Perspective

System Chemistry in Catalysis: Facing the Next Challenges in Production of Energy Vectors and Environmental Remediation

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Abstract: Most of the catalytic processes that assist the production of either renewable energy vectors or degradation of environmental pollutants rely on the interplay among different factors that can be purposely regulated, in order to improve the overall efficiency of reactions. This perspective analyzes some recent examples of 'systemic catalysts', which are based on the modification of the reaction microenvironment and exploitation of concurrent/parasitic reactions or different types of chemical looping, in order to bypass some drawbacks that cannot be easily circumvented by standard approaches. Innovative extensions of those concepts and strategies might inspire new breakthroughs in a variety of key catalytic cycles characterized by high complexity.

Keywords: system chemistry; smart catalysts; CO$_2$RR; OER; environmental pollutants

1. Introduction

System chemistry investigates non-equilibrium systems that are based on homeostatic interactions among different species and require a continuous input of energy to operate [1,2]. Complex and dissipative systems are hallmarks of biology and, in general, life science [3–5]. On the other hand, most of the research activity tends more generally towards reductionistic approaches, which are often necessary to investigate specific processes or phenomena. However, most of the real systems are inherently complex. In addition to pharmacology, biochemistry and fundamental research on the origin of life, which are all directly linked to the world of biology, several fields of environmental (including atmospheric chemistry and precision agriculture) and computational chemistry, as well as materials science, are striving to cope with such a complexity. For example, over the last few years a few systems of technological interest have been developed by exploiting autocatalytic processes, such as oscillating reactions. They have been focused on the creation of self-sustained actuators [6–8], touch sensors [9], or paper-based devices for the temporary storage of self-expiring graphical information [10]. From a more fundamental viewpoint, autocatalytic surface reductions have been investigated to tune the growth of metallic nanoparticles [11], while bistable reactions have been exploited to control gold nanoparticle formation and self-assembly [12].

In the context of catalysis, the study of redox and photoredox catalysts, which takes advantage of coupling between different redox cycles, is another field in rapid expansion. In particular, the so called “synergistic catalysis”, which exploits the combined action of two catalysts and two catalytic cycles to generate new chemical bonds, is an impressive demonstration of systemic catalysis [13,14].

Recently, the translation of system chemistry principles applied to catalysts operating at the solid state over a macroscale was reported by Prins and co-workers [15]. This work
demonstrates the promotion of the catalytic activity of gold nanoparticles through the exploitation of kinetic asymmetry in the energy consumption generated by light irradiation of a photoresponsive hydrogel.

Although heterogenous catalysis could represent another natural playground to apply some of the key concepts and strategies that result from a global analysis of complex systems, this approach is still quite underdeveloped.

This perspective will briefly analyze, from a system chemistry viewpoint, some of the processes that are currently intensively explored for producing renewable energy vectors or chemicals and destroy/transform environmental pollutants. We will try to highlight the key reaction dynamics in which a catalyst is requested to operate according to smart and adaptive criteria.

Non-exhaustive examples of materials and strategies taken from recent literature—most of the papers have been published between 2017 and 2020—as well as future challenges in catalyst’s design will be discussed.

2. Systemic Catalysts: Design Strategies and Selected Examples
2.1. Dynamics of Factors that Influence the Performances of a Catalyst

Temperature fluctuations, availability of reactants, poisoning of active sites, concurrent side reactions, structural and microstructural modification are among the main factors that influence the catalyst’s performances. In many real cases, these parameters undergo significant variations during a process, with direct influence on the rate determining step of a given reaction.

For example, in low-temperature combustion (LTC) processes, a major source of instabilities is caused by kinetic and thermokinetic oscillations, originated from a complex interplay among many competitive elementary reactions, which either release and dissipate (e.g., combustion, which is exothermic) or absorb (e.g., pyrolysis, endothermic) heat [16].

Chemical engineering is used to simulate catalytic processes by taking these dynamic modifications into account. In general, the effects of temperature and pressure/concentration changes can be predicted and mitigated.

Moreover, in some notable cases, such as reforming reactions utilized for production of syngas (or combined production of syngas and ethylene, as illustrated in Figure 1), concurrent endo- and exothermic processes are coupled to achieve autothermal conditions, in which the exothermic reaction provides the heat for the endothermic one [17,18].

![Figure 1](image_url)

**Figure 1.** Example of oxidative coupling in autothermal reactions for the combined production of syngas and ethylene. See [17] for details.

However, in most of the cases, quantitative predictions of variations in a catalyst’s structure and microstructure are extremely challenging. For this reason, in-situ characterization under operando-like conditions is often the only way to obtain reliable data. In
In this context, a number of characterization techniques based on synchrotron radiation have been gaining ever-growing interest in the last years [19].

In parallel, lab-scale tools and new analytical methods based on operando-like spectroscopies and the synergistic combination of complementary techniques (see, for example, all-dielectric optical antennas for mass spectrometry and Raman/FTIR spectroscopy multimodal analysis) have been recently developed in order to characterize chemical reactions in real-world conditions, getting rid of interferences that are usually caused by the use of conventional signal enhancers, such as plasmonic nanoparticles [20–26].

