

## Smart catalytic materials for energy transition

Energy transition, and the related chemistry transition due to their strong nexus, is creating a major worldwide change in the current production system, driven initially by social and environmental pressures (cleaner production, reduced greenhouse gas emissions), but today instead is pushed by economic (renewable energy sources are becoming progressively the more economic energy form) and geopolitical (energy security) motivations. Oil and natural gases are the building blocks of the current refinery and (petro) chemistry, but going beyond fossil fuels is the challenge associated with this transition. This has also major implications on the technologies and processes actually in use, further pushed from another emerging direction associated with the progressive change from centralized to delocalized productions, for a better link with the territory and the local resources. The combined effect of these two emerging directions determines a radical change in the energy and chemical production systems, with major technological implications. Current process technologies in the area of chemical and fuel production cannot just be adapted, they need to be fully redesigned (also in terms of concepts, materials, engineering) to address the new challenges of using renewable energy sources in delocalized productions (small-scale production at the regional level using local resources and in strong symbiosis to other local productions).<sup>1</sup>

Catalysis, particularly based on the use of solid catalytic materials, was one of the key enabling technologies of the current refinery and petrochemistry, with other 90% of the processes using heterogeneous catalysts and an economic impact (direct and indirect) of about one-third of the gross domestic product. This transition in the energy and chemistry requires thus to redesign catalysts because they need to operate under different conditions and for different targets. Rather than operations at high temperatures and sometimes also higher pressure, with heat as the main medium to provide/withdrawn energy to sustain the reaction, the use of renewable energy sources requires to change the catalytic technology, for example, using photons and/or electrons to drive the catalytic reactions, with operations typically at (or close to) ambient conditions. Thus, changing from thermal to

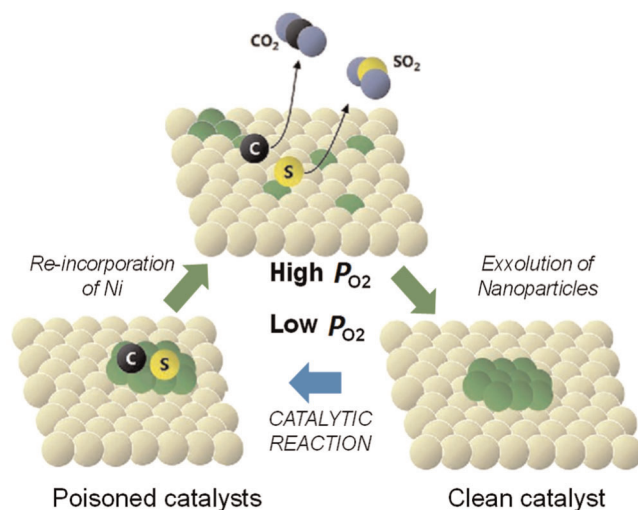
photo/electrocatalysis requires a full rethinking of the conceptual aspects of catalyst design.<sup>2</sup> This opens new possibilities for the area of smart catalytic materials.

The definition of "smart catalytic materials" refers to those where their catalytic performances can be changed by using an external stimulus and thus may be developed a system controlled by artificial intelligence (AI) able to vary dynamically the response, based, for example, to changes in the feed or to reaching some level of deactivation. A sensor may monitor the variation and give feedback to an AI. For example, in the case of deactivation of a solid catalyst, AI may induce a self-regeneration (in-situ) of the catalyst by an external stimulus. Some catalysts present in nature, such as enzymes or macrocyclic complexes, possess a self-regenerative functionality or they can self-adapt to external responses. For example, in photosynthesis machinery, there are self-reparation functions that limit activity when too intense light is present. However, these are not considered as "smart catalytic systems" because there is no possibility to control these systems by AI, and these systems are the result of evolution processes, not of any specific ad-hoc synthesis procedures.

