NZE targets by accounting for the high costs required for their realisation and amortisation time. The introduction of next-generation technologies will likely be shifted after 2050. We thus suggest that it is preferable to invest directly in the next generation and put enough resources to accelerate their exploitability within the year 2035-2040. This possibility largely depends on research investment and the identification that this is the preferable approach. On the other hand, without this turning in terms of priorities, the *e*-fuels will play a quite minor role in the future energy scenario, less than 1%, as predicted in various scenarios (Shell Sky or estimation by the International Energy Agency, see ref. [15] for details).

3. Catalysis to electrify the chemical production in the short-term scenario

In contrast to the urgency in accelerating the development of solutions to decarbonise chemical production, as clearly emerges from Figure 1, it is hard to have clear indications from publications

and ongoing debate regarding priorities in the short term. H₂ is often indicated as a panacea, but production by electrolysis is quite an energy-intensive operation, requiring 50-55 kWh per kg H₂ on average for state-of-the-art electrolysers. Some improvement in electrolysis could be possible towards the theoretical limit of ~40 kWh per kg H₂, but it remains an energy-intensive operation. H₂ is a high-energy energy vector which cannot be efficiently used to provide heat by combustion to furnaces, accounting for over 50% of the energy used in energy-intensive industries (EII) [37].

Depending on the temperature of furnace operations, energy efficiency may be low as 46% [39]. By combining with the inefficiencies in H₂ transport/storage and the fact that up to about 2040-2045, the fraction of RES in the electrical energy mix will be lower than about 50% [40], the use of H₂ in furnaces will not result in the necessary lowering of the carbon footprint required by the roadmap to NZE (Figure 1). Direct use of electrical energy will be preferable in (most of) the furnaces. The use of a methane-green H₂ mix in fired furnaces, even if a relatively mature technology, will not be an effective solution to meet the GHG reduction targets [41] and likely will be a solution delaying the introduction of more effective technologies, as commented for PtX.

In terms of the impact of the electrification of furnaces on catalysis, it is mainly focused on the electrification of chemical reactors [42]. The more straightforward approach uses electrical (ohmic) heating rather than direct or indirect heating by FFs combustion. This approach is also called power-to-heat. If this occurs external to the reactor body where the catalyst is located, this change has minor implications on the catalyst design. Due to intermittent electricity supply, even if stabilisation through electrical storage units is mandatory, higher fluctuations in the reactor temperature could be possible. Catalyst design could be improved for a more stable activity in the presence of these fluctuations.

However, using external electrical boilers to heat reactants or fluid external to the reactor zone where the solid catalyst is located does not require changes to the catalyst's form, shape and composition. The use of FFs will be reduced, and energy efficiency will be slightly better than for FFs-fired boilers [43]. Nevertheless, this approach will hardly achieve the reduction targets for GHG. In addition, it will highly depend on the availability (locally) of large amounts of renewable electrical energy. Due to the competition with other uses (mobility, etc.), it may be predicted that the amount of green electrical energy will not be available for significant electrification of furnaces.

A further issue is a fluctuation in RES. Introducing electrical energy storage solutions to provide 24h operations will reduce efficiency. An effective impact on GHG emissions will occur only in a high renewables grid scenario [43]. In addition, there are high costs in retrofitting the current chemical reactors, especially in the chemical energy sector (which includes refineries). In short, electrification is incentivised only when additional benefits such as process intensification [42,44,45] derive from

the switch to the new electrification technology, not just the reduction in GHG emissions, if not motivated by very high carbon taxes.

The electrification of the chemical reactors, when coupled with a proper novel catalyst design, could offer such a type of innovative element motivating the change. Up to now, however, quite limited specific studies in this direction are present in the literature [46-50]. Rather than have an external electrical boiler, electrification of the chemical reactor could be realised a) by inserting electrical resistances directly in a body on which the catalyst is supported, or b) by applying an electric current to a resistive conductor (metallic support, for example) where the catalyst is supported. The catalyst results in direct contact with the electrically heated surface. Therefore, heat transfer is more efficient. A faster response to induced changes in the temperature to respond to fluctuations in the feed is also present.

An additional advantage is that the temperature of the catalyst layer can be different (in the $\pm 20-50^{\circ}\text{C}$ range) to the temperature of the fluid (reactant) in contact with the catalyst. This temperature gradient offers clues to improve selectivity or stability. The catalyst must be redesigned to exploit these novel possibilities.

An alternative is magnetic heating. A rapidly alternating magnetic field may generate, either directly in the catalyst or in support on which the catalyst is deposited, eddy currents inducing heating by the Joule effect or magnetic hysteresis losses when a ferromagnetic material is present. The latter effect is predominant in magnetic nanoparticles. The effect is well established but not exploited industrially except in a few cases. The advantage is an even short distance heating and the possibility to induce fast fluctuations in the temperature. Redesign of the catalyst is necessary. For example, a core-shell design in which a nanoparticle's core is sensible to magnetic heating, and the catalyst is on the shell of the nanoparticle. High-temperature gradients between the catalyst nanoparticle and the surrounding fluid could be possible, realising, for example, superfast cooling when the product moves out of the catalyst surface.

Periodic fast modulations in the temperature also offer largely unexploited possibilities, for example, modulating adsorption-desorption or cyclically inducing fast desorption of poisoning elements (CO on Pt, for example) by a periodic fast raise in the catalyst temperature. Inducing periodic fast modulations in the catalyst temperature can induce metastable states for the catalysts with enhanced performances. Forced periodic temperature modulations have been shown to enhance the conversion of formic acid over a TiO_2 thin film catalyst [51]. In general, however, studies on how to exploit this possibility are missing. An improvement in rate and selectivity deriving from unsteady-state operation associated with periodic temperature forcing itself is not a novel effect [52]. Still, the timescale

offered by temperature modulations associated with fast changes in magnetic-induced heating opens a new, possibly disruptive field.

Microwave/RF (radio frequency) heating is also an alternative to heat the catalytic reactor zone. It is based on the rapidly alternating electric field of the microwave that generates heat by moving dipolar molecules or ions in liquids. It thus induces the heating of the liquid around the catalyst particles rather than the catalyst itself, which often interferes with the effect. Thus, microwave/RF heating is used mainly for homogeneous or non-catalytic reactions. However, heating could also occur through the so-called "dielectric lossy" solid nonmagnetic materials. Carbon materials (e.g., C black, carbon nanotubes or fibres, carbon fibre and graphene-like materials) could be selectively heated by this effect.

In some industrial cases, microwave/RF heating is already used to synthesise fine chemicals. However, the main challenge is to achieve uniform heating in a larger-scale reactor. Furthermore, proposed solutions are challenging to scale up. Applications up to now have not explored more advanced solutions for process intensifications which use modulations in the applied field to induce unsteady-state operations [53]. Still, a series of advanced possibilities exist [54]:

- (i) creation of hotspot zones by non-uniform distribution of electromagnetic field on the catalyst surface;
- (ii) selective heating of catalyst zones (the surface rather than the bulk of the catalyst, a specific area of the catalyst having a different composition to other parts even at a nanoscale level;
- (iii) selective heating of some of the adsorbed species (adsorbed species have a dipole moment and thus can be selectively heated under microwave irradiation, leading to accelerated adsorption-desorption cycle and enhanced rate of reaction).