In-situ studies revealed that most of the heterogeneous catalysts evolve their structure and microstructure during the process, so that their original properties are often very different from those observed in working regime [27,28]. In general, a progressive deactivation is a common fate for all the catalytic systems, however in many cases the performance of a catalyst reaches its maximum after several catalytic cycles.

Smart “switchable” catalysts, able to respond and adapt to drastic changes of the external parameters are going to be developed in many contexts [29]. These types of catalysts are designed to control diffusion dynamics and aggregation states as a function of changes of different stimuli—such as temperature, pH, ionic strength, light, magnetic, and electric fields.

However, a systemic approach in catalyst’s design is not limited to the exploitation of these types of external stimuli, but aims at envisioning different scenarios during a catalytic reaction, in order to identify the most critical steps and, hopefully, transform limitations and drawbacks into advantages. This means that the horizons of several catalytic processes should be broadened through the interconnection/coupling among different and even concurrent reactions. To do that, a preliminary evaluation of all possible reactions occurring under working conditions should be carefully carried out.

For example, the dry reforming methane reaction,

\[ \text{CH}_4 + \text{CO}_2 \rightleftharpoons 2 \text{H}_2 + 2 \text{CO} \quad \Delta H^\circ = +247 \text{ KJ/mol} \]  

(1)
can be accompanied by a number of other concurrent reactions, such as the water–gas shift reaction

\[ \text{CO}_2 + \text{H}_2 \rightleftharpoons \text{H}_2\text{O} + \text{CO} \quad \Delta H^\circ = + 41 \text{ KJ/mol} \]  

(2)

Other related reforming reactions can occur

\[ \text{CH}_4 + 2 \text{H}_2\text{O} \rightleftharpoons 3 \text{H}_2 + \text{CO} \quad \Delta H^\circ = +206 \text{ KJ/mol} \]  

(3)

\[ \text{CH}_4 + 2 \text{H}_2\text{O} \rightleftharpoons 4 \text{H}_2 + \text{CO}_2 \quad \Delta H^\circ = +165 \text{ KJ/mol} \]  

(4)

Moreover, coke formation, which is one of the main causes of catalyst’s deactivation, is directly influenced by temperature and pressure conditions. In particular, methane decomposition

\[ \text{CH}_4 \rightleftharpoons \text{C} + 2 \text{H}_2 \quad \Delta H^\circ = +75 \text{ KJ/mol} \]  

(5)
is an endothermic reaction, i.e., favored at high temperature. On the other hand, CO disproportionation to carbon coke and carbon dioxide

\[ 2 \text{CO} \rightleftharpoons \text{C} + \text{CO}_2 \quad \Delta H^\circ = -172 \text{ KJ/mol} \]  

(6)

occurs at low temperature and high pressure.

This means that carbon coke can be formed at both high and low temperature. As a result, temperature cannot be exploited as a helpful factor to avoid its formation. However, playing with the equilibrium law of mass, it would be possible to shift Equation (6) towards the formation of CO by adding CO$_2$. At the same time, low temperature and high concentration of CO$_2$ can induce the formation of C coke at low temperature, through the following reactions

\[ \text{CO}_2 + 2\text{H}_2 \rightleftharpoons \text{C} + 2 \text{H}_2\text{O} \quad \Delta H^\circ = -90 \text{ KJ/mol} \]  

(7)
This example illustrates the complex systems of chemical reactions that can take place in gas reactions involving small and simple molecules, such as CO, CH, CO, O, H, H, O, yet analogous arguments can be easily extended to the chemistry of N, NO, NH, SO, and volatile organic compounds.

In general, the design of a catalyst cannot avoid investigating a given process from a systemic viewpoint of complex side reactions.

This applies also to electrocatalysis, where different concurrent reactions can occur in the same potential window. One example is given by chlorine evolution, which competes with oxygen evolution in water splitting processes based on salt water [30]. Along the same line, the selectivity and overall efficiency of a photocatalytic reaction can be strongly modulated by controlling the parameters that govern a system [31].

2.2. Selected Examples of Systemic Catalytic Strategies

Here we will analyze few examples, taken from recent literature, in which catalytic reactions take advantage of the development of systemic catalysts to improve reaction kinetics and/or selectivity.

In particular, in this perspective we will focus our attention on reactions utilized for production of energy vectors and degradation of environmental pollutants.

Different general strategies, which are alternative or complementary to static catalytic systems, can be sketched out (Figure 2). Figure 2a outlines a general process, in which the initial reagents interact to give rise to different intermediates, which eventually evolve in the formation of a targeted compound and, in many cases, other side-products. This reaction flow can be purposely altered by manipulating the catalyst’s local environment at a certain intermediate stage, in order to limit or suppress the formation of byproducts (Figure 2b). The manipulation of catalyst's local environment can be also introduced to directly convert undesired byproducts into product(s) (Figure 2c), and several loops can be designed by a synergistic combination of different possible pathways (Figure 2d). This scheme represents only a few experimental strategies that can be applied in different real cases. Many other variations can be introduced and adapted to each specific process.

