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Heterogeneous Catalysis: Understanding for Designing, and Designing for Applications

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The ultimate goal in catalysis research is the ab initio design of catalysts by introducing the active sites that selectively drive the reaction to form the desired product. This objective may, in principle, be achieved with molecular catalysts, since the nature of the active sites can be rationalized and simulated by computational chemistry, and the catalyst can then be synthesized. Moreover, the reaction mechanism can be followed at the molecular level by means of microkinetic studies, labeling experiments, and operando spectroscopy. In the case of heterogeneous catalysis, the situation is more complex, since the reaction occurs at the usually ill-defined solid–gas or solid–liquid interfaces. The inhomogeneity of these surfaces makes the determination of the exact structure of an active site a difficult task if one takes into account the dynamics of the surface in the presence of reactants, and the fact that, sometimes, the real active site may be generated only under the actual reaction conditions. Therefore, additional difficulties exist for simulating the exact nature of active sites on solid catalysts, to study the reaction, and to obtain detailed microkinetic models in such complex systems.

The inherent difficulties for finding general models based on fundamental knowledge at the molecular level for the a priori design of solid catalysts, and the very strong economic and strategic impact of heterogeneous catalysis, have directed researchers to follow a more empirical strategy. In fact, it is possible to say that heterogeneous catalysis has mainly advanced by accumulated knowledge, trial and error, and judicious interpretation of results. Despite the introduction of high-throughput and combinatorial methods that certainly can be useful in the process of catalysts optimization, it is recognized that the generation of fundamental knowledge at the molecular level is key for the development of new concepts and for reaching the final objective of solid catalysts by design. The two methodologies, that is, a more pragmatic one that can produce catalysts, without an in-depth knowledge of the process at the molecular level, and a second one based on the deep understanding of the catalytic phenomena at the molecular level, will evolve together and will positively interact. A fundamental knowledge-based methodology should strongly help to go beyond incremental improvements and to make larger steps in the development of heterogeneous catalysis. Fortunately, researchers are currently capable of systematically undertaking that task. Indeed, research on catalysis with solids, by being interdisciplinary, both participates in and benefits from the advances in nanomaterials preparation, computational chemistry, and operando spectroscopic characterization of realistic catalysts and reaction conditions. All these techniques, combined with a good understanding of microkinetics and the mechanism of the catalytic process, as well as reactor design, should allow us to generate the necessary knowledge for understanding the molecular interactions at solid–gas and solid–liquid interfaces, and this can finally lead to the design and synthesis of efficient solid catalysts.

Generation of fundamental knowledge at the molecular level is key

I already mentioned that it is desirable to design solid catalysts with well-defined uniform single or multiple active sites that supply the desired selectivity to the catalytic process. This is exactly how nature has built the enzymes where the active sites are isolated and well-defined. The above characteristics are necessary, but not sufficient to achieve the extraordinary selectivity of the enzymes. Other key properties such as molecular selection by means of weak interactions and geometrical parameters, as well as "directed" adsorption and transition-state stabilization, are of paramount importance for explaining the great catalytic activity and selectivity of the biological systems. Moreover, heterogeneous catalysts should be versatile enough to overcome some of the limitations of natural enzymes. When moving into artificial catalysis, homogeneous catalysts such as transition-metal complexes and organocatalysts have been particularly successful for generating well-defined, single isolated sites where the electronic properties could be modified by a judicious choice of ligands and functional groups. However, the extension of those catalysts to more demanding experimental conditions, as well as catalyst recovery, can be a limi-