There are thus significant possibilities, but they are still largely unexplored in a more systematic way [55]. Indeed, a specific novel design for the microwave-heated reactor would be necessary to exploit these possibilities properly [56,57].

In conclusion, except for the first case (coupling the catalytic reactor with an electrically-heated reactor), a general redesign of both the catalysts and reactor geometry and characteristics is necessary to take full advantage of the electrification. In addition, innovative catalysis, largely unexplored, opens by fully exploiting the novel possibilities offered in terms of

- (i) creating structured temperature gradients,
- (ii) modulations in temperature profiles at the nanoscale [58],
- (iii) operations in unsteady-state catalyst conditions.

Thus, substituting the use of FFs with electrical energy as a supply also becomes an opportunity for innovation, improvement in performance and process intensification. On the other hand, the scale-up of these solutions, except the first, remains challenging, with a technology maturity which can be indicated at a TRL value between 3 and 5, or even lower for the more advanced solutions. The main challenge is coupling reactor and catalyst modelling and experimentation under dynamic conditions.

4. Directly electrified chemical processes for a medium-term scenario

In a medium-term scenario (year range 2030-2040), we may expect to see the introduction of directly electrified chemical processes on the market, e.g., processes where RES provides the energy necessary for the reaction directly, in the form of either activated reactants (as in plasma-catalysed processes) [59] or of charged species generated on the surface of the catalyst by application of potential, e.g, electrocatalysis [12,60-63] or by light absorption in a semiconductor, e.g. photocatalysis [64-66]. These technologies are also indicated with the term power-to-chemicals lumps. Although all these technologies will likely play a role in the medium-term scenario for ultra-low carbon chemical production, electrocatalysis is currently at a higher level of TRL development (various processes are in pilot plant experimentation). Reasonably thus, it will be the first introduced commercially [12,67].

While in principle, photocatalytic processes would be preferable to electrocatalytic ones because they integrate the stage of using direct sunlight, there are a series of aspects limiting the industrial effectiveness of photocatalytic processes to the electrocatalytic ones:

- i) The catalytic surface must be directly irradiated by solar light, and thus process intensifications (such as those possible by using stacked electrocatalytic reactors) are difficult to realise;
- ii) The current density generated by light adsorption is typically low, of the order of 10 A/cm², and thus productivity is low; in electrocatalytic processes, the current density can be up to two orders of magnitude higher;
- iii) Direct solar-driven processes highly depend on irradiation intensity and thus depend on meteorological aspects, localisation, etc., while different sources of green electricity could be used for electrocatalysis.

Except perhaps in a few cases (such as H₂ photo- or photoelectro-catalytic production [68]), the issues to solve to bring photocatalysis to the status of industrial use in chemical synthesis processes are more severe than for electrocatalysis. Plasma-catalytic processes [59] are also a valuable option. Still, energy efficiency, control of the selectivity, productivity, and reactor scale-

up are among the crucial aspects to solve to bring to a commercial level plasma-catalysis technology for chemical synthesis. However, there are some specific areas, for example, the direct synthesis of fertilisers from the air [69,70], for which plasma-catalysis appears as one of the promising directions for industrial realisation.

In addition to the differences commented on above, electrocatalysis is the area of "reactive" catalysis explored for a more extensive range of possible applications, differently from photo- and plasma-catalysis studied in a restricted range of reactions. We will thus focus the discussion here mainly on electrocatalysis. There are two dominant areas of investigation regarding the use of electrocatalysis in chemical processes [12]:

1. CO₂ electroreduction to a range of products [71-76], from simple two-electron reductions (CO, HCOOH formation) to more complex electrocatalytic syntheses such as the 6e⁻ reduction to methanol or the more complex conversion paths involving C-C bond formation as in the production of ethanol and higher alcohols (isopropanol), light olefins, or acids such as acetic and oxalic acids.
2. N₂ electro-conversion to NH₃ [77-82] with more limited studies on the N₂ electro-oxidation to NO_x and thus produce nitrate after adsorption in water [83,84] for direct air to fertiliser process.

The third relevant area of investigation of electrocatalytic processes is their use for converting biomass-derived platform chemicals to produce large-volume chemicals or monomers. This area could be considered an extension of the established area of organic electrosynthesis [85,86], but the objectives and approaches are significantly different. Electrosynthesis is one of the synthetic tools for preparing speciality and fine chemicals, in some cases also on an industrial scale, typically structured by classes of target reactions such as type of bond activated (C-H activation, for example) or type of reaction (cyclisation, coupling, carboxylation, dehalogenation, etc.). These processes' energy efficiency, current density, electrode cost, continuous flow operations, easy downstream operations and separation, etc., are not critical. It is different from the use of electrocatalysis for synthesising large-volume (bulk) chemicals. Therefore, even if electrocatalytic technologies to produce bulk or fine chemicals share common aspects, they can be considered different topics, not differently from what occurs in heterogeneous catalytic processes.

Literature data on the electrocatalytic synthesis of bulk chemicals are limited and focused on a few types of reactions, such as furfurals or glycerol conversion [87]. We may also note that it is still not present in the literature a valid strategy to design the electrocatalysts for these reactions. The common observation is that heterogeneous catalysts effective in converting equivalent thermocatalytic reactions are not effective in electrocatalytic operations.

Various attempts exist to use advanced theoretical and experimental methods to identify the nature of the active sites and design strategies for electrocatalysts of platform biobased molecules [88]. As commented later for the cases of CO₂ and N₂ electrocatalytic conversion, most of these studies essentially apply methods established for thermo-catalysts to the investigation of electrocatalysts. The factors identified are somewhat general and mainly not differentiating heterogeneous conventional catalysis from electrocatalysis (geometric structure of the active sites, presence of surface defects, size and shape of the nanoparticles, etc.). Most of these design criteria apply to particular results and fail to analyse all the results. In addition, do not identify in a predictive way the class of electrocatalysts to be used by hypothesising a conceptual reaction mechanism. Several crucial aspects are not typically considered in electrocatalysis theories or the design of electrocatalysts, among them the role of

- (i) the generation of surface localised charges, which depend on the nanostructure,
- (ii) the presence of an electrical surface field associated with the nanostructure and which generates local variations in the potential and nature of the double layer (thus drastically influencing the electron transfer),
- (iii) the competition between electron and/or energy transfer to adsorbing molecules versus adsorbed molecules,
- (iv) the issue of the presence of a surface charge and its influence over the diffusion of charged intermediates generated in the electron transfer process, etc.

In addition, the other crucial aspect related to the induced surface transformation of the electrocatalyst when a potential is applied is not often considered, even if various proofs are present in the literature on the presence of this (often reversible) transformation [89].

Many authors consider electrocatalysis a type of heterogeneous catalysis for which all approaches are valid for studying the latter. For example, Tang et al. [90] indicated that "heterogeneous electrocatalysis occurring on the electrode surface can be understood in much the same terms as other heterogeneous catalytic processes". We disagree with this interpretation because this definition ignores the relevant aspects mentioned above. A fundamental basis for catalysis also applied to electrocatalysis, is the volcano-type activity plot based on revisions of the old Sabatier concept. This has also been used to predict the existence of optimal catalyst formulations based on the identification of proper descriptors of the catalytic behaviour. The effective electrocatalysts (oxide, hydroxides, etc.) differ from the metal-specific surfaces used in these theoretical approaches. Many other aspects, such as the need for concerted and multi-electron mechanisms, the presence of multifunctional sites, the presence of proton-coupled transformations, etc., indicate that an ad-hoc theory for complex

electrocatalytic transformations is needed.

