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# Nanotechnology: applications and potentials for heterogeneous catalysis

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**Abstract**

Nanotechnology offers the potential to design, synthesize, and control at nanometer length scale. While the catalysis community has many techniques at their disposal to synthesize catalytic materials at such a scale, the ability to fully design and control is still lacking. Examples are presented to illustrate what can nanotechnology do for heterogeneous catalysis to help achieve the goal of designing catalysts for perfect selectivity in a chemical reaction. Some current state-of-the-art approaches and potential limitations are discussed. Some examples of what can catalysis do for nanotechnology are also presented. However, this aspect is much less studied, although it offers rich opportunities for the catalysis community.

*Keywords:* Nanotechnology; Catalysis; Catalyst; Design; Selectivity

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## 1. Introduction

Nanotechnology has gained substantial popularity recently due to the rapidly developing techniques both to synthesize and characterize materials and devices at the nano-scale, as well as the promises that such technology offers to substantially expand the achievable limits in many different fields including medicine, electronics, chemistry, and engineering. In the literature, there are constantly reports of new discoveries of unusual phenomena due to the small scale and new applications. Nano-size noble metal particles have occupied a central place in heterogeneous catalysis for many years, long before recognition of nanotechnology. Thus, it is fitting to critically evaluate the impact of such development on heterogeneous catalysis [1,2].

In the discussion here, nanotechnology refers to techniques that offer the ability to deign, synthesize (or manufacture), and control at the length scale ranging from $<1$ to $>100$ nm. The emphasis in this definition of scope is ‘‘design and control’’, and not only synthesis. Synthesis of materials at nanometer scale has already become routine practice for supported noble metal catalysts after decades of research on the subject. However, there is much room for development to design and control. Thus, our discussion starts with defining what we would like to achieve in heterogeneous catalysis. This is followed by selective examples of how nanotechnology has helped researcher advance toward these goals, that is, examples of *what can nanotechnology do for (heterogeneous) catalysis*.

There is a complementary aspect in the relationship between catalysis and nanotechnology, which is: *what can catalysis do for nanotechnology*? Can catalysis help in the development of nanotechnology and in overcoming critical barriers? This is a much less explored aspect but it deserves attention.

## 2. Nanotechnology for catalysis

A major goal in catalysis research is to design catalysts that can achieve perfect selectivity and desirable activity. Between activity and selectivity, it is commonly accepted that the latter is much more difficult to achieve and control. Thus, it is the focus of our discussion. A reaction of perfect selectivity would generate no waste products, thereby reduce energy and process requirements for separation and purification.

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In nature, biological enzymes operate with very high selectivity. An enzyme is made of protein. The specific order of amino acids in the protein generates functionalities critical for the operation of the enzyme. Like other catalysts, an enzyme has an active site where chemical transformation takes place, such as bond breaking and forming. What distinguishes an enzyme from many other catalysts is the environment of the active site. Often the active site is in a cavity formed by the protein. Along the wall of the cavity are functional groups that help bind the reactant and product. One interesting and perhaps critical characteristic is the fact that the protein is flexible [3], such that the cavity, the active site, and the binding sites move during the course of the reaction to accommodate the adsorption and release of the reacting species.

Therefore, in the synthesis of a designed heterogeneous catalyst, it would be desirable to have complete control over the formation of the active site, the environment around the active site, the binding sites and their locations relative to the active site, and the path to access these functionalities. In other words, we would like to have complete control from the atomic scale to tens or hundreds of nanometer scale.

### 2.1. Active sites for metals

It is now accepted that for metallic catalysts, control at the atomic level is needed to design active sites because the chemical and catalytic properties of atoms at terraces, corners, and edges of a metal crystallite are different, and can be different from atoms at the metal-support interface [4]. In addition, the location of the metal cluster on the support may be important also if its properties are affected by its proximity to the support defects [5].

A much studied method attempting to generate metal clusters with atomic control is to use well-defined organometallic complexes as precursors. In recent years, uniform clusters of identifiable geometry up to five or six metal atoms can be synthesized [6]. Extension of this method to larger clusters, however, is limited by the availability of precursor complexes.

A different approach taken by Somorjai's group is to attempt control of particle size using lithography [7]. Metal clusters are deposited onto a masked, patterned surface. This technique, while offering control of location and separation between metal clusters, does not yet have control at the atomic level. Owing to the current limit in size resolution of the technique, even with the size-reduction lithography, it will be a challenge to produce atomically uniform (identical number of atoms per cluster and its shape) clusters at the nanometer size of interest in catalysis without major breakthroughs in the technology.