Figure 2. Schemes of different catalytic strategies utilized to promote selectivity and yield of a given process: (a,b) systemic approach based on the manipulation of catalyst's local environment for the limitation of byproducts formation; (c) systemic approach based on the manipulation of local environment for the smart conversion of undesired byproducts into targeted products; (d) systemic approach based on design of chemical loops that take advantage of the manipulation of the local environment at different stages of the process and might leverage on concurrent reactions.
2.3. Manipulating the Local Microenvironment: The Case of Copper Catalysts for CO₂ Reduction and Related Reactions

Electroreduction of carbon dioxide (CO₂RR) is one of the most investigated processes to transform CO₂ into value-added products, including carbon-neutral fuels and a variety of C1 (CO, HCOOH, CH₄), C2 (C₂H₄, CH₃COOH, C₂H₅OH), and C3 (CH₃(CH₂)₂OH) chemicals.

In a recent paper X. Wang, A. Xu et al. (Sargent’s group) succeeded in obtaining methane from CO₂RR with high selectivity at current densities >100 mA cm⁻² and Faraday Efficiency of 48% [32]. This remarkable result has been achieved by controlling the local concentration of CO₂ available at the sites of a catalyst made of a 100 nm-thick layer of Cu sputtered on polytetrafluoroethylene (PTFE) membrane. This strategy relied on DFT calculations, which revealed that low selectivity in methane production is originated by the free energy barrier in conversion of CO₂ into adsorbed carboxylates (*COOH), the first step of a sequence of reactions that lead to the synthesis of methane

\[
\text{CO}_2 \rightarrow \text{COOH}^* \rightarrow \text{CO}^* \rightarrow \text{CHO}^* \rightarrow \cdots \rightarrow \text{CH}_4
\]

where the species adsorbed on the Cu catalysts are indicated by an asterisk.

The poor selectivity towards methane formation is due to the C–C coupling reaction, which starts with the formation of OCCOH species and leads to the formation of ethylene. This reaction competes with protonation of CO to CHO, which will evolve up to methane synthesis.

The authors found out that lowering the coverage of CO₂ on the catalyst increases the free energy of COOH*, resulting in lower coverage of CO*. The difference in free energy between CHO and OCCOH shows that a lower coverage of CO* favors methane vs. C₂ selectivity. A systematic analysis of the reaction products at different concentrations of CO₂ (25, 50, 75, 100%) in the reaction gas stream, carried out at different ranges of current density (from 50 to 250 mA cm⁻²) revealed an optimum in methane selectivity for a gas stream with a CO₂ concentration of 75% at 225 mA cm⁻². Using a pure (100%) CO₂ stream, the yield of methane does not exceed 15% in optimal conditions. In parallel, dilute CO₂ streams promote hydrogen evolution reaction (HER). Instead of being competitive, this effect is beneficial for production of methane, as the high concentration of H* promotes the protonation of CO* to CHO*.

This work represents an example of a rational design of heterogeneous catalysts based on a systemic approach, which analyzes all possible reaction pathways and strongly modifies selectivity and yield of products by modifying the catalyst’s local microenvironment (Figure 2b), in particular by playing with easily tunable factors, such as the concentration of reagents and current density.

In another work, Li et al. demonstrated that the same catalyst (Cu on PTFE membranes) can be utilized in CO₂RR to produce ethylene with a Faradaic efficiency of 72% at a partial current density of 230 mA cm⁻², with a full-cell energy efficiency of 20% in a neutral medium [33]. Again, the increase of product selectivity and overall efficiency was based on the controlled manipulation of local environment. In particular, the authors exploited N-aryl-substituted tetrahydro-4,4'-bipyridine molecules to stabilize reaction intermediates. A detailed analysis of the intermediate steps that lead to ethylene formation revealed the crucial role of coordination of CO* on the Cu surface. Experimentally, the maximum Faradaic efficiency is achieved for an intermediate ratio between CO adsorbed in ‘atop’ and ‘bridge’ configurations. The model drawn from computational analyses shows that the water-mediated electron density transfer of the tetrahydro-bipyridine film stabilizes the ‘atop’ CO species, which in turns assist the selective formation of ethylene. A large library of tetrahydro-bipyridine was screened, which allowed to synthesize optimized species, on the basis of their electron-donor efficiency. When tetrahydro-bipyridine has a too strong electron-donor tendency, the number of atop-bound CO exceeds the optimal concentration, with detrimental effects on Faradaic efficiency. Decreased values of Faraday efficiency are observed also for poor-electron donor species that do not allow to stabilize a sufficient number of atop-bound CO molecules.
The use of accessory molecules to modify intermediate steps of a catalytic reactions is very exciting and could be extended to a variety of processes, introducing the concept of dynamic co-catalyst in heterogeneous reactions. Analogous approaches are quite common in homogeneous catalyst, but less diffuse in heterogeneous systems, in which catalyst and co-catalyst(s) are both in solid state.