The term "smart catalytic materials" thus indicates two main classes of catalysts. The first (also called intelligent catalysts) is related to those catalysts having self-regenerative functionalities. This is an area in which significant effort was made about 15 years ago, particularly in relation to automotive emissions control, although finding then limited commercial uses. It was related to the possibility of a cyclic movement of Palladium (Pd) between the outside (as Pd nanoparticles) and the inside (as Pd cations in the lattice) of the perovskite crystal in synchronization with the inherent fluctuations between reductive and oxidative (redox) atmospheres that occur in real automotive exhaust gases. A more recent example is the application of this concept to Lanthanum-doped strontium titanate (LST) materials for advanced SOFC (solid oxide fuel cells) anodes where nanosized nickel catalyst is repeatedly exsolved from and incorporated back into the LST perovskite host structure, to improve durability and sulfur resistance.<sup>3</sup> Figure 1 illustrates this concept.

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**FIGURE 1** A schematic drawing of the concept of self-reparation of a smart material catalyst triggered by oxygen partial pressure ( $P_{O_2}$ ). Reproduced with permission.<sup>3</sup> Copyright 2016, Royal Society of Chemistry

An analogous concept, but not related to regeneration, is the possibility of controlling the catalytic hydrogenation behavior (e.g., in alkyne-to-alkene selective transformation) by changing the amount of carbon incorporated in Pd particles, for example, the presence of subsurface carbon and hydrogen species.

These "smart" functionalities are thus based on a reversible switch between different active forms of a catalytic element in relation to environmental changes to avoid/limit the sintering of metal particles, although not limited to this aspect. Note, however, that it is a common practice in various industrial processes (even if often maintained secret) to make in-situ treatments (sometimes also by adding some chemicals in traces, or making some controlled redox cycles) to reform smaller catalyst nanoparticles from the larger ones, allowing thus to extend the catalyst lifetime.

The second class of "smart" catalysts is based on the concept of "soft matter in catalysis". This term indicates materials (catalysts) when noncovalent bonds play a key role. Note again that many "natural" catalysts (enzymes, etc.) are characterized by the presence of this type of bond. Here, however, the concept of soft matter in catalysis is restricted to those where a controlled procedure of synthesis exists, with thus the possibility of a tailored preparation.

Different typologies of systems may be identified, going from discrete units (where supramolecular assembly creates microenvironments suitable for chemical transformations) to extended systems (macroscopic assembly, polymeric networks) passing through non-discrete units (micelles, emulsions, and microemulsions, for biphasic liquid/liquid). The presence of noncovalent

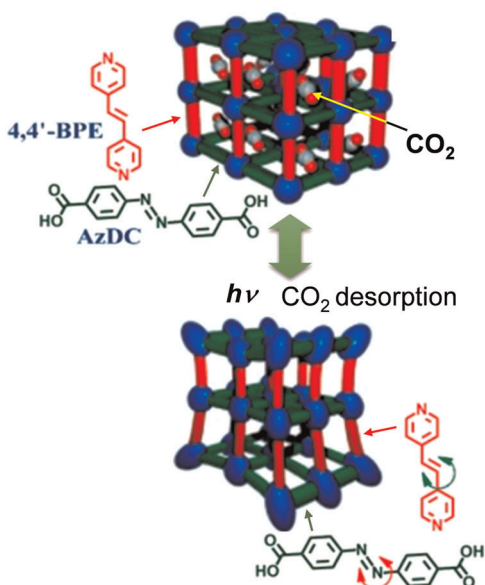
bonds and for example, of a softshell around a catalytic nanoparticle, makes it possible to develop stimuli-responsive materials, which can be externally switched from one state to another.