Applying an electrical potential creates highly reactive species and a complex charged interface (depending on the nanostructured, as commented above) which dramatically changes the electrocatalyst's surface nature and the reaction mechanisms. Even diffusion inside a catalyst particle is a different problem when considering a charged porous material, especially a non-homogeneous charge distribution in a porous medium. A proper understanding of electrocatalysis starts by reformulating the concepts used for heterogeneous catalysis, although advances in precise synthesis and characterisation represent common aspects [91]. Thus, the challenge is to develop the rational bases for the design of electrocatalysis, going largely beyond the current approaches, which fail to adequately identify the electrocatalytic processes' specific nature and characteristics [92].

Electrocatalysis can also be used to generate in-situ the reactants used in the conversion of biobased platform molecules, for example, the H^+/e^- equivalent of H_2 for hydrogenation reactions. Active oxygen species, such as $*OOH$, $*OH$, $*O$ [93] or even singlet oxygen molecules [94], or selective oxidants such as H_2O_2 [95] could also be generated in situ for direct or mediated oxidation reactions. Thus, electrification also offers the advantage of eliminating the need to separate these redox reagents. This aspect could result in a novel process offering potential cost reduction, improved efficiency and reduced GHG emissions. The studies in this direction are still limited, but exciting results are growing. For example, the electrooxidation of propylene into propylene oxide [96].

In addition to direct redox processes at the surface of the electrocatalysts, mediated processes are another opportunity. The use of redox mediators (typically organic compounds, but not limited to them) is a common practice in organic electrosynthesis [97]. However, it is still not systematically explored to produce bulk chemicals. The mediator is involved in a reversible redox reaction initiated at the electrode surface and then transferred to the substrate of interest in the bulk of the electrolyte. Electron transfer mediators can avoid over-oxidation/-reduction of the substrate and mitigate electrode passivation. The kinetic inhibition associated with the electron transfer from the electrode to the substrate can be avoided, and selectivity can be controlled. A mediated electron transfer can occur against a potential gradient, meaning that lower potentials are needed, reducing the probability of undesired side reactions.

Mediated electrochemical reactions are thus hybrids between direct electrochemical conversions and homogeneous redox reactions. Tetramethylpiperidine N-Oxyl (TEMPO), Phthalimide N-Oxyl (PINO) and related N-Oxyl species are also widely used as mediators in electro-oxidation reactions. N-oxyl compounds undergo facile redox reactions at electrode surfaces, enabling them to mediate a wide range of electro-synthetic reactions. On the other hand, their use introduces critical issues of

separation and stability that often become the discriminating elements for industrial processes out of specific small-scale productions of high-added-value chemicals.

4.1 Moving to an *e*-chemistry

The next challenge (developing an *e*-chemistry) can be addressed using the knowledge above [3,4]. By combining primary electrocatalytic reactions of molecules such as H₂O, CO₂, N₂, and CH₄ with the electrocatalytic conversion of bio-derived products, it is possible to produce an extensive range of products forming the skeleton of new chemical production, as demonstrated elsewhere [4]. The requirement is to understand and control the nature of the intermediate species formed in these electrocatalytic processes and use them to build new electrocatalytic paths. This concept is schematically presented in Figure 2 [3].

Fast progress is ongoing in creating the science bases, routes and building block chemicals for this novel *e*-chemistry. Among them may be indicated the direct electrocatalytic conversion of CO₂ to light olefins [98-103] or the non-oxidative electrocatalytic deprotonation of light alkanes to light olefins [104,105]. Other raw materials for chemical production, such as methanol, can also be produced by direct electrocatalytic conversion of CO₂ [106-109]. Direct electrocatalytic reduction of CO₂ may also produce other valuable chemicals for an *e*-chemistry, from ethanol and higher alcohols to acids such as acetic and oxalic acid [110-116]. In addition to the production of aromatics via FFs-free routes [117], it is thus possible to indicate that the bases to develop a disruptive *e*-chemistry exist and accelerating this transformation is necessary to meet the NZE targets. This acceleration also requires the development of fundamental knowledge to address the challenges defined above.

While various scientists still consider this transformation unfeasible, it was before commented on why we consider instead necessary and feasible, although impossible to proven unequivocally.

We have not discussed the role of enzymatic paths and, particularly, the possibilities offered by hybrid electrocatalytic/biocatalytic systems [118]. They represent a valuable tool to realise the *e*-chemistry presented in Figure 2, but not discuss to avoid defusing discussion.

Realising this *e*-chemistry requires expanding the current electrocatalysis approaches and exploring new routes [119,120]. At the same time, an integrated approach combining cell engineering (a crucial parameter [121,122]) with knowledge in electrochemistry, electrocatalysts and electrode development and engineering, process development and assessment is necessary. Still, literature studies are too focused on mechanistic aspects, which may fail to correctly identify the critical aspects of developing the electrocatalysts to address *e*-chemistry challenges. In addition, notwithstanding the area of electrocatalysis is one of those in chemistry with the faster growth of publications and reviews,

the broadness of the approaches, reactions, devices and paths investigated is still limited, with few attempts to explore unconventional possibilities and combinations that nevertheless have the possibility of practical implementation.

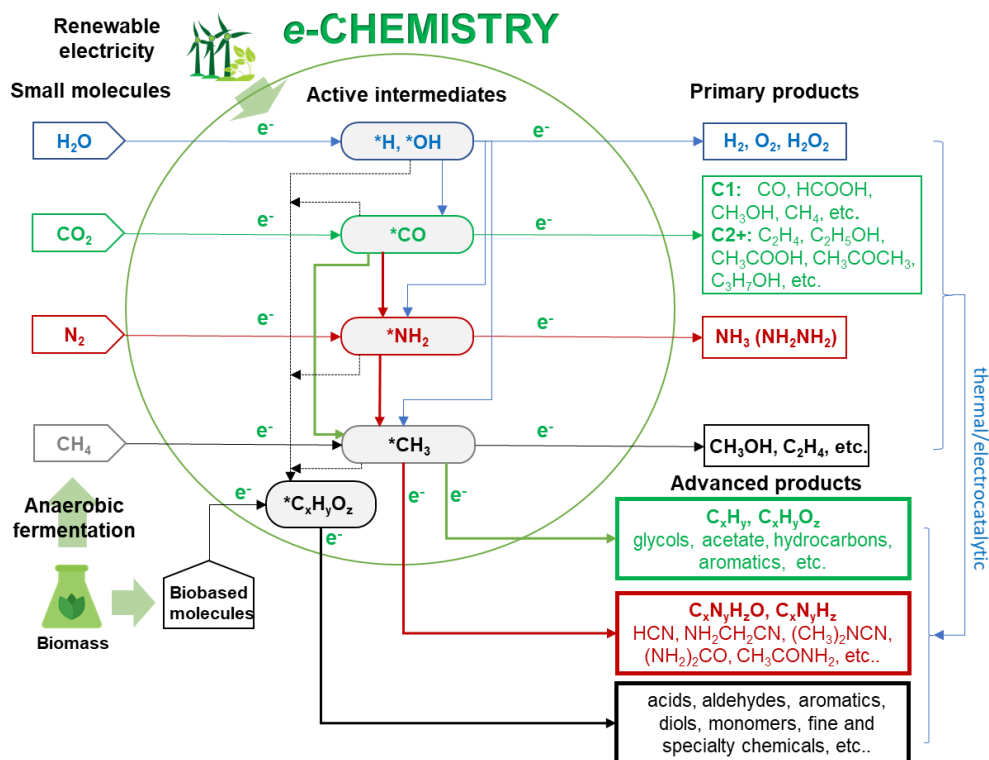


Figure 2. A new framework of electrocatalytically based reactions to develop a new e-chemistry alternative to that based on fossil fuels (petrochemistry). Reproduced with permission from Papanikolaou et al. [3]. ACS copyright, 2022.