Another way to control the local concentration of CO species in CO$_2$RR is represented by nanozymes, a class of inorganic nanoparticles that mimic selectivity and turnover rates of natural enzymes. In a recent work O'Mara et al. demonstrated that Ag/Cu core/shell nanoparticles can simulate enzymatic cascade reaction to produce C$_2$ or C$_3$ products through CO$_2$RR, depending on the potential window at which the process is operated [34]. In this case, CO$_2$ diffuses through the porous Cu shell layer toward the Ag core, where it is partially reduced to CO. CO back diffuses through the copper shell layer, where it is adsorbed and converted, via proton-coupled bimolecular reduction, into C$_2$ or C$_3$ products, which are eventually released outside the shell. This strategy enables to channel the sequence of CO$_2$ reduction reactions into a confined space, with CO molecules that are generated inside the catalyst’s core and are forced to stay in close proximity and interact with the copper shell to form new C-C bonds. Analogous approaches have been recently applied in multi-hollow copper catalysts that concentrate the reduction intermediates and stabilize the formation of Cu$^+$ species that promote the formation of C$_2$ and C$_3$ products [35].

One of the biggest challenges in Cu-based catalysts is their modification during the reaction, which results in significant changes in selectivity. Although in situ characterization techniques have been able to monitor the evolution of surface modification as a function of time under operando-like conditions, the prevention or control of this transformation is still hard to be achieved [36,37]. In general, most of the strategies utilized to protect the Cu functionality and preserve selectivity are based on protective layers, such as reduced graphene oxide or cationic surfactants [38]. The main disadvantage of using coating layers is the reduction of the number of accessible sites, which is detrimental for the reaction kinetics. An alternative strategy is based on the use of Cu nanoparticles that modify their morphology under bias, improving the formation of C$_2$ and C$_3$ products during operation [39].

However, general solutions are still under investigation. A promising strategy, in the case of reactions and processes that require Cu to be kept in reduced (metallic) state, in order to prevent its oxidation, could be inspired by a seminal work of the Linic’s group on ethylene epoxidation [40]. This reaction is normally affected by surface oxidation of the Cu catalyst, which typically occurs under working condition (T = 400–500 °C) and strongly decreases reaction selectivity. This work demonstrated that visible light irradiation (580 nm) can excite localized surface plasmon resonance, leading to the reduction of the freshly formed oxide. This restores the original selectivity and can sustain the reaction under industrial-compatible conditions. Although this approach is indeed quite general and applicable to a variety of plasmonic particles, to date most of the work on plasmon-assisted reactions has been focused on the exploitation of co-catalytic effects related to hot-electron injection or charge separation, not for keeping the catalyst ‘clean’ or preventing its oxidation.

The possibility of exploiting light as auxiliary tool for the control of the efficiency of a catalytic system has been investigated also at the macroscopic scale [41]. This study has led to the development of a photo-actuated shutter that, according to the wavelength of the incident light, enables to regulate the activity of a photocatalyst deposed on the surface of the photoactuator, controlling the occurrence or the inhibition of a photochemical reaction. In this case, a mechanical system is utilized for the control of a classical photocatalytic system and light is exploited as parameter to modify microenvironment conditions of the catalytic system. Under UV illumination, the photoactuator is not active, it maintains a flat configuration and light can be exploited for making the desired photoreaction to occur. On the contrary, under visible illumination the photoactuator movement is activated,
protecting the chemical system from light and inhibiting the occurrence of the photochemical reaction. The value of this approach has been demonstrated in the case of methylene blue photodegradation catalyzed by TiO\textsubscript{2} nanoparticles, but the same principle could be exploited also in the case of different photoreactions.

2.4. Turning Problems into Opportunities: The Case of NiFe for Methane Dry Reforming and Chemical Looping

As discussed in the previous paragraph, CO\textsubscript{2} can react with methane in a dry reforming process to produce syngas, a mixture of hydrogen and carbon monoxide with a molar ratio around 1:1 (reaction 1). Among the variety of metals that have been screened to catalyze this reaction, Ni is one of the most investigated because of its low cost and high activity. In particular, Ni alloys have been extensively studied in view of their superior stability under operational conditions. Müller and co-workers demonstrated that NiFe alloys are able to generate a dynamic dealloying/re-alloying loop in response to changes of microenvironmental conditions during dry reforming, which prevents the formation of carbon coke, improving the overall efficiency of the catalyst [42]. The result is an adaptive catalyst, which is able to maintain its activity by dynamically modifying its phase (Figure 3).