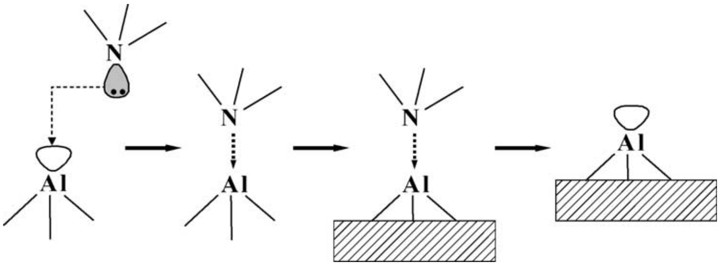
Deposition of small clusters using a STM tip has been demonstrated [8] that could also position metal clusters at desired locations on a flat substrate. The technique can be scaled up using the millipede approach to deposit a large number of clusters simultaneously [9]. Potentially, it can be coupled with dip-pen technology for a continuous supply of the metal precursor [10]. At present, however, these techniques have not yet achieved atomic control. In other words, there is no technique yet to generate supported metal clusters of uniform composition, shape, and size (see note added in proof).

When considering controlling metal clusters at the atomic level, it is important to keep in mind that the clusters may be dynamic, that is, the location of the atoms may respond to the environment. For example, there is direct observation using high resolution electron microscopy that the surface layer of a Pd crystallite restructures [11] and the shape of the crystallite changes [12] upon exposure to oxygen. A thorough understanding of the dynamic behavior of the atoms in a metal crystallite during catalysis would be greatly beneficial to establishing the limit and desirability of atomic control in these systems.

### 2.2. Active sites for oxides

Among oxides, zeolite is the most studied and best understood. For zeolite acids, the active sites are associated with the trivalent substituents in the zeolite framework. Other functionality, such as framework titanium for epoxidation and framework Co for oxidation, are also established. Extraframework active sites, including those introduced by ion-exchange and those synthesized by the ship-in-a-bottle techniques can be readily characterized.

For other oxides, however, the nature of the active site is less well defined. It is common that coordination unsatura-



Scheme 1. Illustrating the soft-chemical technique to synthesize alumina. Starting from the left, an aminoalkoxyaluminum monomer is formed, which is hydrolyzed in a controlled manner to form an alumina the surface of which is covered with Al ions bound to amine adducts. These sites are Lewis acid sites, active for catalysis without post-synthesis calcination.

tion of a cation in the surface is necessary for catalytic activity [13]. The general method to generate coordination unsaturation is by high temperature dehydroxylation of an oxide, which generates a wide range of surface sites. Recently, we explored a different method of preparation, in which we protect the coordination unsaturation site of the precursor during preparation of the oxide, so as to preserve it until the catalyst is formed. We demonstrated this with alumina [14]. Thus, we first converted the aluminum alkoxide precursor into aminoalkoxyaluminum monomers (Scheme 1). The amine ligand serves to protect the coordination unsaturation of the aluminum ion. Controlled hydrolysis of this precursor eventually led to the formation of an alumina surface that contains a much higher concentration of surface coordination unsaturation sites (Lewis acid sites) relative to surface hydroxyls than a conventionally prepared alumina. The new preparation is also much more active for Lewis acid catalyzed aminolysis of epoxide [15]. While this method offers some control of the active site at the atomic level, there is much to be developed before we can achieve the goal of controlling the active sites in general.

### 2.3. Environment around the active sites

Defining and controlling the active site is insufficient to have complete control of a catalytic reaction. As mentioned earlier, using an enzyme as example, the environment plays an important role as well. A very interesting example of how the environment affects selectivity is in the selective terminal oxidation of hexane by Co-AlPO-18 [16]. The high selectivity for 1,6-diacid was interpreted as due to the interaction of hexane with the wall of the cavity, such that the molecule is aligned in such a manner that the terminal carbons are positioned near the framework Co ions to favor their activation. If one desires to exploit such interaction to align the reactant molecule with respect to the active site in other systems, it would be necessary to be able to position the active sites in a cavity by design. Unfortunately, there is yet no known method to control the spatial distribution of cations in a molecular sieve framework.