4.2 Beyond the current fundamental approaches

Addressing the challenges defined in the previous sections for "reactive" catalysis would also require understanding better the differences between "reactive" and "thermal" (conventional) catalysis. In short, these differences were outlined above and discussed in more detail elsewhere [13,15]. We also earlier evidenced that, for example, in the direct electrosynthesis of ammonia from N₂, the analysis of the current state-of-the-art mechanistic studies reveals the limits of the current approaches [13,17]. Notwithstanding relatively similar catalytic results (for selected carbon-based electrocatalysts, among the better reported in the literature), a wide range of different reaction mechanisms and active sites have been proposed [17], supported by theoretical and experimental data. However, the same approaches applied to other electrocatalysis give different and often contradictory conclusions, even if catalytic performances are similar. The conclusion is that these methodologies cannot determine

the relevant mechanistic features determining the catalytic behaviour. The interpretation is that this is because these methods consider the "reactive" catalysis equal to "thermal" ones. Although more studies are necessary, the indication is that reconsidering the fundamentals of the catalysis approach is necessary. It is necessary to determine how "reactive" catalysis should be analysed from a different perspective to the "thermal" ones.

A paradigm of thermal catalysis mechanistic models is that the reaction occurs on specific active sites where the energy of interaction of the adsorbed species is analysed, but not considering how the energy transfer to overcome the activation barrier(s) is provided. Based on the physics of solids (but not applied to catalysis), the energy transfer should be provided, in principle, by phonons (solid vibrations). In the case of "thermal" catalysis, the onset temperature for activity determines the minimum reaction temperature at which reactants' thermal vibrational models are enough to provide the energy to overcome the activation barrier. Electrocatalysis and, generally, "reactive" catalysis operates below this onset reaction temperature. Without the application of an electrical potential, light illumination or generation of non-thermal plasma, the activity of the catalyst is virtually zero. Thus, providing the energy selectively to chemisorbed species to overcome the activation barrier becomes crucial.

Phonons are typically extended solid vibrational modes without sufficient energy to induce the catalytic transformation. Local phonons would be necessary to provide an effective and selective energy transfer. For this reason, the concepts of catalysis determined by local phonons or the energetic profile of the adsorbate-active site's interaction are strongly correlated. Still, they analyse the catalytic mechanism from a different perspective.

When charges (induced by the application of electrical potential or by light absorption in a semiconductor) are present, they can interact with localised phonons, creating excitons, polarons and other species (as plexciton, deriving from the interaction between plasmon and exciton [123]). These aspects are well-known in the physics of solids but ignored in catalysis, except for some studies on photocatalysis [124-127]. These species may be able to realise a proton-coupled multi-electron transfer (PCMET) which is a key to creating low-energy and selective paths in electro- and photo-catalysis [12,128]. This mechanistic path is typically not considered in "thermal" catalysis approaches. How charges are trapped at the active sites and how they modify the nature of the catalytic process are aspects well accounted for by looking from the local phonons (and related aspects) perspective to design selective electro- and photo-catalysis. On the contrary, they are not considered in classical "thermal" catalysis approaches.

Gordiz et al. [129] recently indicated that "phonon catalysis could lead to an entirely new field of

research". However, they only showed the contributing phonons to the ion hop in solids computationally. By exciting selected solid phonon modes (between 8 and 20 THz) of a model ion conductor (Ge-substituted Li_3PO_4), they evidenced an increase in ion diffusivity by several orders of magnitude. Tian et al. [130] studying MoS_2 - WSe_2 heterojunctions by spatially resolved electron energy-loss spectroscopy evidenced the presence of localised phonon modes at the interface between these nanoparticles, suggesting their role in determining the catalytic performances of these materials. Engineering the exciton–phonon interactions allows for controlling photocatalysis in bismuth oxybromide [131]. Luo et al. [132] discussed how hot carriers and phonon modes act in concert to contribute to the photocatalysis reaction mechanisms. McEwen and coworkers [133] showed that the electric field, whether externally applied or intrinsically present, significantly affects the behaviour of many materials relevant to catalysis.

Thus, there are limited and scattered indications in the literature on the role of localised phonons and related species in determining the behaviour of electro- or photocatalysts and how understanding these effects could be crucial to making a disruptive design of these "reactive" catalysts.

We suggest that looking at "reactive" catalysis from the perspective of localised phonons and the species generated by their interaction with charges offers a new disruptive approach to catalysts, particularly "reactive" catalysis. Among the critical aspects to analyse are the following:

- The mechanism of electron/energy transfer to adsorbed molecules through localised phonons
- The relation between nanostructure and localised phonons, how the latter interacts with localised charges, and how the nanostructure of the catalyst can be designed to promote this interaction
- How defects, edges, etc. (in "reactive" catalysis) rather than being active sites have the role of creating localised phonons instead
- How localised phonons and related species can be tuned to realise an effective resonance with the adsorbed species to control their selective transformation
- How excitons and related species can be effective in realising multiple electrons and PCMET transfer and how this offers novel paths to control selectivity in electrocatalysis
- The use of these concepts in designing novel strategies for developing effective "reactive" catalysts
- The difference between "reactive" and "thermal" catalysis
- The concept of phonon catalysis and how it can be a generalised method to design catalysts from a different perspective.

5. Artificial leaf devices for a long-term scenario of distributed production of chemicals and fuels

In a longer-term scenario, between 2040-2050, the main catalysis challenge in the high-tech scenario is the development of highly integrated devices able to realise in a single unit all the complete set of necessary functionalities to allow a distributed production of chemicals and fuels. We can use the production of fertilisers from the air as an example of this kind of artificial leaf device.

Figure 3 reports the concept of an artificial leaf for direct fertiliser synthesis from the air.