![Figure 3](image)

**Figure 3.** Example of self-regulating phase-change catalyst. See the main text and [42] for details.

An important point to note is that Ni maintains its metallic state (Ni\textsuperscript{0}) either in the presence or absence of Fe. Thus, Fe is not active per se in dry reforming reaction, but plays an indirect key role, which can be understood by considering the different competitive reactions occurring in dry reforming

\[
\begin{align*}
\text{CH}_4 & \rightleftharpoons 2 \text{H}_2 + \text{C} \quad \text{(10)} \\
\text{CO}_2 + \text{Fe} & \rightleftharpoons \text{CO} + \text{FeO} \quad \text{(11)} \\
\text{C} + \text{FeO} & \rightleftharpoons \text{CO} + \text{Fe} \quad \text{(12)}
\end{align*}
\]

In NiFe alloys, during the interaction with CO\textsubscript{2} Fe is partially oxidized to FeO (reaction 10), which induces partial dealloying of the catalyst. FeO forms few nm-thick small domains that locate preferentially on the catalyst surface, protecting Ni from coke formation (reaction 9). As a result of this interaction with carbon, FeO is reduced back to Fe (reaction 11), which is reincorporated in Ni lattice (realloying). This beneficial Fe redox cycle avoids Ni deactivation and allows to sustain dry reforming. The best performances were observed for a Ni\textsubscript{4}Fe composition. This is an example of active protection or catalyst ‘self-healing’. Unlike the case of plasmonic reduction, which should be externally activated by light irradiation, in this case the catalyst directly exploits coke formation, the major drawback of dry reforming, for restoring the catalyst to its initial state.

This example introduces two key concepts in design of systemic catalysts.
The first is related to the possibility to turn detrimental, yet unavoidable, effects into positive (or even essential) factors to control the process course.

For example, D.Y. Chung et al. suggested to exploit Cr(VI) reduction to Cr(III) to oxidize CO2 the CO adsorbed on Pt catalyst, which usually causes inactivation of the catalysts in direct methanol fuel cells [43]. This idea suggests an intriguing way to employ contaminated wastewater as an additive for the production of fuels (Figure 4).

![Diagram of catalyst deactivation and regeneration](https://example.com/diagram.png)

**Figure 4.** Scheme representing the use of toxic or unwanted reagents/byproducts to prevent catalyst’s deactivation. See [43] for details.

However, several critical issues remain still open, as in real water the concentration of a given pollutant cannot be sufficient to the scope and, in any case, it cannot be controlled a priori. In addition, the simultaneous presence of other interfering species with uncontrolled concentration makes the exploitation of the external chemical inputs a non-trivial task.

The second concept is chemical looping, which has been extensively investigated in the Müller’s group, for example in production of pure H2 or syngas from methane [44–46]. The idea at the basis of chemical looping is the generation of a sequence of chemical reactions, aimed at obtaining a specific product that allows to use and regenerate a catalyst through a circular process originated from concurrent reactions (Figure 2d).

For example, as illustrated in Figure 5, pure H2 can be obtained from methane in three steps that have been designed to utilize and regenerate a metal oxide catalyst through a redox cycle.

![Diagram of chemical looping process](https://example.com/diagram.png)

**Figure 5.** Example of chemical looping-based process for the production of H2 from CH4, using metal oxide as catalyst. See the main text and [44,45] for details.
In particular, methane is exploited to reduce the metal oxide, typically Fe$_2$O$_3$, (step 1) to metallic Fe, which is in turn partially re-oxidized to Fe$_3$O$_4$ by reacting with steam to generate highly pure H$_2$ (step 2) and then fully oxidized in air to restore the Fe$_2$O$_3$ pristine state (step 3).

In this loop, methane is combusted with molecular oxygen that is extracted from Fe$_2$O$_3$ through a thermally-driven reduction. The metal oxide plays as the oxygen carrier, which avoids the combustion products to mix with either steam or H$_2$. As a result, no additional steps of H$_2$ separation and purification are required. This process is strongly dependent on the redox stability of iron oxide, which can be controlled by means of interactions with supporting substrates such as TiO$_2$, Al$_2$O$_3$, MgAl$_2$O$_4$, and ZrO$_2$. Müller and co-workers observed that the addition of Mn$_2$O$_3$ and ZrO$_2$ to the Fe$_2$O$_3$ oxygen carrier improves the overall redox performances, allowing to achieve a stable production of highly pure H$_2$. In particular, the formation of a Fe$_{75}$Mn$_{20}$Zr$_5$ solid solution limits the high-temperature induced sintering and prevents the deposition of carbon coke that normally originates from methane cracking [43]. In another example, the same group demonstrated that the addition of Cu to Ca$_2$Fe$_2$O$_5$ oxygen carriers contributes to the stable production of pure H$_2$ with high yields [44]. At the origin of this improvement of performances there is the reversible exsolution/reincorporation of Cu nanoparticles. From a conceptual viewpoint, this behavior resembles the dealloying–alloying cycle discussed for NiFe catalyst. Here, Cu exsolution promotes methane oxidation, whereas its re-incorporation is essential to regenerate the pristine oxygen carrier. Reoxidation can be obtained by air exposure and it is a hallmark of Cu. Analogous experiments carried out with Ni in lieu of Cu revealed that exsolved Ni cannot by reincorporated into the Ca$_2$Fe$_2$O$_5$ lattice, probably because Ni and Fe form NiFe alloys that tend to segregate separately.

