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Review

Creating and mastering nano-objects to design advanced catalytic materials☆

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ABSTRACT

New developments in the synthesis of nano-materials have opened new possibilities for creating and mastering nano-objects in order to design novel advanced catalytic materials. This concise conceptual review will give a glimpse into this fast growing research area discussing some of the possibilities in this direction, the perspectives and the gap to reduce to develop selective catalysts for complex multi-step reactions. Emphasis is given to the opportunities offered by a tailored nano-design of the catalysts, from exploiting nano-confinement effects and supramolecular active sites synergies in nano-reactors to the new possibilities offered by new concepts such as the reduction of the relaxation time between two consecutive turnover cycles on a single active site and forcing a vectorial active site sequence in complex, multistep reactions. Other aspects discussed include the development of hierarchic pore structure to maximize catalyst effectiveness, metal complexes confined with solid cavities and the concept of nano-reactors, nanostructured composites and ordered 1D-type metal oxides. It is shown how significant progress in nano-materials has still not corresponded with progress in understanding the relationship between nanostructure and catalytic performance and the development of a more general strategy on the design of next-generation nano-catalysts.

1. Introduction

The significant changes in the worldwide economic and social panorama during the last decade have further stimulated the chemical and energy industries to reconsider their business strategies in terms of raw materials and energy resources, impact on the environment and the sustainability of their production [1–3]. One of the examples is the creation of the European Technology Platform on Sustainable Chemistry (www.suschem.org) from the joint effort of the European Chemical Industry Council (Cefic) and the European Association for Bioindustries (Europabio) to define a common vision and strategic roadmap to revitalize chemistry and biotechnology innovation in Europe. The aim was to strengthen the industrial competitiveness through a sustainability vision [4].

Because of these changes, a revitalization of the research on catalytic materials and industrial catalysts was observed in the last decade, with the opening of new area and in general a shift of the R&D activities with respect to those present in the last century [5]. For example, the increasing share of biofuels in the energy pool caused a fast growth in R&D activity to develop new catalysts and related catalytic processes [6,7]. Biomass is rich in oxygen and is composed of polymeric-like macro-units (cellulose, hemi-

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cellulose, and lignin). Novel catalysts to deconstruct selectively these macro-units to smaller platform molecules (sugars, phenol derivatives, etc.) and to convert these by selective elimination of oxygen are necessary, while acid catalysis prevails in an oil refinery and catalysts able to insert oxygen into the hydrocarbon are necessary in petrochemistry. Thus, conceptually new catalysts are necessary to create a bio-based economy. In addition, several of the catalytic reactions for biomass transformation require combining homo/heterogeneous catalysis with biocatalysis, creating the need for new catalysts [7].

The push towards more sustainable industrial chemical processes has also accelerated the need for new catalysts to be able to perform in a single reactor more complex transformation to reduce process complexity, energy consumption and waste production [5]. Also in this case conceptually new catalyst design is required to achieve this goal [7]. The effort towards process intensification and the use of micro-reactors has also increased the need for a new catalyst design to improve the performance.

The last decade was also characterized by intense research effort on the synthesis of novel nano-materials [8,9], for example by (i) surface assembling [10] or nano-casting [11] to create tailored inorganic micro- and nanostructures, (ii) assembling nanoscale building blocks at solution/solid interface to create ordered tubular nanostructures [12], (iii) synthesizing novel nanostructured carbons (as tubes, fibers, graphenes, mesostructures, etc. with a variety of novel sp^2 and/or sp^3 configuration or functional properties) [13], (iv) using different assembling or template strategies to create 3D hollow nano-architectures [14] or multilevel interior-structured hollow 0D or 1D micro/nano-materials [15], (v) using aerogel or aerogel-like nanostructures to fabricate appropriate nano-scale building blocks with suitable void space and disorder as design components [16] or specific architecture (multiple junctions) in metal nanoparticles supported over metal oxides [17], where the presence of perimeter sites at the boundary between the metal nanoparticles and the oxide is important to determine the catalytic reactivity in simple reactions such as CO oxidation or water-gas shift reaction [18]. While increasingly sophisticated synthesis methods are available to control the (i) nanostructure of materials [19,20], (ii) hierarchic organization of the mesoscale in advanced materials [21–25], and (iii) nature of the active sites in nanoporous materials [26,27], still limited data are available, however, on the correlation between the nano-scale architecture of the catalysts and their catalytic activity, particularly in complex catalytic reactions [28,29] which are more demanding in terms of nano-architecture of the catalyst centres with respect to simpler reactions like CO oxidation or model reactions [30].