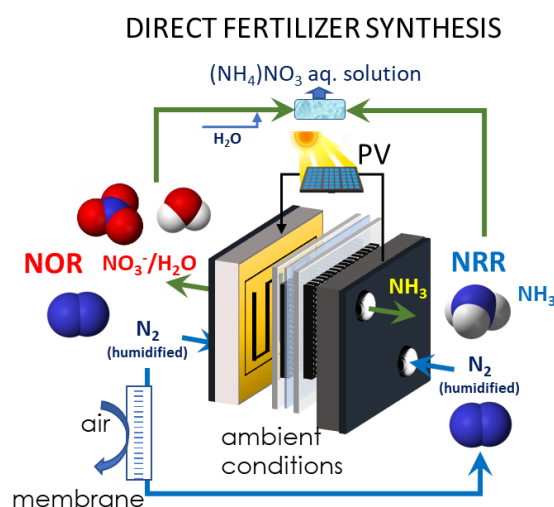


Figure 3. Concept of the artificial-leaf device for directly synthesising fertilisers (ammonium-nitrate aqueous solution) from the air. The device integrates a membrane for direct on-device production of N₂ from the air and a photovoltaic (PV) module to generate the necessary photocurrent to drive the electrocatalytic devices, where the anode contains an electrocatalyst for N₂ oxidation (NOR) and the cathode an electrocatalyst for N₂ reduction to ammonia. Both electrocatalysts should be highly productive/selective and not sensitive to the other components (such as traces of O₂) present in the N₂ flow from the membrane-integrated unit.

Changing the production model from a centralised (a few mega plants) to a distributed model is the grand challenge for chemical and refinery production [134-136]. It offers more flexible adaptability to a highly variable market and strongly reduces investments, the environmental impact and costs for transport/distributions. A distributed model integrates with the local resources rather than along the value chain. It also generates new opportunities for symbiosis and investments, offering better resilience and reduced geopolitical dependence [137]. All these elements create a competitive environment based on innovation.

It is a development model different from the current global-scale model, which evidences strong

limits. Distributed production requires efficient small-medium scale plants well integrated with the territory and the local resources/needs, with a modular plant scheme allowing faster time to market and great flexibility of operations. The technologies discussed above have these characteristics but require innovative catalysis for their realisation.

Conceptually similar artificial leaf devices could also be considered for CO₂ direct conversion in (industrial) emissions without the need for separate capture and purification of the carbon dioxide. They offer possible closure of the carbon cycle in various productions. By avoiding a separate capture and treatment of CO₂, this novel technology drastically cuts the costs, as mentioned before, regarding solar fuels. A range of possible devices could be considered by tailoring the electrocatalysts and choosing the anode and cathode reactions.

Rather than use standard PV units, it is possible to consider advanced PV units that integrate a flow redox battery component and thus operate continuously (24 h) and not only when sunlight is present. A photoactive cathode or anode, rather than a separate PV module, leads to more compact devices. Still, the issue mentioned before of insufficient current density [68] must be solved first.

Materials, including catalysts, should be low cost, not based on critical raw materials and prepared with easy methods for mass production. While ideally, all critical raw materials should be avoided in preparing electrodes, it should be recalled that the sustainability evaluation should consider i) the amount needed in relation to the world availability of the element and ii) the recyclability. For example, Ir is often used in anode electrodes. It is a rare element, and even if used in small amounts in electrodes, it may still create issues for a larger-scale application. On the contrary, Ti is classified as rare material but used as TiO₂ in photocatalysts. Its consumption in 2020 was about 6.45 Mtons for the paint and coatings industry. In an electrode, it is used in mg amounts. Thus, its use in preparing electrodes will have a minor impact. The problem of the recyclability of electrodes, except for batteries, was not addressed. The low-cost industrial manufacturing of electrodes is also still an aspect scarcely investigated.

Advanced 3D-like electrodes to improve performances for unit electrode geometrical area is compulsory to have low costs of production, but still, many fundamental issues on how to realise an efficient 3D electrode have to be first solved.

Easy product recovery in continuous operation cells is also mandatory, as well as minimising the cost of cell manufacture. Still, too limited attention is given in the literature on these studies, which also have implications for developing effective electrocatalysts. Compact cells operating without a liquid electrolyte (indicated often as gas-phase electrocatalytic cells; the membrane separating the anode and cathode zone acts as the solid electrolyte) are necessary [138-140], but it is demonstrated that

different electrocatalysts are required for optimal operations in these cells to the conventional ones (with large electrolyte volumes) on which the vast majority of the studies focus.

Finally, a short economic consideration because artificial-leaf devices are often considered too costly. Cost targets (Capex, capital expenditure) are about 20-30% higher than those projected for electrolyzers (below 600-700 €/kW). Still, considering the higher value of the products obtained with respect to H₂ and process intensification, their implementation is feasible.

6. Conclusions

This short discussion of the priorities of catalysts for a future high-tech scenario to meet the NZE targets evidence a series of challenges for catalysis in the short-, medium- and long-term timescale, e.g. up to 2030, between 2030-2040 and 2040-2050, respectively. We suggest that these targets are feasible if enough resources are dedicated. However, the catalysis community should try to turn the current approach by clearly identifying the critical aspects that focus the research. It is also necessary from one side to expand the range of possible applications and, from the other side, the concepts and methods used in understanding and designing "reactive" catalysts with respect to conventional heterogeneous catalysts.

In a short-term scenario, the design of novel "thermal" catalysts to exploit the new opportunities given by the electrification of the chemical reactors was indicated as the main priority. The innovation opportunities were presented mainly to realise i) structured temperature gradients inside the reactor and ii) operations under fast dynamic temperature control. Both require the development of innovative catalysts. At the same time, it was also indicated that solutions in which electrification is limited to produce H₂ by electrolysis (the series of PtX processes to produce the so-called *e*-fuels) represent a solution that, even if already at high TRL, could delay the passage to the next generation of solutions. The 2nd generation technologies are required to address the NZE targets.

The main challenge in the medium term is the direct electrification to produce chemicals and fuels, including energy vectors. However, it was evidenced that the literature approaches still look at a limited range of reactions and solutions. These do not account for the extensive range of creative possibilities. Their potential has to evaluate in the frame of the transitions to a new carbon-neutral and FFs-free chemistry. A better understanding of the intermediates formed in the electrocatalytic process and how to exploit them to create new synthesis paths is the challenge which opens a full range of new possibilities. Only a few of them were discussed.

Developing more solid bases for understanding electrocatalysts and designing them is compulsory. We have suggested looking at these aspects from the perspective of localised phonons and their

interaction with charges to generate excitons. However, this is just some initial concept that has to be explored and proven.

Finally, developing artificial-leaf-type solutions is the priority in the longer-term scenario. These devices integrate all the necessary functionalities, including the possibility of operating without a separate unit to capture/purify the reactants (such as N₂ or CO₂). These devices are the key to realising a distributed production overcoming the many limits of the current model of centralised production

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Acronyms

CC	climate change
EII	energy-intensive industries
FFs	fossil fuels
GHG	greenhouse gas
NZE	net-zero emissions
RES	renewable energy sources

