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## Engineering of supported nanomaterials

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### Abstract

This brief review analyzes the parameters that can be used to guide the generation of hierarchic systems that include inorganic and/or biological nanoscale objects. Importance of interface effects and geometrical factors are underlined. The mutual influence between the substrate and the deposited material is an important factor to determine the most appropriate set of parameters for the synthesis of nanomaterials with desirable properties for industrial applications.

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### 1. Introduction

This brief review is an attempt to combine existing data about the mutual influence and interaction between supporting media (matrix) and supported material (active phase) to establish general dependencies in the engineering of nano-systems used in a wide variety of processes.

### 2. Factors influencing multicomponent systems

#### 2.1. Synergy between components

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Chemistry of materials is presently facing the challenging task of producing hierarchically structured hybrid nanocomposite materials. The design and successful processing of a new generation of smart materials with molecular interfaces that promote efficient self-assembly and charge-transfer is important for the development of heterogeneous catalysis, photocatalysis, light harvesting, hybrid organic/inorganic surface chemistry, etc.<sup>1-3</sup>.

At present, it is possible to couple the catalytic power of biological enzymes with semiconductor nanomaterials, or to immobilize them in voids of nanoporous supports. A clear design strategy is necessary to organize and control the molecular interactions. In heterogeneous catalysis most catalysts consist of a two-part system: a porous matrix, traditionally considered as an inert support, and the supported dispersed active phase. However, this complex multicomponent material can be modified by altering each component independently allowing to tune the properties of the resulting system. Modern chemistry permits to prepare porous materials with defined pore size and chemistry. Together with the well-developed methods of nanoparticle synthesis new possibilities arise to produce materials with predetermined properties. Structure relations and electronic properties are mutually important for both the support and the dispersed active phase. Table 1 shows examples of the combinations of variables in such a system.

Table 1. Examples of interactions between the elements of two-part systems

	Matrices	Supported materials
Structure (geometry); size and shape effects; connectivity of nanopores.	Zeolites. Mesoporous matrices, such as oxides and mixed oxides. Porous metals. Porous xerogels. Sol-gel materials. Porous carbon. Carbon nanomaterials. Aerogels. Porous Silicon. Polymer-based porous materials. Two-dimensional mesoporous membranes.	Pore-confined nanoparticles. Cluster stabilization. Size and shape of nanoparticles. Cluster sieving effects. Immobilization of enzymes.
Electronic properties; surface functionalization for subsequent anchoring.	Composition of the matrices. Ratio of components in multicomponent supports, for example Si/Al ratio of zeolites. Hydrophobic/hydrophilic interactions on the surface. Presence, concentration and strengths of Bronsted and/or Lewis acid centers. Interfaces and interphases in multicomponent materials.	Metal nanoparticles. Bimetallic systems. Semiconductor nanoparticles. Luminescent nanomaterials. Magnetic nanoparticles. Quantum size effects. Interfaces and interphases in multicomponent materials.

The same material supported on two matrices of different composition but equal structure shows dissimilar properties due to alterations generated by the interaction of the material with the supports. An example of this effect is the influence of the Si/Al ratio on the formation of different supported metal nano-species and on their stability<sup>4-6</sup>.

Currently, no clear model has been proposed yet for the events that take place during the nucleation of transition metal nano-particles (NPs) on a support surface. The use of diverse types of supporting materials leads to differences in terms of simplicity and efficiency of nucleation and in the resultant particle size and NPs dispersion<sup>7</sup>. Experimental efforts are needed to understand how the support interacts with transition metal NPs, how its composition influences the final NPs properties, and to elaborate protocols for choice and use of such materials.

In catalysis metal-support interaction plays an essential role. For example, CO or CO<sub>2</sub> hydrogenations are interesting catalytic reactions as they are alternatives to produce fine chemical feedstock, hence avoiding the use of fossil sources<sup>8</sup>. The Fischer–Tropsch synthesis (i.e., CO/H<sub>2</sub> and CO<sub>2</sub>/H<sub>2</sub> reactions) was studied for monodispersed Co nanoparticles. Although 10 nm Co NPs cannot be reduced at 250 °C while supported on TiO<sub>2</sub> or SiO<sub>2</sub>, cobalt oxide performs much better than fully reduced cobalt when supported on TiO<sub>2</sub>. In fact, the results indicate a 10-fold enhancement for the CO<sub>2</sub>/H<sub>2</sub> reaction rate and 2-fold for the CO/H<sub>2</sub> reaction rate when Co/TiO<sub>2</sub> treated at 250 °C in H<sub>2</sub> is used, versus Co/TiO<sub>2</sub> treated at 450 °C. Inversely, activity of cobalt supported on SiO<sub>2</sub> has a higher turnover frequency when cobalt is metallic<sup>8</sup>. The reaction product distributions may be tuned depending on the support and the oxidation state of cobalt.