One approach to attempt to control the relative positions of sites (active sites and binding sites) is to synthesize the area of interest by an unit-by-unit approach. That is, starting with an active site, ‘‘spacer’’ atoms or units are added one by one until a desired separation is obtained before the second functional site is added to the ensemble. We have started research along this direction. Fig. 1 shows a siloxane chain synthesized by such unit-by-unit approach. Starting from a single unit siloxane, a disiloxane is synthesized by adding another single unit to it. By repeating the procedure, trisiloxane, tetrasiloxane, and pentasiloxane were synthesized. [17].

Other approaches have been explored. One is molecular templating technique. Starting with a templating molecule that contains functional groups that can be linked to siloxane, a silica is formed by reacting the siloxane with other silica precursors. Consequently the template is enclosed in a cavity of silica. Cleaving the template from the silica gel with generation of catalytically active functional groups then generates active sites anchored to the silica wall at positions directed by the template [18]. This is schematically shown in Fig. 2 At present, such method offers some, but not precise control over positioning of the active sites.

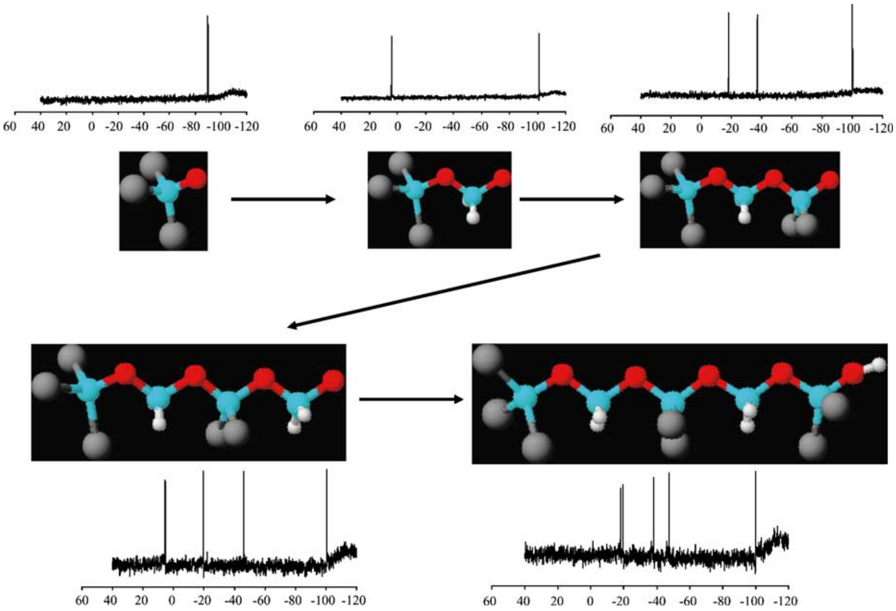


Fig. 1. Schematic drawing showing the unit-by-unit synthesis of a siloxane chain. Starting with a single siloxane, additional units are added stepwise to form disiloxane, trisiloxane, tetrasiloxane, and pentasiloxane. The $^{29}$Si NMR spectra show the presence of different Si atoms in each of the chains [17].

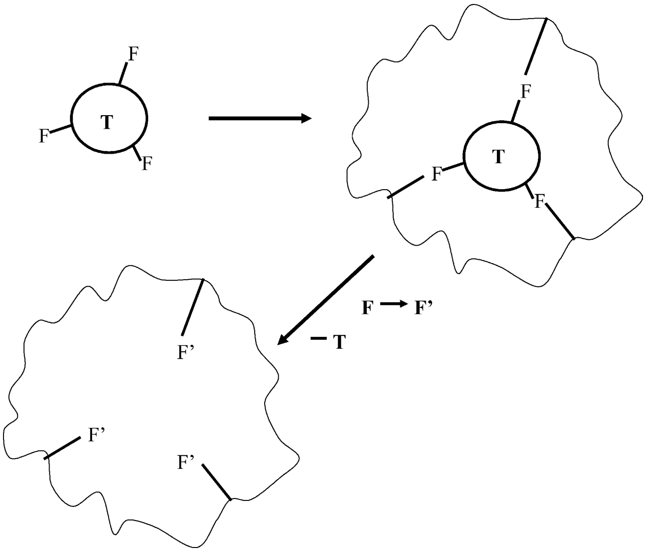


Fig. 2. Schematic drawing to show control of positioning of active sites on a cavity wall by molecular templating technique. A matrix is formed around a template molecule T that possesses three functional groups F as linking groups to the cavity wall. After removal of T and, at the same time, converting the linkage into catalytic active sites F', a cavity containing active sites F' at locations directed by T is formed.