These studies highlight the importance of designing the components of a process through a careful evaluation of the structural dynamics occurring in the solid phase. In the case of syngas production, Donat and Müller demonstrated that a proper modification of LaFeO$_3$ perovskite oxygen carriers, obtained by a partial substitution of Sr$^{2+}$ (15%) in the La$^{3+}$ sites and Al$^{3+}$ (5%) in Fe$^{3+}$ sites enables to promote a bulk phase transition that allows to transform methane and carbon dioxide in syngas with a H$_2$/CO $\approx$ 1 thorough chemical looping [46].

Overall, chemical looping is a very interesting and universal approach, especially for high temperature reactions. In this regard, other remarkable examples applied to the ‘drop-in’ generation of syngas fuels directly from solar irradiation, have been reported by Steinfeld and co-workers [47]. These studies demonstrated that a solar concentrator can be exploited to drive the endothermic reduction of the metal oxide catalyst, which is then reoxidized by reacting with steam and/or CO (Figure 6). Among the large variety of MO/MO$_{1-x}$ metal oxide couples that have been tested, the CeO$_2$-CeO$_2$$_x$ system was particularly investigated, as it offers key advantages in terms of faster kinetics and improved stability and selectivity in comparison to other couples, such as those based on ferrites. Ceria was able to drive water and carbon dioxide splitting and produce syngas with a H$_2$/CO ratio that can be easily controlled by tuning the amount of water and carbon dioxide introduced in the reaction medium [48]. The solar-to-fuel efficiency of these systems, which was quite limited (<1%) up to few years ago, has impressively grown in the last few years (around 5–6%) and it is expected to target the theoretical limit (20–30%) in the next future.

In spite of still existing challenges, all strategies discussed in this paragraph represent an advancement of the concept of switching catalysts, which are becoming an emerging frontier also in heterogeneous catalysis [29].
The catalytic activity of Ni electrodes is regulated by the formation of oxyhydroxide (NiOOH) species in the course of the process, which occurs in alkaline conditions at 1.4 V vs. reversible hydrogen electrode (RHE). Previous works by Boettcher and co-workers pointed out the role of Fe impurities in mediating the catalytic activity [50]. The work of Koper’s and co-workers shows that alkali ions have a direct effect in OER, even in the absence of iron. In particular, the combination of in situ Raman and impedance spectroscopy enabled the authors to postulate a new mechanism at the basis of the enhanced catalytic effect, which relies on the formation of a superoxo NiOOH-M+ intermediate with different M+ alkaline metals. These superoxo species are more stabilized when larger alkali metals

2.5. Systemic Approaches for Oxygen Evolution Reaction (OER)

Water splitting is a key process for the production of H₂ from renewable sources. However, the sluggish kinetics of oxygen evolution reaction (OER) is a major bottleneck, which strongly impacts on the performances of electrochemical and photoelectrochemical cells, as well as on the development of photocatalytic artificial leaves. OER is a four-electron reaction, which usually implies a sequence of multiple reaction steps, influenced by formation of different intermediate species [47].

Thus, the catalysis of OER can strongly benefit from systemic approaches. In a recent paper, the Koper’s group demonstrated that alkali cations can be a powerful factor for enhancing OER catalysed by Ni-based electrodes [49], as illustrated in Figure 7.

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Figure 6. Example of chemical looping-based process for the production of syngas, using metal oxide (e.g., CeO₂ or ZnO) as a catalyst. See the main text and [46,47] for details.

Figure 7. Example of manipulation of local microenvironment to improve OER. Enhancement of the activity of a Ni-based catalyst by alkali ions. See the main text and [49] for details.
(such as Cs⁺) are utilized as the M⁺ source. Although the details of this superoxo-assisted oxygen evolution are still under investigation, the effects on the overall OER processes are remarkable and clearly observed in both purified (i.e., iron-free) and non-purified electrolytic solutions. This example broadens the horizons of OER catalysis, which in the last years has been largely taking advantage of the dynamic modifications of the catalyst’s chemical composition [51–53], nanoalloying [54], and interactions with the substrate [55,56].

Another major goal in this field is represented by water splitting from sea, or in general, saline waters.

As mentioned before, the main issue in this regard is to keep OER separated from chlorine evolution (CER), which is not trivial as overpotential makes these two reactions concurrent in the potential range utilized to run water splitting. This competition originates from the different kinetics of the two processes. In particular, CER is a two-electron reaction that can be accomplished in a single catalytic step, which makes it faster than OER. Moreover, recent simulations revealed that OER and CER share the same catalytic centers. A way to tackle this competition was proposed in 2018 by Vos et al. and it is based on the deposition of a MnOₓ coating on the surface of IrOₓ catalysts, which are normally utilized to promote OER in acidic conditions [57]. The MnOₓ layer prevents CER, yet allowing free in-and-out access for water, protons and oxygen to the IrOₓ catalytic centers. Strasser and co-workers recently utilized a systemic approach to solve the problem of OER vs. CER selectivity [58]. The idea is based on water electrolyzers that utilized different electrolyte solutions to feed cathode and anode. In addition to the above-discussed competition between OER and CER as regards the potential range, the presence of chlorine ions in the water electrolyzer is detrimental for anion exchange membranes that are utilized to separate the cathodic and anodic compartment. The authors observed that NiFe-layered double hydroxide (NiFe-LDH) employed as catalyst for anodic OER exhibits optimized performances in alkaline environments, whereas saline water induces strong corrosion of both catalyst and porous transport layer. In order to circumvent this detrimental effect and allow NiFe-LDH catalysts to operate at their maximum efficiency, the electrolyzer was designed with a continuous feed of KOH solution at the anode, whereas the cathode is directly fed by seawater. This simple modification of the system enabled the electrolyzer to operate with superior performances in comparison to analogous, yet symmetric, cells.

