

# Supported metal nano particles and their scope in catalysis

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Catalysis and heterogeneous catalysts are essential to our present technology. Inexpensive transportation fuels, high-temperature lubricants, chlorine-free refrigerants, high-strength polymers, stain-resistant fibres, cancer treatment drugs, and many thousands of other products required by modern societies would not be possible without the existence of catalysts. These critical materials mediate the pathways by which chemical reactions occur, enabling the highly selective formation of desired products at rates that are commercially viable. Catalysts are also essential for the reduction of air and water pollution and contribute thereby to reducing the emissions of products that are harmful to human health and the environment. A recent article discussing the economic contributions of catalysis noted that “one-third of material gross national product in the U.S. involves a catalytic process somewhere in the production chain”. The majority of the industrial catalysts are high-surface-area solids onto which an active component is dispersed in the form of very small particles.

Nano catalysis is a new scientific area, if it is considered as the rational building of materials from basic structural units that are assembled on supra-molecular length scales to yield nanostructured inorganic polymers in small crystals that provide large surface areas. The control of a catalyst at supra-molecular length scales and the orientation of in situ characterization towards this aspect is broadening this research area, where atomic-level knowledge that might lead to a full definition of synthons (active sites) is still desperately needed. The similarity of this approach to that of biocatalysis is obvious. The degree of sophistication with which active sites in enzymes are fine-tuned by linking them into the complex network of an organic polymer made of chemically “simple” basic structural units is much higher than one can hope to achieve in purely inorganic systems. Catalysts in homogeneous catalysis, with their sophisticated ligand design, are intermediate in the comparison of chemical complexity and structural control.

Nanocatalysis requires a massive increase in understanding the synthetic processes in inorganic chemistry. Adapted in situ characterization methods and full chemical understanding of the “unattractive” environment of aqueous solutions are missing scientific essentials in obtaining the necessary fundamental insight. Chemical preparation pathways using aqueous methods are preferred as they provide great synthetic variability and give access to bulk quantities of active materials. The definition of structures for active sites or synthons will be a limiting factor for progress in this field. Besides the continuing insight into catalytic processes from the aspect of chemical physics, the much increased performance of ab initio theory can, with its hierarchical methodology, provide predictive clues for structures that may be worthwhile candidates in for synthetic nanocatalysis. As the design of nanocatalysts based on detailed synthetic understanding must still be considered a long-term objective, it is essential to apply a suitably modified high-throughput experimentation strategy that looks at the non-compositional parameter space for achieving visible breakthroughs in catalysis science using the “nanoconcept”. To achieve these breakthroughs, a massive increase in funding is vital to take nanocatalysis to a level where it is no longer considered to be a “mock-up” or an alternative to “conventional” catalysis, but rather where it is augmented by principles of physical chemistry, chemical engineering, and supramolecular inorganic chemistry, which may lead to the acquisition of the supporting fundamental knowledge that will be required to fully understand these processes.

Metals are among the most important catalysts, being used on a large scale for refining of petroleum, conversion of automobile exhaust, hydrogenation of carbon monoxide, hydrogenation

of fats, and many other processes. The metal is often expensive and may constitute only about 1 wt % of the catalytic material, being applied in a finely dispersed form as particles on a high-area porous metal oxide support.

The smaller the metal particles, the larger the fraction of the metal atoms that are exposed at surfaces, where they are accessible to reactant molecules and available for catalysis.

Particles ranging in size from roughly 1 to 50 nm exhibit physical and chemical properties that are intermediate between those of the smallest element from which they can be composed (such as a metal atom, the stoichiometric unit of a metal oxide) and those of the bulk material.

Boudart classified supported metals into three categories according to particle size, as follows:

(1) Metal particles larger than about  $50 \text{ \AA}$ , which have surface structures resembling those of chunks of the bulk metal.

(2) Supported metal particles in the size range  $10\text{-}50 \text{ \AA}$ , which have been regarded as the ones of most interest because changes in the particle size lead to significant changes in properties for many catalytic reactions.

(3) Supported metal particles with diameters  $<10 \text{ \AA}$ , which are henceforth referred to as clusters to distinguish them from the larger particles (or crystallites).

Supported metal clusters were barely mentioned in Boudart's 1985 review<sup>2</sup> because only little was known about them then. The moieties have dimensions of 1 to 20 nm and are often referred to as nanoparticles.

Metal nanoclusters have physical properties differing significantly from their bulk counterparts. Metallic properties such as delocalization of electrons in bulk metals which imbue them with high electrical and thermal conductivity, light reflectivity and mechanical ductility may be wholly or partially absent in metal nanoclusters, while new properties develop. Now days supported clusters are rapidly gaining attention because methods have been developed to prepare and characterize them and because a catalyst incorporating such clusters (platinum in the pores of LTL zeolite, Pt/ LTL zeolite) has found industrial application for selective reforming of naphtha to give aromatics.