Molecular templating is also used to shape the cavity around an active site. In one example [19], a template that resembles the reaction transition state bound to the active site was used. After forming the cavity around this template, the portion nonessential for the active site was removed. The resulting cavity can accommodate reactants that fit the shape better than molecules that do not, thus favoring reaction of these reactants. That is, the technique offers some control of selectivity. This technique was used to generate a more selective catalyst for hydrogenation of aryl ketones.

Templating using ordered surfactant molecules is a heavily studied technique first applied to prepare MCM41 type of materials [20]. Using this technique, regular channels of diameter ranging from about 2 nm up to 10 nm can be prepared. The original application was to prepare siliceous materials, but the technique has been successfully extended to many other oxides [21]. Using the same principle and with spherical styrofoam beads, siliceous materials containing regular spherical cavities can be prepared (Fig. 3) [22]. In fact, cavities of other shapes can be prepared using the appropriate templates. Such techniques, while versatile in preparing cavities and channels, are limited by the templates available. Furthermore, it will take further development to design cavities containing functional groups at specific positions.

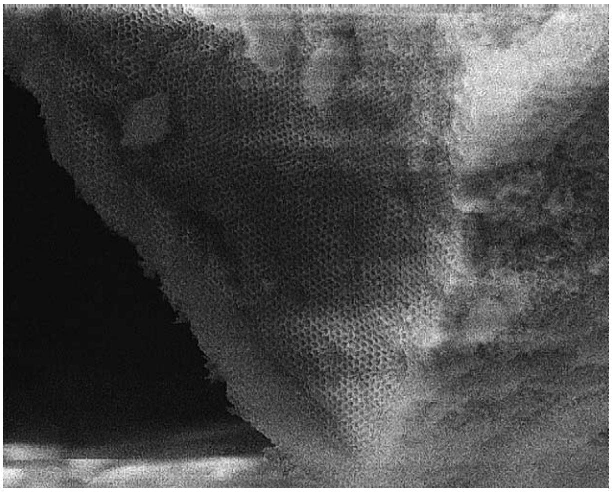


Fig. 3. SEM picture of a siliceous material containing uniform cavities of about 400 nm diameter, formed using regularly packed, 400 nm diameter styrofoam beads as template.

### 2.4. Reaction engineering

An area of great potential for new discovery is application of nanotechnology to reaction engineering. Here, the discussion emphasizes on control at the macromolecular level to influence chemical reaction, more specifically controlling when an active site is active and selectivity.

Researchers have successfully modified enzymes to effect on-off switching of catalytic activity. For example, by incorporating a polymer whose conformation responds to small changes in temperature into an enzyme near the active site, it was possible to switch on and off the enzyme reversibly by a small temperature swing [23]. Extending this concept to catalysts in general, it should be possible to design catalyst systems where there is a movable segment, controlled by a hinge, that brings a blocking group to or retrieve it from an active site, thereby turning the catalyst off and on (Fig. 4). One could even think of constructing a molecular-sized box big enough just to contain a stoichiometric number of the reactant molecules (Fig. 5). Then, only

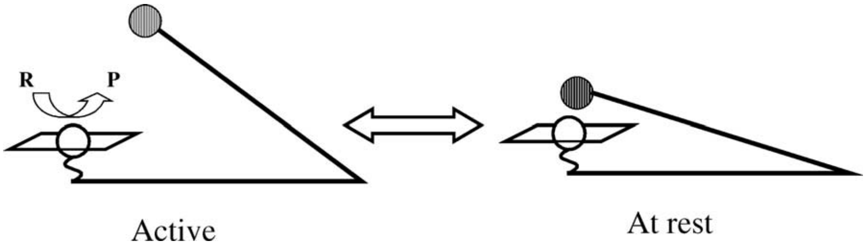


Fig. 4. Schematic drawing illustrating the concept of on-off switchable active sites. The circle in a square planar ligand represents the active site where reactant R reacts to form product P. When the active site is blocked by a blocking group (shaded sphere), the active site is at rest.