Although many challenges remain to be addressed on the road towards seawater electrolysis, all the new strategies are expected to pass through a careful analysis of the overall system, including concurrent reactions and external factors that can be wisely exploited to assist the catalyst action.

Moreover, photocatalytic water splitting, as well as direct generation of solar fuels, draws inspiration from photosynthesis. In this regard, a number of catalytic systems based on the Z-scheme approach have been designed and investigated in detail over the past years (Figure 8). Here we observe that the Z-scheme, which is based on coupling between two photosystems connected by means of a common redox pathway, is a natural field of application of system chemistry, with a large number of factors that can be controlled to maximize photon capture and reaction efficiency, such as the recent exploitation of multiphoton conversion and inorganic or hybrid optical nanoantennas [59–61]. The reader can refer to many excellent and updated reviews for a comprehensive overview [62,63].
Environmental remediation is another sector of catalysis in which a systemic approach can allow to achieve major breakthroughs. Although most of the literature is focused on the catalytic degradation of specific targets, real systems are characterized by the simultaneous presence of many chemical species with extremely variable concentrations. Moreover, the concentration of these chemical species can vary not only from one system to another, but also in the same system as a function of time under the mutual influence of different environmental factors (pH, partial pressure, temperature, mass transport, etc.). This is the case, for example, of pollutants dispersed in water (rivers, sea, lakes, aquifers, ground-, waste-, and tap water), whose nature and relative concentration is typically unpredictable a priori and largely influenced by the above-mentioned factors. Analogous, or even greater, complexity is characteristic of atmospheric pollutants and, in general, atmospheric chemistry, where meteorological factors play a key role in determining the oscillations of relative concentration of gaseous species. In view of finding a practical application in such complex and challenging environments, a catalyst should be able to cope with a variety of pollutants, interfering species and dynamic modifications of the external factors (Figure 9).

For this reason, most of the catalysts and strategies tested on lab-scale cannot be extended to real systems. This gap can be bridged only by shifting the paradigm of catalyst’s design from specificity to generality. In other words, researchers are realizing that the quest for optimized catalysts specifically designed for the degradation of a given target, should be accompanied with the generation of systemic catalysts that can be active against different classes of compounds. In a recent paper, alginate-based active blends...
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have been employed as a coating layer for the most common ceramic photocatalysts (e.g., TiO$_2$) and catalytic supports (Al$_2$O$_3$ and ZrO$_2$) to adsorb cationic charged pollutants by means of a synergistic combination of electrostatic attraction and chemical affinity [64].

This concept of general decontaminant has been expanded in a recent paper focused on the development of photocatalysts for the degradation of different types of organic pollutants in water [65].

These photocatalysts were rationally designed as modular systems, consisting of catalytic centers made of silver nanoparticles, which play the double role of catalysts and optical antennas, embedded into alginate hydrogel bubbles, which are utilized as dynamic sponges to adsorb polluted water. The silver nanoparticles are functionalized with β-Cyclodextrin, which are characterized by a general affinity towards aryl- and heterocyclic ring-moieties. As most of the organic pollutants—such as dyes, biphenyls, and pharmaceutical compounds—contain these types of rings, these receptors act as universal scavengers for a large variety of pollutants. This pan-specific capture of organic pollutants represents an important advancement in comparison to previous works, which are often focused on the removal of individual compounds.

Moreover, the presence of plasmonic silver nanoparticles allows not only the ultrasensitive detection of water pollutants by portable Raman spectrophotometers, but also their efficient, light-driven degradation. In particular, two types of effects can be exploited: (a) the dynamic aggregation of the nanoparticles, induced by pollutant capture, which enables photo-assisted pollutant degradation or (b) pollutant light absorption capabilities. In this case the pollutant itself cooperates in its degradation. In the case of methylene blue, whose photosensitization produce singlet oxygen species, the pollutant can be utilized to destroy other pollutants, including bacteria or viruses, thus the overall catalyst is formed and evolves in the course of the process. Moreover, the pollutant capture-mediated aggregation of plasmonic nanoparticles is an efficient way to exploit local plasmonic heating. This opto-thermal effect, which has been intensively investigated in the last years, represents a general way to induce the degradation of recalcitrant pollutants that do not absorb light in the visible. The plasmonic bubbles take advantage of this effect to efficiently remove antibiotics from water under direct sunlight irradiation, with obvious advantages for real world applications. In another recent work, Wei et al. applied plasmonic heating generated by silica-stabilized Janus gold nanorods to activate peroxydisulfate and promote oxidation of different classes of persistent organic pollutants under solar illumination [66]. The degradation processes depend on the complex interplay among different phenomena, including photothermal heating, injection of hot-electrons and electron shuttling.