References

1. McKinsey & Company, The net-zero transition. What it would cost, what it could bring, *McKinsey Global Institute Report*, January 2022.
2. K. M. Van Geem, B. M. Weckhuysen, *MRS Bull.*, 46 (2021) 1187–1196.
3. G. Papanikolaou, G. Centi, S. Perathoner, P. Lanzafame, *ACS Catal.*, 12 (2022) 2861–2876.
4. G. Centi, S. Perathoner, *Green Chem.*, 24 (2022) 7305-7331.
5. J. Schot, L. Kanger, *Research Policy*, 47 (2018) 1045-1059.
6. L. Kanger, J. Schot, *Env. Innovation and Soc. Transitions*, 32 (2019) 7-2.
7. P. Lanzafame, S. Abate, C. Ampelli, C. Genovese, R. Passalacqua, G. Centi, S. Perathoner, *ChemSusChem*, 10 (2017) 4409.
8. D. Saygin, D. Gielen, *Energies*, 14 (2021) 3772.
9. C. vom Berg, M. Carus, M. Stratmann, L. Dammer, Renewable Carbon as a Guiding Principle

for Sustainable Carbon Cycles. Renewable Carbon Initiative (RCI), Febr. 2022. Available at: www.renewable-carbon-initiative.com

10. CEFIC, Restoring sustainable carbon cycles, Position paper May 2022. Available at: <https://cefic.org/app/uploads/2022/05/Cefic-position-on-Restoring-sustainable-carbon-cycles.pdf>
11. A Navarrete, G Centi, A Bogaerts, Á Martín, A York, G Stefanidis, *Energy Technology*, 5 (2017) 796–811.
12. S Perathoner, G Centi, *Catal. Today*, 330 (2019) 157-170.
13. G. Centi, S. Perathoner, *Catal. Today* 387 (2022) 216-223.
14. A. Bogaerts, X. Tu, J. C. Whitehead, G. Centi, L. Lefferts, O. Guaitella, F. Azzolina-Jury, H.-H. Kim, A. B. Murphy, Schneider, T. Nozaki, J. C. Hicks, A. Rousseau, F. Thevenet, A. Khacef, M. Carreon, *J. Phys. D: Appl. Phys.*, 53 (2020) 443001.
15. G. Papanikolaou, G. Centi, S. Perathoner, P. Lanzafame, *Chinese J. Catal.*, 43 (2022) 1194-1203.
16. D. M. Koshy, S. S. Nathan, A. S. Asundi, A. M. Abdellah, S. M. Dull, D. A. Cullen, D. Higgins, Z. Bao, S. F. Bent, T. F. Jaramillo, *Angew. Chem. Int. Ed.*, 60 (2021) 17472.
17. G. Centi, S. Perathoner, *Small* 17 (2021) 2007055.
18. J. Čejka, P. Nachtigall, G. Centi, *Chem. Soc. Rev.* 47 (2018) 8066 – 8071.
19. S. Mitchell, J. Perez-Ramirez, *Nature Comm.*, 11 (2020) 4302.
20. T. Toyao, Z. Maeno, S. Takakusagi, T. Kamachi, I. Takigawa, K.-i. Shimizu, *ACS Catal.*, 10 (2020) 2260-2297.
21. B. W. J. Chen, L. Xu, M. Mavrikakis, *Chem. Rev.*, 121 (2021) 1007-1048.
22. G. Zhan, P. Li, H. C. Zeng, *Adv. Mater.*, 30 (2018) 1802094.
23. Y. Shi, Z. Lyu, M. Zhao, R. Chen, Q. N. Nguyen, Y. Xia, *Chem. Rev.*, 121 (2021) 649-735.
24. C.J. Heard, J. Čejka, M. Opanasenko, P. Nachtigall, G. Centi, S. Perathoner, *Adv. Mater.*, 31 (2019) 1801712.
25. P. Lanzafame, S. Perathoner, G. Centi, S. Gross, E.J.M. Hensen, *Catal. Science & Techn.*, 7 (2017) 5182-5194.
26. Y. Du, H. Sheng, D. Astruc, M. Zhu, *Chem. Rev.*, 120 (2020) 526-622.
27. K. R. G. Lim, A. D. Handoko, S. K. Nemani, B. Wyatt, H.-Y. Jiang, J. Tang, B. Anasori, Z. W. Seh, *ACS Nano*, 14 (2020) 10834-10864.
28. Y. Sun, L. Han, P. Strasser, *Chem. Soc. Rev.*, 49 (2020) 6605-6631.
29. L. Zhang, Z.-J. Zhao, T. Wang, J. Gong, *Chem. Soc. Rev.*, 47 (2018) 5423-5443.
30. C. Guo, V. Ran, A. Vasileff, S.-Z. Qiao, *Energy & Envir. Sci.*, 11 (2018) 45-56.
31. C. Zhao, M. Xi, J. Huo, C. He, L. Fu, *Mater.Today Phys.*, 22 (2022) 10060.

32. L. M. Azofra, L. Cavallo, J.-M. Basset, M. Harb, *J. Phys. Chem. C*, 125 (2021) 8488-8496.
33. Y. Wang, D. He, H. Chen, D. Wang, *J. Photochem. and Photobiol., C: Photochem. Rev.*, 40 (2019) 117-149.
34. J. S. Adams, M. L. Kromer, J. Rodriguez-Lopez, D. W. Flaherty, *JACS*, 143 (2021) 7940-79.
35. A. Corma, E. Corresa, Y. Mathieu, L. Sauvanaud, S. Al-Bogami, M. S. Al-Ghrami, A. Bourane, *Catal. Science & Techn.*, 7 (2017) 12.
36. McKinsey & Company, Net-Zero Europe Decarbonization pathways and socioeconomic implications, *McKinsey Global Institute Report*, Nov. 2020.
37. S. Perathoner, K.M. Van Geem, G.B. Marin, G. Centi, *Chem. Comm.*, 57 (2021) 10967-10982.
38. G. Centi, S. Perathoner, A. Salladini, G. Iaquaniello, *Front Energy Res.*, 8 (2020) 567986.
39. London Energy Transformation Initiative (LETI). *Hydrogen. A decarbonisation route for heat in buildings?* LETI, London (UK), Feb. 2021.
40. International Energy Agency (IEA), *Net Zero by 2050: a Roadmap for the Global Energy Sector*, IEA Paris (France), May 2021.
41. S. Timmerberg, M. Kaltschmitt, M. Finkbeiner, *Energy Conv. and Mgm.: X*, 7 (2020) 100043.
42. A. I. Stankiewicz, H. Nigar, *React. Chem. Eng.*, 5 (2020) 1005-1016.
43. C. Schoeneberger, J. Zhang, C. McMillan, J. B. Dunn, E. Masanet, *Adv. in App. Energy*, 5 (2022) 100089.
44. S. Haase, P. Tolvanen, V. Russo, *Processes*, 10 (2022) 99.
45. F. Kapteijn, J. A. Moulijn, *Catal. Today*, 383 (2022) 5-14.
46. Ž. Ponikvar, B. Likozar, S. Gyergyek, *ACS Appl. Energy Mater.*, 5 (2022) 5457-5472.
47. M. Ambrosetti, A. Beretta, G. Groppi, E. Tronconi, *Front. Chem. Eng.*, 3 (2021) 747636.
48. E. Meloni, G. Iervolino, C. Ruocco, S. Renda, G. Festa, M. Martino, V. Palma, *Energies*, 15 (2022) 3588.
49. S. T. Wismann, J. S. Engbæk, S. B. Vendelbo, F. B. Bendixen, W. L. Eriksen, K. Aasberg-Petersen, C. Frandsen, I. Chorkendorff, P. M. Mortensen, *Science*, 364 (2019) 756-759.
50. K. M Van Geem, V. V Galvita, G. B Marin, *Science*, 364 (2019) 734-735.
51. T. Ellwood, L. A. Živković, P. Denissenko, R. Sh. Abiev, E. V. Rebrov, M. Petkovska, *Processes*, 9 (2021) 2046.
52. P. L. Silveston, R. R. Hudgins, *Chem. Eng. Sci.*, 59 (2004) 4043 – 4053.
53. T. K. Houlding, E. V. Rebrov, *Green Process Synth.*, 1 (2012) 19-31.
54. P. D. Muley, Y. Wang, J. Hu, D. Shekhawat, *Catalysis*, 33 (2021) 1-37.
55. V. Palma, D. Barba, M. Cortese, M. Martino, S. Renda, E. Meloni, *Catalysts*, 10 (2020) 246.
56. A. Martínez González, A. Stankiewicz, H. Nigar, *Catalysts*, 11 (2021) 369.