The importance of small particles to the performance of catalysts has stimulated extensive efforts to develop tools for their characterization. Originating from the fields of physics, chemistry, materials science, and chemical engineering, this area of study is now often referred to as nanoscience.

zeolites are the most widely used catalysts in industry. They are crystalline microporous materials which have become extremely successful as catalysts for oil refining, petrochemistry, and organic synthesis in the production of fine and speciality chemicals, particularly when dealing with molecules having kinetic diameters below  $10 \text{ \AA}$ . Zeolite supports are important because the steric restrictions offered by the cages limit the sizes of clusters that can form in them, and the restrictions of the apertures limit what can enter and leave the cages. Thus clusters can be trapped in zeolite cages. The cages are small enough to exert solvent-like effects on clusters within them, and the cages may cause the cluster structures and properties to be different from those of clusters in solution or on the more nearly planar surfaces of amorphous supports.<sup>32</sup> Confinement in cages may hinder cluster interactions and increase cluster stability. Because of the regularity of structure of crystalline materials, clusters in their cages may be easier to characterize structurally than clusters in amorphous materials.

Despite these catalytically desirable properties of zeolites they become inadequate when reactants with sizes above the dimensions of the pores have to be processed. The presence of the mesopores in the crystallites of a given zeolite should basically increase the accessibility of large

molecules to the external opening of the pores. In other words, and from the stand point of large reactant molecules, the presence of mesopores in the crystallites of the zeolite would be equivalent to increasing the external surface of the zeolite making a larger number of pore openings accessible to the reactant.

The use of porous environments with defined pore sizes and characteristics as supports for nanoparticles allows the generation of specific adsorption sites, creating a partition between the exterior and the interior pore structure. It also has the added advantage of inhibiting particle growth to a particular size regime as well as reducing particle aggregation. Furthermore, by selecting and manipulating the textural properties of the porous support (sometimes in unison with a reduction step), it should be possible to control the size and shape of the resulting nanoparticles.

Metal oxides offer high thermal and chemical stabilities combined with a well-developed porous structure and high surface areas ( $4100 \text{ m}^2 \text{ g}^{-1}$ ), meeting the requirements for most applications. They can also be easily prepared and further functionalized, adding value to their use as supports and/or catalysts.

Within the broad domain of oxidation chemistry, oxygenations (i.e. the take-up of oxygen) constitute an important and diverse sub-class, including such differing processes as metal corrosion, deterioration of biological and man-made materials, combustion, and artificial partial oxidation. The last area refers to the selective introduction of functional groups for example in alcohols, aldehydes and carboxylic acids, without over-oxidizing the desired product. Such oxygenated molecules are used as building blocks in nearly all branches of chemical industry, ranging from polymer synthesis to medicinal chemistry. This industrial interest explains the massive increase in the number of scientific publications. One of the reasons is the higher oxidizability of the partial oxidation products, compared to the parent substrates, leading to an inherent selectivity problem. Partial oxidations are therefore considered a scientific challenge with direct industrial relevance. Although in principle both homogeneous and heterogeneous catalysts can be used to achieve this goal, usually solid catalysts are preferred because of easy handling (viz. recycling) and downstream processing considerations.

Supported metal clusters are a new class of catalyst. It may be fruitful to search for reactions for which supported metal clusters have catalytic properties superior to those of conventional supported metals. Several reports can be found on a wide range of applications of various supported bimetallic nanoparticles and metal nanoparticles in catalysis including Ru-Pt, Au-Pt, and Ag, Pd & Pt respectively. The key applications of the most commonly employed metals will now be briefly reviewed based on their number of publications.

Au being the most employed metal for such catalytic applications. Pd, and to a minor extent Pt, Rh and Ag metal nano-particles (MNPs) have also been reported to be active and selective in oxidation processes and hydrogenation process. Among the other reported examples, the oxidation of alcohols and selective hydrogenation of aldehyde are of great importance as a key transformation in organic synthesis. Many reports can be found on the uses of supported Au and Pd MNPs and bimetallic nano particles are using a wide range of oxidants. Recent research efforts have focused on the oxidation of glycerol, a widely available chemical that is currently obtained as a by-product of biodiesel production.

These are some out lines given about supported nano particles and clusters and their scope. In nano range the activity of born catalysts (active metals) increases very drastically. However industrial acceptance of a catalyst for a process is possible if the new material gives low product cost than currently adopted, i.e. gold can never accepted as industrial catalyst.

By converting a metal in to nano range we can make it active. Now on behalf of industrial point of view we all have to think to make metals active, which are industrially viable by converting them in nano range. Still there are lots of scopes remaining for nano in the production of specialty chemicals.

Overarching such nitty-gritty aspect is to motivate the development of nano clusters and nanoparticles supported on porous materials, (since they are also in nano range and also active) to enhance the activity of metals belongs to the first series and to make them industrially viable.

References:

- Ive Hermans, Eyal S. Spier, Ulrich Neuenschwander, Natascia Turra, Alfons Baiker *Top Catal* (2009) 52:1162–1174
- A. Corma *Chem. Rev.* 1995, 95, 5594-14
- J. P. Wilcoxon, B. L. Abrams *Chem. Soc. Rev.*, 2006, 35, 1162–1194
- Robin J. White, Rafael Luque, Vitaliy L. Budarin, James H. Clark, Duncan J. Macquarrie *Chem. Soc. Rev.*, 2009, 38, 481–494
- Alexis T. Bell *Science* 2003, 299, 1688
- B. C. Gates *Chem. Rev.* 1995, 95, 511-522