In general, all reactions involving the formation of radical species can be approached from a systemic chemistry viewpoint. In 2019 Huang et al. demonstrated the possibility to induce decomplexation of Cu(II)-EDTA complexes and removal of Cu(II) species from real industrial wastewater by exploiting autocatalytic reactions triggered by UV irradiation of chlorine, which is usually utilized for water disinfection [67]. Decomplexation is a key step in heavy metal recovery, as complexing agents effectively protect heavy metal ions from oxidation. In this regard, autocatalytic processes represent a major breakthrough for advanced oxidation processes (AOP), which are normally based on UV/H$_2$O$_2$, UV/persulfate and photo-Fenton reactions and, in real systems, decrease their efficiency by interactions with other interfering species and/or due to pH variations [68].

In the work of Huang [67], the production of highly efficient Cl radicals is sustained by the continuous interconversion of Cu(I)/Cu(II) that proceeds through concurrent ligand-to-metal and metal-to-ligand charge transfer. As a result, Cu(II)-EDTA decomplexation follows an autocatalytic kinetics and the rapidly formed CuO precipitates and can be easily recovered without need of any further pH adjustment. Again, an appropriate exploitation of concurrent intermediates can overcome unsolved problems for traditional catalysis.

All these approaches open the door to a variety of exciting applications for system chemistry. In the next future, the researchers could envision and design systemic catalysts through a synergistic combination of some of the concepts discussed above. In
particular, catalysts that are able to assist the degradation/conversion of wide classes of chemical species, such as those containing an aromatic ring, which are characteristic of a large variety of pharmaceutic compounds and many types of other organic pollutants, or fluorinated alkyl compounds, which encompass a few thousand different chemicals, could be rationally combined in catalytic cycles based on the synergistic interactions among external agents, reaction intermediates and byproducts (Figure 10). This kind of strategy could enable the simultaneous processing and transformation of different pollutants in real world environments.

![Figure 10. Scheme representing an example of systemic catalytic cycles based on synergistic interactions among different catalysts, reaction intermediates (Int 1, 2, . . . , n) and byproducts and exploited for producing safe and value-added compounds from environmental pollutants.](image)

3. Conclusions and Outlook

This perspective briefly discussed some recent examples of catalytic processes in complex systems, focusing the attention on approaches and strategies that are able to exploit such a complexity for improving catalytic performance. In addition to smart catalysts, which are able to adapt and respond to external stimuli, the rational manipulation and control of the local microenvironment is a key aspect in the design of any catalytic system operating in real world conditions.

In particular, we observed that research in the field of production of energy vectors from renewable sources can take full advantage of a detailed analysis of intermediate products and concurrent reactions. In general, most of the reactions promoted by heterogeneous catalysts are severely affected by the limited lifetime of intermediates, which makes their spatial confinement and activation into specific reaction pathways crucial factors to achieve high turnover frequency and selectivity. In this regard, biology offers a rich palette of inspirational examples, such as enzymes and coupled reactions involved in biological cycles and photosynthesis (Z-scheme).

Significant efforts in this direction have been reported in recent research works, aimed at triggering cascade reactions by means of artificial enzymes (nanozymes) or focused on stabilizing intermediate species in favorable configurations and regulating the access to catalytic active sites. Several successful cases of application of chemical looping concepts to high-temperature reactions, such as syngas production or hydrogen purification, have been reported in the last 2–3 years, and their number is expected to continuously grow in the near future.

No matter the strategy applied for promoting the activation of small molecules (CO₂, H₂O, CH₄, CO, NH₃, etc.) utilized to generate energy vectors, solar fuels or value-added products, in the research community there is an ever-increasing attention to find solutions that go beyond the static approaches that have been normally utilized so far.
A particularly interesting feature of systemic strategies is that, in some cases, detrimental factors, such as the formation of byproducts or the presence of contaminants, can be turned into useful, or even key, ingredients for improving the efficiency of the overall catalytic process. This kind of symbiosis could become a new paradigm in the design of catalysts, also for environmental remediation, which is an inherently complex field.

The examples discussed from this perspective also note the importance of achieving detailed information about all the factors and reaction pathways that can occur in a given process and their mutual interactions. In the case of complex systems, this could be a formidable task to accomplish. However, the giant leaps forward in development of machine learning and artificial intelligence-based algorithms can represent a powerful tool for catalyst’s design. At present, these algorithms are intensively utilized for screening among a variety of possible combinations of materials and compositions, in order to find optimal solutions for heterogeneous catalysis [69]. These analyses mainly rely on thermodynamic data and DFT simulations. However, the synergistic integration of these algorithms with experimental data obtained from in-situ and operando-like characterization techniques [70,71] could lead to the design of groundbreaking, alternative catalytic systems that are able to harness complexity to find out-of-the-box solutions to compelling problems, especially in the fields of energy vectors and environmental remediation [72].

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