Influence of the supported catalyst on the support material was shown for the case of gold<sup>9</sup>, and especially for the gold NPs supported on TiO<sub>2</sub>, for which the phase composition depended on the supported material<sup>10-12</sup>. Despite significant research efforts, the technology in this field remains largely an art<sup>13</sup>. Improving the support properties of

a selected material is, in general, empirical. The synthesis of materials with predetermined properties demands that they can be deliberately manipulated.

Among oxide nano-porous support varieties, zeolites and mesoporous materials have advantages due to their high surface area, ion-exchange capacity, and possibility to stabilize small metal particles via their insertion into the ordered porosity of the structure. For example, more than 200 zeolite structures with different topology are known with a range of channel diameters and cavities from  $\sim 2.5$  till  $\sim 15$  Å<sup>14</sup>.

### 2.2. Effect of cation concentration and matrix acidity

Ion-exchange properties of zeolites permit simple synthesis of sulfide and oxide nanoparticles. Semiconductor ZnS and ZnCdS nanoclusters were embedded in Na-mordenite (NaMor)<sup>15</sup>. Synthesis was done by ion exchange of NaMor using a mixture of CdCl<sub>2</sub> and ZnCl<sub>2</sub> solutions followed by sulfidation treatment. These ZnS and ternary ZnCdS nanoclusters exhibit blue shift in the absorption edges related to the relative ion concentrations. These results are important for photo-catalysis and non-linear optical applications.

NPs may be stabilized either in pores (as a small clusters) or on the external surface of the matrix (as large particles, which exceed the pore diameter). Fabricating of metal and semiconductor NPs assemblies of uniform size and shape distribution can be done by their confinement within molecular sieves. In line with this “cluster-sieving effect” the effect of metal NPs stability variation was observed when the zeolite SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio (MR) was changed. This dependence was explained by variations of zeolite acid properties under the influence of compositional changes. High concentrations of strong Bronsted acid sites favor the stabilization of silver clusters inside the pores, while at low concentrations of weak Bronsted acid sites the stabilization of silver clusters preferably takes place on the outer surface. Furthermore, silver incorporation into a silver mordenite matrix also affects its properties. As a result, four different types of Lewis acid sites existing in the starting H-mordenite material disappeared, and at the same time, new different Lewis acid sites appeared<sup>4</sup>. These examples confirm the strong interaction between the carrier and the deposited material.

### 2.3. Role of temperature

Effects of temperature on the alterations of the properties of the system consisting of the carrier and the supported material were studied by observing the changes in microstructure and phase transition behavior of TiO<sub>2</sub> obtained by a sol-gel method. Addition of gold to the Au-TiO<sub>2</sub> system enhanced the transformation of brookite to anatase, and retarded the transition of anatase to rutile; but when treated at 500 °C, the brookite phase disappeared.

Although gold retarded the transformation of anatase to the rutile phase, it was unable to maintain the porous structure of TiO<sub>2</sub> caused to collapse in BET surface area to  $\leq 1$  m<sup>2</sup> g<sup>-1</sup> at 700 °C. Moreover, there is no evidence of the substitution of Ti<sup>4+</sup> ions by gold, but gold was found to be bonded to the surface of TiO<sub>2</sub> as metallic gold. If any Au<sup>3+</sup> ions were present, they may be localized in interstitial positions in the TiO<sub>2</sub> matrix and this could contribute to the transition of anatase to the rutile phase<sup>10</sup>. Thus, the phase transitions in the carrier can be caused by the deposited substance.

### 2.4. Immobilization of biocatalysts

Enzymes are key biomolecules that act as catalysts in several crucial biochemical reactions, therefore, they have been used in medical and biotechnological processes. However, due to their proteinaceous origin they exhibit thermo and chemical lability, and are affected by the exposure to organic solvents, high concentrations of salts, changes in pH, mechanical pressure, etc. These forces induce the unfolding of their tridimensional structure (known as denaturalization) and to the consecutive loss or reduction in enzyme activity.

To avoid denaturalization and improve the catalytic properties of enzymes, scientists proposed to adsorb and immobilize enzymes either inside the nanoporous voids of porous materials or by chemical bonding to the surface of nanomaterials. Enzymes were immobilized in solid supports, particularly on silica gel, but it was only after the invention of mesoporous materials by Mobile researchers in 1992<sup>16</sup> that their application to immobilize

biomolecules, including enzymes, became extensive. It was clearly demonstrated that this process improves enzyme stability and catalytic activity, product specificity and resistance to extreme conditions<sup>17</sup>.

Enzyme immobilization is useful when the biocatalyst or the resulting products are important for purification or reuse processes. Several methods of biomolecule immobilization exist; but physical adsorption is still the simplest, although it involves only weak interactions, such as hydrogen bonding, hydrophobic and Van der Waals attraction and does not prevent the enzyme to leach into the media.