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tation for a number of chemical processes. Solid catalysts, on the other hand, are more robust and can be applied to almost any set of experimental conditions. Unfortunately, as already mentioned, it becomes difficult in the case of solids to generate large and regular surfaces with well-defined, single, and homogeneously distributed active sites. Furthermore, the limited flexibility of solids and the challenge to achieve a uniform atomic composition for the neighbors and next-nearest neighbors of the active sites limit the fine-tuning for molecular adsorption and transition-state selection and stabilization. Advances in this direction have been achieved with the design and synthesis of zeolites and zeolitic materials that can act as molecular sieves for reactant selection. Moreover, well-isolated single or multiple active sites can be introduced on the zeolite walls, and are accessible to reactants through regular pores and cavities that can influence the reactant adsorption and transition-state stabilization. These materials have become extraordinary solid catalysts for many important reactions. Nevertheless, there are some important issues that have yet to be addressed. The first one is the design and synthesis of zeolites with the active sites exclusively located in the desired framework positions. The second one, which is more difficult to overcome, is the limited flexibility of the framework for molecular adaptability required for optimization of transition-state energy and entropy. A third one is to achieve chiral centers in zeolites and zeolitic materials whose chirality could be transferred to a large variety of molecules. Achievement of these three objectives will help to push solid catalysis to another dimension.

Increasing the flexibility of solid catalysts has been attempted by synthesizing hybrid organic–inorganic structured solids containing active sites in either one or both components. Such solids include hybrid zeolites, periodic mesoporous organosilicas (PMOs), metal–organic frameworks (MOFs), and, in general, hybrid organic–inorganic catalysts, which all also offer the possibilities introduced by the organic component to design multifunctional solid catalysts. It is possible to imagine hybrid catalysts with multiple active sites integrated with enzymes, molecular catalysts, metal and metal oxide nanoparticles, and acid and base centers that may act in a coordinative fashion for catalyzing multistep reactions, in a one-pot or even in a cascade reaction mode.

Although solid catalysts have always been associated with the field of nanomaterials (since they involve nano-/mesoporous solids, metal and metal oxide nanoparticles, or even composite materials), it is fair to say that more recent developments in materials science have allowed us to improve and rationalize the shape and size of metal and metal oxide catalysts, synthesize materials (such as nitrides and carbides) with higher surface areas, or prepare multimetal catalysts, among others. In some cases, such as with gold, a very important increase in catalytic activity has been observed when metal particle size was reduced to a diameter of 1–2 nm. The possibilities to control nanoparticle size, shape, and composition should help to prepare solid catalysts in where noble metals are substituted by non-noble metals such as copper, cobalt, or iron.

> *It is desirable to design solid catalysts with well-defined uniform single or multiple active sites*

We are now coming to the point where the use of single atoms or small metal clusters of 3–10 atoms can improve metal-catalyst activity by more than three orders of magnitude when they interact through their frontier orbitals. What is more interesting is that such systems can be modeled and molecular interactions and reactivity of homo- and heteronuclear metal clusters can be studied “in silico”, thus opening further possibilities for the design of catalysts. There is no doubt that there are still limitations for their practical use, and stabilizing “naked” atoms and clusters is a challenge. However one should not forget that their industrial use will be dictated by the turnover numbers that can be achieved before the complex clusters vanish, in a similar way to some transition-metal complexes that are currently used in industry. Moreover, if the stabilization of naked metal atoms and clusters is generally achieved, it will be of much interest to investigate whether they catalyze the formation and breaking of non-activated C–C and C–H bonds, C–H bond functionalization, and also chemo-, regio-, and enantioselective hydrogenation or oxidation reactions.

Our responsibilities as scientists should not be limited to increasing the knowledge of the nature and behavior of matter, but we should also use that knowledge for improving the living standards of humankind. Therefore, we have to be aware of the social megatrends in order to anticipate future problems for achieving sustainable growth. Issues such as population growth, an aging society, healthcare, climate change, and limited resources, as well as an increased demand for sustainability, miniaturization, automated systems require an early response from science and technology. Chemistry, and certainly catalysis, can play an important role in health, sustainability, and energy, as well as food and clean water production. It certainly appears that in the challenge of creating a sustainable future, understanding the fundamental basis of molecular interactions at the solid–gas and solid–liquid interfaces, together with the knowledge required to design solid surfaces for achieving the desired catalytic interactions is a must.

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