Different possibilities exist from switchable catalysis allowing to control the diffusion dynamics to systems where a change in the aggregation state can be induced externally.<sup>4</sup> The change of state of the catalyst can be induced by temperature, or even more interestingly by light, for example. This allows to control the diffusion of reactants or activators to the active sites, thus switching from a low to a higher reaction rate or the opposite. The most common case is that of metallic nanoparticles embedded in a stimuli-responsive hydrogel matrix or metallic nanoparticles functionalized with stimuli-responsive units. The alternative possibility is that of systems where an external stimulus (pH, ionic strength, or other stimuli) modifies the state of aggregation and consequently the reactivity. For example, catalyst nanoparticles embedded in a pH-responsive polymer matrix. There is a range of novel possibilities limited only by creativity. For example, changing the redox state of a catalytic site in a conductive substrate by an electrochemical stimulus like modulations in the applied potential to induce dynamics in the catalytic performances, which may increase the performances.

There is, thus, a range of possibilities to control the catalytic properties, exploiting, for example, the metastable properties and which can be controlled externally in different ways, from light illumination or application of a magnetic field, changes in pH, temperature, and so forth. Although these concepts are known for at least a decade, they have not found practical application, except in limited cases because often they do not have the necessary robustness for use. However, the increasing demand for novel catalysts to address the new challenges related to energy transition and chemistry has created new needs to develop advanced catalysts having these characteristics, for example, artificial photosynthesis devices.

For example, photoresponsive adsorbents (based on metal-organic framework materials) allow a pore-sized variation in response to a light stimulus and stimulated desorption of  $CO_2$ .<sup>5</sup> Figure 2 shows schematically this concept. Although not yet developed, this is the basis to create membranes equivalent to those present in leaves, which allow to operate directly with  $CO_2$  from the air. Thus, by extending this concept, it is possible to consider photoelectron catalytic (PEC) devices able to operate directly in the sun-driven reduction of  $CO_2$  to chemicals/fuels capturing  $CO_2$  directly from the air, a giant step towards the uses of these devices for a sustainable future.

In general, there is increasing attention toward hybrid PEC water-splitting devices, where combining light



**FIGURE 2** Light irradiation leads to the isomerization of the photoresponsive ligands, which distorts pore structures of the framework, allowing desorption of  $\text{CO}_2$ . Reproduced with permission.<sup>5</sup> Copyright 2019, American Chemical Society

harvesting with water redox catalysis, make it possible to limit electron-hole recombination and promote interfacial charge transfer. A range of novel possibilities can be introduced with external control of these aspects, for example, by inducing controlled modulations in the redox catalysis component or in heterojunction formation.

There are other examples of this emerging area of smart catalytic materials evidencing the relevant role for the future of catalysis and thus which requires the necessary attention to pass from curiosity-driven research to a more systematic analysis of the possibilities offered to design the next-generation catalysts for the energy transition. While inducing changes in the state of the catalyst by modification in temperature, or in the environment (pH, solvent, ionic strength), can have a limited practical impact (mainly to the separation of the catalyst for its recycle), the more exciting new direction is that of catalysts (particularly, photo and electrocatalysts) which behavior can be modulated in real-time from external inputs (light, potential applied, magnetic field, etc.). This opens the new field of externally modulated catalysis, which includes the area of dynamic restructuring. Especially in catalysis with renewable energy sources (photo, electro, and plasma catalysis), these novel possibilities are exciting.

It is worth to note, however, that there are relevant issues to transfer these results to practical applications, starting from the cost and robustness (particularly, under operations with real feeds containing various possible poisoning elements), to not-least the issues in the scale-up of

the synthesis to large scale. These are not intrinsic barriers, and adequate effort could solve them when the increase in the performances justify the costs of development. There is a continuous improvement in the knowledge of how to prepare industrial catalysts with precise control of the nanostructure. While for traditional heterogeneous catalysis, this effort has been translated to few successful novel catalysts, for the limited incentives (alternatives more economic solutions often exist), the situation is different for the novel area of catalysis with renewable energy sources, where higher demand for novel solutions exists.<sup>2</sup>

These smart catalytic materials introduce an additional level of complexity, with issues in terms of cost, robustness and stability, and the possibility of industrialization. However, they open a new field requiring a more extensive investigation to evaluate more correctly whether they remain an academic interesting area or instead represent a true novel, disruptive possibility.

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