57. P. Yanab, A. I. Stankiewicz, F. E. Sarabi, H. Nigar, *Chem. Eng. Sci.*, 232 (2021) 116383.
58. N. Haneishi, S. Tsubaki, E. Abe, M. M. Maitani, E.-i. Suzuki, S. Fujii, J. Fukushima, H. Takizawa, Y. Wada. *Sci. Rep.*, 9 (2019). 222.
59. A. Bogaerts, X. Tu, J. C. Whitehead, G. Centi, L. Lefferts, O. Guaitella, F. Azzolina-Jury, H.-H. Kim, A. B. Murphy, Schneider, T. Nozaki, J. C. Hicks, A. Rousseau, F. Thevenet, A. Khacef, M. Carreon, *J. Phys. D: Appl. Phys.*, 53 (2020) 443001.
60. A. Yazdani, G. G. Botte, *Current Opinion in Chem. Eng.*, 29 (2020) 89-95.
61. A. P. O'Mullane, M. Escudero-Escribano, I. E. L. Stephens, K. Krischer, *ChemPhysChem*, 20 (2019) 2900.
62. J. Wyndorps, H. Ostovari, N. von der Assen, *Sustainable Energy Fuels*, 5 (2021) 5748-5761.
63. J. Liu, J. Ma, Z. Zhang, Y. Qin, Y.-J. Wang, Y. Wang et al., *J. Phys. Mater.* 4 (2021) 022004.
64. D. M. Arias-Rotondo, J. K. McCusker, *Chem. Soc. Rev.*, 45 (2016) 5803.
65. Y.-J. Xu, *Front. Catal.*, 1 (2021) 708319.
66. M. Melchionna, P. Fornasiero, *ACS Catal.*, 10 (2020) 5493–5501.
67. G. Centi, G. Iaquaniello, S. Perathoner, *BMC Chem. Eng.* 1 (2019) 5.
68. V. Romano, G. D'Angelo, S. Perathoner, and G. Centi, *Energy & Environ. Sci.*, 14 (2021) 5760.
69. L. R. Winter, J. G. Chen, *Joule*, 5 (2021) 300-315.
70. E. Vervloessem, M. Aghaei, F. Jardali, N. Hafezkhiani, A. Bogaerts, *ACS Sustainable Chem. Eng.*, 8 (2020) 9711–9720.
71. W. Zhang, Z. Jin, Z. Chen, *Adv. Sci.*, 9 (2022) 2105204.
72. P. Saha, S. Amanullah, A. Dey, *Acc. Chem. Res.*, 55 (2022) 134-144.
73. W. Ma, X. He, W. Wang, S. Xie, Q. Zhang, and Y. Wang, *Chem. Soc. Rev.*, 50 (2021) 12897.
74. G. Wang, J. Chen, Y. Ding, P. Cai, L. Yi, Y. Li, C. Tu, Y. Hou, Z. Wen, L. Dai, *Chem. Soc. Rev.*, 50 (2021) 4993-5061,
75. X. Tan, C. Yu, Y. Ren, S. Cui, W. Li, J. Qiu, *Energy & Env. Sci.*, 14 (2021) 765-780.
76. G. Centi, S. Perathoner, *Green Carbon Dioxide: Advances in CO₂*, Wiley & Sons (2014).
77. G. Zhang, Y. Li, C. He, X. Ren, P. Zhang, H. Mi, *Adv. Energy Mater.*, 11 (2021) 2003294.
78. L. Shi, Y. Yin, S. Wang, H. Sun, *ACS Catal.*, 10 (2020) 6870-6899.
79. R. Shi, X. Zhang, G. I. N. Waterhouse, Y. Zhao, T. Zhang, *Adv. Energy Mater.*, 10 (2020) 2000659.
80. S. H. W. Kok, J. Lee, L.-L. Tan, W.-J. Ong, S.-P. Chai, *ACS Mater. Lett.*, 4 (2022) 212-24.
81. S. Chen, S. Perathoner, C. Ampelli, C. Mebrahtu, D. Su, G. Centi, *Angew. Chem. Int. Ed.*, 129 (2017) 2743-2747.
82. D. Mallamace, G. Papanikolaou, S. Perathoner, G. Centi, P. Lanzafame, *Int. J. Molec. Sci.*, 22

(2021) 139.

83. M. Anand, C. S. Abraham, J. K. Nørskov, *Chem. Sci.*, 12 (2021) 6442.
84. C. Dai, Y. Sun, G. Chen, A. C. Fisher, Z. J. Xu, *Angew. Chem. Int. Ed.*, 59 (2020) 9418.
85. A. Dey, T. B. Gunnoe, V. R. Stamenkovic, *ACS Catal.*, 10 (2020) 13156-13158.
86. A. Shatskiy, H. Lundberg, M. D. Kaerkaes, *ChemElectroChem*, 6 (2019) 4067-4092.
87. L. Du, Y. Shao, J. Sun, G. Yin, C. Du. Y. Wang, *Catal. Sci. Technol.*, 8 (2018) 3216-3232.
88. B. Garlyyev, J. Fichtner, O. Piqué, O. Schneider, A. S. Bandarenka, F. Calle-Vallejo, *Chem. Sci.*, 10 (2019) 8060–8075.
89. C. Genovese, M. E. Schuster, E. K. Gibson, D. Gianolio, V. Posligua, R. Grau-Crespo, G. Cibin, P. P. Wells, D. Garai, V. Solokha, S. K. Calderon, J. J. Velasco-Velez, C. Ampelli, S. Perathoner, G. Held, G. Centi, R. Arrigo, *Nat. Comm.*, 9 (2018) 1-12.
90. C. Tang, Y. Zheng, M. Jaroniec, S-Z. Qiao, *Angew. Chemie Int. Ed.*, 60 (2021) 19572-19590.
91. G. Centi, J. Čejka, *ChemSusChem*, 12 (2019) 621-632.
92. J. Masa, C. Andronesco, W. Schuhmann, *Angew. Chem. Int. Ed.*, 59 (2020) 15298–15312.
93. G. Yang, Y. Jiao, H. Yan, Y. Xie, C. Tian, A. Wu, Y. Wang, H. Fu, *Nat. Comm.*, 13 (2022) 3125.
94. G. Chen, Y. Sun, R. R. Chen, C. Biz, A. C. Fisher, M. P. Sherburne, J. W. Ager III, J. Gracia, Z. J. Xu, *J. Phys. Energy* 3 (2021) 031004.
95. E. Jung, H. Shin, W. H. Antink, Y-E. Sung, T. Hyeon, *ACS Energy Lett.*, 5 (2020) 1881–1892.
96. J. Ke, J. Zhao, M. Chi, M. Wang, X. Kong, Q. Chang, W. Zhou, C. Long, J. Zeng, Z. Geng. *Nat Commun* 13 (2022) 932.
97. R. Francke, R. D. *Chem. Soc. Rev.*, 43 (2014) 2492-252.
98. L. Kuo, C.-T. Dinh, *Current Opinion in Electrochem.*, 30 (2021) 100807.
99. J. Chen, T. Wang, Z. Li, B. Yang, Q. Zhang, L. Lei, P. Feng, Y. Hou, *Nano Res.*, 14 (2021) 3188.
100. C. Xiao, J. Zhang, *ACS Nano*, 15 (2021) 7975.
101. W. Ye, X. Guo, T. Ma, *Chem. Eng. J.*, 414 (2021) 128825.
102. T. K. Todorova, M. W. Schreiber, M. Fontecave, *ACS Catal.*, 10 (2020) 1754.
103. S. Nitopi, E. Bertheussen, S. B. Scott, X. Liu, A. K. Engstfeld, S. Horch, B. Seger, I. E. L. Stephens, K. Chan, C. Hahn, J. K. Nørskov, T. F. Jaramillo, I. Chorkendorff, *Chem. Rev.*, 119 (2019) 7610.
104. W. Wu, H. Hu, D. Ding, *Cell Reports Phys. Sci.*, 2 (2021) 100405.
105. D. Ding, Y. Zhang, W. Wu, D. Chen, M. Liu, T. He, *Energy Environ. Sci.*, 11 (2018) 1710.
106. Z. Li, N. H. Attanayake, J. L. Blackburn, E. M. Miller, *Energy & Env. Sci.*, 14 (2021) 624.
107. S. Zhang, X. Jing, Y. Wang, F. Li, *ChemNanoMat*, 7 (2021) 728.
108. H. Guzman, N. Russo, S. Hernandez, *Green Chem.*, 23 (2021) 1896.