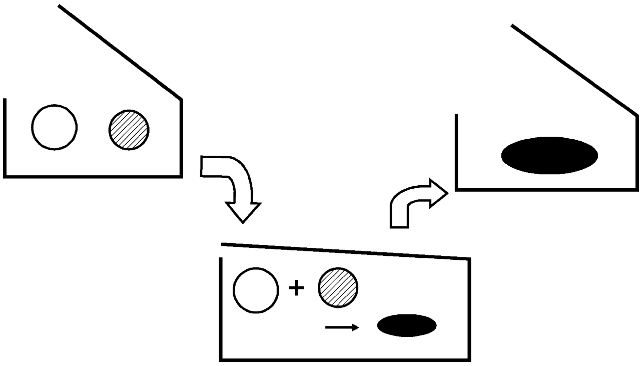


Fig. 5. Nanoreactor of the size of the mean-free path of the reactants, containing molecular hinge to control the reaction by closing the reactor. The two circles represent two reactant molecules, which can react to form the product represented by the oval. Since the box can only contain two molecules, only the desired reaction can proceed in the nanoreactor.

the desired product can be formed, since a wrong mixture in the box would not react. The necessary ingredients needed to bring this concept to reality are already known. For example, wall materials of different properties, from carbon as in carbon nanotubes to organic-inorganic hybrids [24], to inorganic oxide (e.g. MCM41) are known. Molecular hinges, the most important component, are also known. For example, the orientation of ligands around a metal ion can be reversibly changed through change in the oxidation state of the ion [25]. Other switching mechanisms employing light excitation, pH changes, and others are possible [26]. With ingenuity, these could be adapted for reaction engineering applications.

### 2.5. *Catalysis for nanotechnology*

Thus far, applications of catalysis to nanotechnology are limited. Two examples will be cited here for illustration.

Catalysts are used in forming carbon nanotubes. Metal catalyzed decomposition of carbon monoxide or hydrocarbon to form carbon nanotubes has been observed over two decades ago by T. Baker, but it was until recently that their unique properties were recognized. For practical applications, it is important to be able to control the dispersion in properties of the nanotubes such as wall thickness (single wall or multiwall), tube diameter, helicity, and length. Research has shown that catalytic synthesis offers much better potential to control the formation of the tubes than less-well controlled thermal decomposition. Various catalysts have been investigated, and some have been found to be effective in generating multiwall tubes, whereas others effective for single wall tubes [27]. Recently, synthesis of tubes of a rather narrow dispersion of tube diameter and helicity was reported, catalyzed by a Co-Mo catalyst [28].

The second example involves using catalytic reaction to supply energy for motion of small particles. Mallouk et al. at Penn State University coated one end of small particles with Pt, and the remaining part with Au. Upon placing the particles in a hydrogen peroxide solution, Pt-catalyzed decomposition of hydrogen peroxide occurs and the action propels the particles into a forward motion [29]. The exact mechanism that causes the motion is still under investigation. One possibility is the change of surface tension at the reaction end.

These examples demonstrate that catalysis can play an important role in the development of nanomaterials and nanomachines. However, at present, there are very few examples reported although there are many opportunities available.

## 3. Conclusion

There is little doubt that the catalysis community is following developments in nanotechnology closely and attempts to capitalize on these developments to further the goal of custom-designing catalysts to achieve perfect selectivity in a catalytic reaction. Much progress has been made, but many challenges remain. These challenges include the need to control the relative locations of the active sites and binding sites, controlling the atomic details of the active sites, and incorporate flexible openings and cavities. In reaction engineering, nanotechnology offers the opportunity to control reactor operation at the molecular level. One example is incorporation of molecular switches for active sites. It is expected that as the achievable limits are expanded, new applications will arise. In all these developments, in addition to inventing methods to achieve them in a laboratory, a significant hurdle is the need to develop reliable methods for mass production before significant commercialization is possible.

On the other hand, there is much less attention paid to use catalysis to enable nanotechnology. While catalytic synthesis of carbon nanotubes is being pursued, there is generally a lack of examples in which catalysis plays a pivotal, enabling role. It is likely that such opportunities are present and waiting to be discovered. It should be highly beneficial to pursue them.

## Note added in Proof

Preparation of metal nanoparticles of a narrower size distribution than conventional methods has been reported using the dendrimer-assisted method [30], which is consequent to starting with uniform-size dendrimer molecules and close to stoichiometric binding of metal precursors to them. Bimetallic particles can be made also [31], although a uniform composition has yet to be achieved.

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