The existing gap with respect to the precise control possible in organometallic and metallo-organic catalysts has also been considerably reduced in solid nano-catalysts [31,32] in the last decade. This progress in R&D of tailored catalytic nano-materials put in a different perspective the traditional discussion about the advantages and limits of homogeneous versus heterogeneous catalysis [33–37] with the need to overcome this dichotomy in a new integrated vision [5]. This concise conceptual review has the aim to provide some of the potential possibilities, and reduce the aforementioned gap, in creating and mastering nano-objects for the design of advanced catalytic materials to address the societal challenging of sustainable production and energy [38].

2. Catalysis and the nano-dimension

Catalysis is a molecular phenomenon and similarly to homogeneous catalysis by metal-complexes in solid catalysis, the reaction occurs on an active site, i.e. involving the rupture and creation of bonds at the distance of the coordination sphere. However, a more rigid structure of the active centres is present and limited possibilities to tune the electronic structure of the active metal centre exist. Both these factors contribute to typically lower selectivities for heterogeneous catalysis in single reactions with respect to homogeneous catalysis by metal complexes, although the former are able to perform selectively complex multistep reactions, which often cannot be made by homogeneous catalysts [5].

The surface sites on a solid material (for example, hydroxyl groups) may act as ligands to prepare supported metal complexes, in order to combine the advantages of homogeneous catalysts (better intrinsic control of the nature of the active centre) to those of heterogeneous catalysts (easy separation, higher productivity, etc.), and also to prepare single site catalysts. This was the base concept for the large effort towards a “surface organometallic chemistry” [39]. However, the surface sites present on the support may interact with the metal complexes. This interaction often gives rise to a lowering of the performance of the supported metal complex with respect to those of the analogous homogeneous complex. An approach explored to overcome this problem was to tether covalently the metal complex to the supports, i.e. to introduce a flexible spacer (linker) between the metal complex and the support [40–43]. In some cases, the supported metal-complexes showed improved performance [44,45]. The direct anchoring of the metal complex to the surface through covalent bonding may change the electronic state of the metal centre or force an unusual configuration of the metal complexes, which can reflect positively in its reactivity or can improve the performance by assisting the coordination of the incoming molecules. Novel active reaction spaces can be thus designed by (i) influencing the coordination of the central metals, (ii) chemical interaction at metal–surface interface, and (iii) three-dimensional architecture at the surface sites [37,46]. Therefore, not only the specific nature of the active centre, but also the environment around the active sites is relevant in determining the catalytic behaviour, similarly to enzymes where the flexible protein-structure determines the access and coordination of the reactants to the active sites.

Additional effects are possible due to the presence of an ordered 3D structure. A good example is offered from microporous (zeolite) materials having active site centres located inside the ordered pore structure. Due to the molecular-size dimensions of the channels and access cavities in microporous materials, the well-known effects of shape selectivity are present: restriction on diffusion of reactants and/or products, and on transition state [47–49]. Chiral zeolitic materials can also combine both shape selectivity and enantioselectivity [50]. Another effect is related to the change in the local nano-environment. This concept can be exemplified by the case of Ti-silicalite (TS-1), industrial catalyst for the selective oxidation of various substrates using H_2O_2 [51]. TS-1 has approximately the same composition as the Shell epoxidation (industrial) catalyst based on Ti ions supported on amorphous silica [6]. Both these catalysts are selective in the synthesis of propene oxide from propene, but TS-1 uses H_2O_2 as the reactant, while hydroperoxides (for example, ethylbenzene hydroperoxide) are necessary in the case of the Shell catalyst [5]. The difference is related mainly to the local environment around the Ti active sites. TS-1 is hydrophobic and water molecules essentially do not diffuse inside the channels of TS-1 zeolite, where the Ti ions are localized. In the Shell catalyst the Ti ions are accessible to water molecules. The catalyst is able to epoxidize 1-hexene with H_2O_2, if a “water-sponge” is present which scavenges the H_2O formed during the reaction. TS-1 is instead active in aqueous solutions of H_2O_2 (usually a water/methanol solvent is used), because the hydrophobic character of the local environment around the active sites (nano-environment) creates a local water-free-like solvent.