109. S. Sarp, S. Gonzalez Hernandez, C. Chen, S. W. Sheehan, *Joule*, 5 (2021) 59.
110. D. Gao, R. M. Aran-Ais, H. S. Jeon, B. Roldan Cuenya, *Nature Catal.*, 2 (2019) 198.
111. A. V. Rayer, E. Reid, A. Kataria, I. Luz, S. J. Thompson, M. Lail, J. Zhou, M. Soukri, *J. CO₂ Utiliz.*, 39 (2020) 101159.
112. C. Ampelli, C. Genovese, B. C. Marepally, G. Papanikolaou, S. Perathoner, G. Centi, *Faraday Disc.*, 183 (2015) 125.
113. X. Sun, Q. Zhu, X. Kang, H. Liu, Q. Qian, J. Ma, Z. Zhang, G. Yang, B. Han, *Green Chem.*, 19 (2017) 2086.
114. F. Guo, B. Liu, M. Liu, Y. Xia, T. Wang, W. Hu, P. Fyffe, L. Tian, X. Chen X. *Green Chem.*, 23 (2021) 5129.
115. C. Genovese, C. Ampelli, S. Perathoner, G. Centi, *Green Chem.*, 19 (2017) 2406.
116. E. Schuler, M. Demetriou, N. R. Shiju, G.-J. M. Gruter, *ChemSusChem*, 14 (2021) 3636.
117. Y. Chen, A. Vise, W. E. Klein, F. C. Cetinbas, D. J. Myers, W. A. Smith, T. G. Deutsch, K. C. Neyerlin, *ACS Energy Lett.*, 5 (2020) 1825.
118. S. Guo, T. Asset, P. Atanassov, *ACS Catal.*, 11 (2021) 5172-5188.
119. G. Centi, S. Perathoner, *Chem. Comm.* (2022), submitted.
120. G. Centi, S. Perathoner, *Current Opinions in Chem. Eng.*, (2022) accepted.
121. D. Giusi, M. Miceli, C. Genovese, G. Centi, S. Perathoner, C. Ampelli, *Appl. Catal. B: Env.*, 318 (2022) 121845.
122. D Giusi, C. Ampelli, C. Genovese, S. Perathoner, G. Centi, *Chem. Eng. J.*, 408 (2022) 127250.
123. R. Yang, Y. Cheng, Y. Song, V. I. Belotelov, M. Sun, *Chem. Rec.*, 21 (2021) 797– 819.
124. H. Wang, W. Liu, X. He, P. Zhang, X. Zhang, Y. Xie, *J. Am. Chem. Soc.*, 142 (2020) 14007– 14022.
125. W. Xie, L. Tian, K. Wu, B. Guo, J. R. Gong, *J. Catal.*, 395 (2021) 91-104.
126. A. R. S. Kandada, C. Silva, *J. Phys. Chem. Lett.*, 11 (2020) 3173–3184.
127. D. Zhang, P. Wang, J. Wang, Y. Li, Y. Xia, S. Zhan, *PNAS*, 118 (2021) e2114729118.
128. A. Pannwitz, O. S. Wenger, *Chem. Commun.*, 55 (2019) 4004-4014.
129. K. Gordiz, S. Muy, W. G. Zeier, Y. Shao-Horn, A. Henry, *Cell Reports Phys. Sci.*, 2 (2021) 100431.
130. X. Tian, X. Yan, G. Varnavides, Y. Yuan, D. S. Kim, C. J. Ciccarino, P. Anikeeva, M.-Y. Li, L.-J. Li, P. Narang, X. Pan, J. Miao, *Sci. Adv.*, 7 (2021) eabi6699.
131. H. Wang, S. Jin, A. Wang, X. Jiang, W. Liu, X. Zhang, W. Yan, K. Yu, J. Zhao, Y. Xie, *CCS Chem.* (2022), Just Published. DOI:10.31635/ccschem.022.202101748
132. S. Luo, X. Ren, H. Lin, H. Song, J. Ye, *Chem. Sci.*, 12 (2021) 5701-5719.

133. F. Che, J. T. Gray, S. Ha, N. Kruse, S.L. Scott, J.-S. McEwen, *ACS Catal.*, 8 (2018) 5153-5174.
134. S. Lier, M. Grünewald, *Chem. Eng. Techn.*, 34 (2011) 809-816.
135. F. Cavani, G. Centi, S. Perathoner, F. Trifiró, *Sustainable Industrial Chemistry*, Wiley-VCH, Weinheim - Germany, 2009.
136. A. Stankiewicz, T. Van Gerven, G. Stefanidis, *The Fundamentals of Process Intensification*, Wiley-VCH, Weinheim - Germany, 2019.
137. A. Appolloni, G. Centi, N. Yang, *Current Opinion in Green and Sustainable Chem.* (2022), accepted.
138. C. Ampelli, G. Centi, R. Passalacqua, S. Perathoner, *Catal. Today*, 259 (2016) 246-258.
139. S. Perathoner, G. Centi, D. Su, *ChemSusChem*, 9 (2016) 345–357.
140. J. Proost, *Int. J. Hydrogen Energy*, 44 (2019) 4406-4413.