### 2.5. Influence of support size into enzyme

When immobilizing enzymes into mesoporous materials, there are two main aspects to be defined: the pore size and the type of support for the protein. Selection of support material is made by the size of enzyme to be confined in the pore; but also the possible interaction between support and supported material have to be taken into account. Large particle supports will immobilize more proteins, but this will reduce the number of enzymes that have access to the reagent because of the distance between each other or due to macromolecular crowding<sup>18</sup>.

These phenomena can be indirectly determined by measuring immobilization efficiency, known to be the ratio between specific activity of the immobilized enzyme and specific activity of the free enzyme<sup>19</sup>. Thus, immobilization efficiency depends on pore filling and on the chemical properties of the selected support and protein. In addition, enzymes immobilized inside the pores of materials may undergo conformational changes resulting in a modification of enzyme activity<sup>20</sup>. Large pore diameter also affects the surface of the support diminishing the surface curvature, which affects secondary protein structure and reduces enzyme activity.

### 2.6. Immobilization processes are influenced by acidity

According to their charge, proteins may be neutral, positively or negatively charged; the charge state is determined by their isoelectric point (pI). For example, at pH values below their pI, proteins exhibit a net positive charge but they have a negative charge when the pH is above the pI. Acidity affects both enzyme conformation and the support surface, and consequently the electrostatic interactions between both of them. Acidity or alkalinity can shift the structure of an enzyme and its capacity to be immobilized in a suitable material<sup>21</sup>.

Physical adsorption of enzymes into mesoporous materials is usually done in a buffer solution, since the amount of protons is essential to avoid repulsion between support and enzyme. To achieve successfully biomolecule immobilization it is important to know the pI for both enzyme and support. A simulation of molecular dynamics using ribosomal protein supported on a flat silica surface at different pH values showed that enzyme orientation is highly dependent on pH<sup>22</sup>. Sabirianov et al. corroborated this in another simulation using fibronectin supported in nano-structured zirconia<sup>23</sup>.

### 2.7. Influence of the environment inside the pore

Solvent composition inside the pore may not be the same as in the immobilization solution; in this sense, the availability of water inside the pore can affect orientation of solvent molecules, diffusion rates, density and change in viscosity<sup>24</sup>. The maintenance of enzyme structure is related to its hydration, i.e. the availability of water in the vicinity of the enzyme that may affect its structure and catalytic activity. Therefore, there is a need to understand how to modify the properties of the support and the solvent composition, with the aim of controlling enzymatic activity and other catalytic parameters.

The influence of the support on immobilized enzymes is affected by folding forces driven by the changes on the surface or inside the pore of the support; in this sense, Winter has demonstrated that hydration and excluded volume are determining factors for the stability of confined proteins<sup>25</sup>. Moreover, it was reported that small pores increase the stability of proteins by 15 kcal/mol<sup>26</sup>.

It is known that in silica mesoporous materials, water molecules close to the pore walls may form bonds to the silanol groups located at the surface of the material. The linkage of water molecules is different between materials; for example in SBA-15 they bond more strongly than in MCM-41<sup>27,28</sup>.

Functional groups are used as anchors for covalent binding and as linkages with the amino acid residues of the targeted enzyme; they can also affect the size of the pore entrance and consequently the enzyme-trapping capacity of the material<sup>29</sup>. Exposure of these groups in nanomaterials is related to the surfactant molecules used during synthesis, and to the template extraction method. Calcination is the most commonly used method; however, it causes the conversion of some hydrophilic silanol groups into hydrophobic siloxane groups affecting enzyme confinement inside the support pores<sup>27,30</sup>. This can be avoided by extracting the template with ethanol which preserves the silanol groups; but some template remains inside the pores limiting the lodgment of enzymes inside the voids<sup>31,32</sup>. Using an HNO<sub>3</sub>-H<sub>2</sub>O<sub>2</sub> mixture completely removes the pluronic P123 from SBA-15 and leaves a high density of silanol groups exposed in the support<sup>33</sup>. Such parameters as support surface and matching size of pores are critical to achieve high enzymatic activity in organic solvents<sup>34</sup>.

### 3. Conclusions

Physical and chemical parameters, such as temperature, geometry, size and shape of the pores, composition, acidity, ion concentration, surface functionalization, hydrophobic/hydrophilic interactions, etc., can affect the properties of complex systems consisting of a porous matrix and embedded nanoparticles of the supported material. Most of these physical and chemical parameters are interdependent.

To develop engineering of the nanomaterials with the predetermined properties, the mutual influence of support and supported materials must be considered. It is crucial to consider the relations between electronic properties and structure in both supported material and supporting matrices; and combine their physical and chemical parameters to find out an appropriate combination of them to build or obtain a high performing material with required stability, activity and selectivity.

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