Catalysis

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Bridging the Materials Gap in Catalysis: Entrapment of Molecular Catalysts in Functional Supports and Beyond**

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coordination chemistry · heterogeneous catalysis ·
porous materials · single-site catalysts ·
supported catalysts

Dedicated to Professor Gerhard Ertl

It's all over town: In view of the forthcoming shortage of natural resources, the demand for more efficient chemical processes for the conversion of energy and matter, especially with respect to carbon management, is growing rapidly.[1] For this reason, catalysis is of paramount importance and truly a key technology; which is confirmed by the fact that more than 80% of today's processes in the chemical industry rely on catalysis. However, the necessity to use natural resources more efficiently calls for the development of new, more efficient catalysts.

The range of complexity of catalysts is enormous, ranging from a single atom in a suitable environment (single active site) to molecular compounds, atoms of clusters adsorbed on solid surfaces, to complex active sites embedded in protein matrices in biological catalysts. Accordingly, active sites or models thereof can be categorized in three different groups, namely homogeneous, heterogeneous, and biological catalysts. Combining these traditional fields of catalysis could provide an understanding of processes in different length scales and thus establish a basis for the development of new catalysts. The desire to benefit much faster from the progress made in the different branches of catalysis and to achieve maximum synergism has led worldwide to the foundation of new catalysis research centers, including the recently established Cluster of Excellence in the Berlin region "Unifying Concepts in Catalysis" (UniCat).[2] In all such research centers, one of the main aims is to bridge the gap between homogeneous and heterogeneous catalyses.

The main advantage of homogeneous catalysts is that specificity, activity, and selectivity are given by their molecular architecture; therefore, reaction mechanisms can be rationalized and tuned in a controlled and predictable fashion. The opposite is also possible: by a specific modification of the catalyst, reaction paths can be influenced in a controlled and predictable manner. However, the use of (typically) organometallic catalysts beyond the laboratory scale requires their recovery and re-use. Therefore tremendous efforts have been made to transform a homogeneous into a heterogeneous catalyst by immobilization on an insoluble solid support. This approach of incorporating isolated ions, atoms, molecular complexes, or clusters on surfaces or in pores of otherwise inert supports has been labeled "surface organometallic chemistry".[3] Much work has also been devoted to the grafting of organometallic complexes on supports by long and flexible linkers.[4]

In these approaches, most often an inert support is used, which usually consists of amorphous silica and therefore only serves as spatial and geometrical component in such heterogeneous composites. The question arises as to why more than 90% of the weight of the material (not to mention the volume fraction) should solely contribute to the generation of surface area. Or, put another way, can a heterogeneous catalyst be prepared that is based on an organometallic complex, but where any part of the catalyst represents a certain valuable function besides generation of surface area?

Such a catalytic system that is based on an immobilized organometallic catalyst might be obtained by replacing the silica support by another, functional material. Indeed, like silica, various other materials can be (nano)structured, including metal oxides,[5] metals,[6] carbon materials,[7] and polymers.[8] Immobilization of organometallic complexes on such materials is however still scarce, except for metal complexes on titania or transparent conducting oxides, which are used for dye-sensitized solar cells,[9] whereas metal particles or clusters supported on metal oxides have been widely used as heterogeneous catalysts.[10] Nevertheless, when metals are supported on transition metal oxides, the active sites on such catalysts are difficult to identify, if at all present,

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even if the character of the metal–surface interaction, the presence of coordinatively unsaturated sites, and defects can be analyzed or adjusted in detail.[11,12]

Organometallic complexes on the one hand and pure metals on the other hand represent the two major but opposing concepts of single-site and multi-site catalysts. The term "multi-site" expresses that no exclusive active single site can be identified, as there is a great deal of surface mobility of compounds on supports.[13] In a new and exciting approach, Yosef et al. combined these two "opposing forces" in the heterogenization of an organometallic catalyst into a metal.[14] Intriguingly, the rhodium complex used is still intact and accessible after its entrapment in silver, and the composite [metal complex]@metal catalyst was active for catalytic hydrogenation reactions. The same group has already pioneered the incorporation of organic molecules and polymers into metals.[15] In particular, their process of entrapment is so mild that the organic compounds stay intact, and even chiral compounds maintained their chirality upon entrapment.[15c] Furthermore, it was shown that the organic molecules are still accessible for further reactions. Such organic@metal composites indeed have the potential to expand the properties of metals to typical organic features; thus, for example, acidic or chiral "metals" could be prepared.[15b,c]

The extension of this concept to the immobilization of an organometallic complex in a metal certainly opens up new possibilities for heterogeneous catalysis. Immobilization was accomplished by mixing a silver salt together with a complex derived from the chemical reaction of chloro(1,5-cyclooctadiene)rhodium(I) dimer with 3-(diphenylphosphino)benzenesulfonic acid (Figure 1). The complex thus formed features an anionic sulfonic acid group and phosphorus atoms, which ensures water solubility and also leads to strong interactions between the silver ions and the complex. In fact, reduction of the silver ions with elemental zinc results in the precipitation of silver, with the organometallic complex entrapped in the metal (Figure 2). In this case as well, the metal complex is still accessible from the outside but cannot be washed out even by "good" solvents, which makes the entrapment principally different from a simple adsorption on the metal surface. Most astonishingly, the organometallic complex still possesses good catalytic activity for catalytic hydrogenation reactions of styrene or diphenylacetylene.

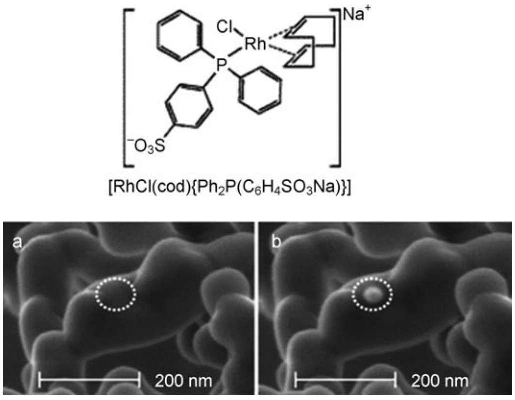

Figure 1. Chemical structure of the entrapped rhodium(I) catalyst and high-resolution SEM images for [Rh]@Ag sample showing the leaching out of the organometallic dopant owing to the high energy of the electron beam (circled area): a) first image, and b) image taken after a few seconds. Reproduced from Reference [14] with permission.

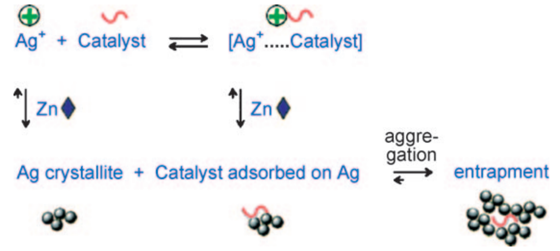

Figure 2. Proposed mechanism for heterogeneous entrapment. Reproduced from Reference [14] with permission.

This composite architecture, metal complex@metal, opens up a wide variety of possibilities: As the support is highly conductive, the catalyst can be easily incorporated into electrode assemblies. The sea of electrons provided by a metal can protect the entrapped metal from reduction, which is indeed the case for the example given herein under homogeneous reaction conditions. A metal or even alloy as support could also be considered, which furthermore acts as catalyst for a certain part of a consecutive reaction cascade, thus enabling novel synergistic effects towards unifying concepts in homogeneous and heterogeneous catalysis. The new family of complex@metal composites by Yosef et al. is therefore an important example of bridging the materials gap between homogeneous and heterogeneous catalysis.

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