A Simulation Study on the Structure of Bimetallic Nanoparticles Synthesized in Microemulsions

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A Simulation Study on the Structure of Bimetallic Nanoparticles Synthesized in Microemulsions

M. de Dios, F. Barroso, and C. Tojo

Abstract Monte Carlo simulations were carried out to study the different structures showed by bimetallic nanoparticles synthesized in microemulsions. It is observed that the difference in reduction rates of both metals is not the only parameter to determine the metals segregation, playing the interdroplet channel size a relevant role. The reduction rates difference determines nanoparticle structure only in two extreme cases: when both reactions take place at the same rate a nanoalloy structure is always obtained; if both reactions have very different rates, the nanoparticle shows a core-shell structure. But in the large interval between both extreme cases, the nanoparticle structure is strongly dependent on the intermicellar exchange, which is mainly determined by the surfactant film flexibility, and on reactants concentration. This result is very promising for the preparation of bimetallic nanoparticles with a given structure.

Keywords bimetallic nanoparticles • nanomaterials • microemulsions • reduction rate • microheterogeneous reaction media

Introduction

Studies of bimetallic nanoparticles received great attention from both scientific and technological communities because of most of the nanoparticle catalytic activity depends on their structural aspects [1]. Among the various structural aspects it is of most important to control the homogeneity, dispersion and alloying extent as they have profound influence on the surface properties which affect to catalytic activity and stability of the bimetallic nanoparticles. There-fore, control of composition distribution of bimetallic nanoparticles is crucial to the improvement of particle properties.

The bimetallic particles will be in a core-shell structure or alloy form, depending on the preparation route, miscibility and reduction kinetics of metal ions. As an example, bimetallic particles like Au/Ag are reported to exhibit Ag core and Ag/Au alloyed-shell type of structure by the seed-growth method [2]. However, if the reductions are simultaneous in presence of a capping agent, Au/Ag nanoparticles form homogeneous alloy [3]. When they are reduced simultaneously by the microemulsion method, Au/Ag nanoparticles can form homogeneous alloy [4] or an enriched in Au core-enriched in Ag shell structure [5], depending on the preparation conditions.

Among the methods used for nanosized particle synthesis, the microemulsion route is one of the most important methods to control the particle size, because the surfactant-stabilized droplets provide a microenvironment for the preparation of nanoparticles by exchanging their contents and preventing the excess aggregation of particles. But microemulsion itself is a very complicated system, and different simulation results show that the dynamics of intermicellar exchange plays an important role in the kinetics [6-9]. Likewise, experimental data supports this result. For example, Au/Pt alloys [10] and Au/Pt core-shell particles [11] had been prepared using different microemulsions. It seems fair to say that no definitive conclusions may be established about the control of particle structure. In line with our ongoing effort to evaluate the particles synthesis in microemulsions [7-9,12,13] we have aimed here to study the factors affecting nanoparticle structure.

Model Formulation

The computer simulation of the formation of nanoparticle in microemulsions was carried out using the model previously reported [7-9]. Briefly, each simulation began with a random

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distribution of three microemulsions droplets randomly located on a three-dimensional lattice: one microemulsion contains molecules of the metal salt A, other the metal salt B, and another the reductor R. The reactants are distributed throughout the droplets using a Poisson distribution.

Two micelles chosen randomly are allowed to collide (due to Brownian motion), fuse and redisperse. Upon collision and they can establish a water channel forming a transient dimmer (fusion), exchanging their contents (reactants, products and/or growing particles). Exchange criteria depend on the species inside the droplets (see Ref. [8,12] for details). The micellar dynamics is affected by changing the surfactant, the chain length of the oil phase and the cosurfactant [6,7,14-19]. The surfactant film flexibility is the ability to depart from the optimal curvature. Surfactants can be flexible or rigid, depending on the strength of the interactions at both sides of the interface. To simulate this phenomenon the surfactant film flexibility around the droplets is related to the ease with which channels communicating colliding droplets can form. Film flexibility also places a limit on the size of the particles traversing the interdroplet channels. The flexibility parameter (f) is the maximum size of the particle which can be exchanged: particles with more than f products are not allowed to pass from one droplet to another. In this way, a highly flexible film allows the interchange of larger particles than a rigid one. The ripening relies on mass transport from smaller to larger droplets: if a droplet containing a small particle collides with another droplet containing a greater one, the smaller particle will traverse the interdroplet channel to be added to the larger one. The species inside micelles, reactants and growing particles, can be exchanged if the droplets stay long enough together and if the size of the channel communicating colliding droplets is large enough [12]. Since a reactant molecule is smaller than a particle, it is assumed that the main factor determining the reactant interdroplet transfer is the dimer stability, and the channel size would not be so important. On the contrary, the channel size will be relevant when the exchanged material is a particle (products aggregate), which has to be transferred as a whole. The k_{ex} simulation parameters govern the exchange of reactants and non-aggregated products and they are related to the dimer stability. The larger the dimer stability the longer two water pools stay together and more molecules can be transferred during a collision. The material exchange parameters (f and k_{ex}) rise together: an increase of the flexibility implies not only the exchange of larger particles, but also a quicker exchange of reactants.

In order to include different reaction rates, only a percentage v of reactants inside the colliding droplets leads to products. The fastest reaction is v=1 (100% reactants transform

in products). Because there are two different metal salts, two different reaction rate parameters have to be considered: the reduction rates of the metal salt A^+ ($A^+ + R \rightarrow A$) and B^+ ($B^+ + R \rightarrow B$) are determined by v_A and v_B respectively.

The nanoparticles growth may be limited by the size of the drops. The influence of droplet size was studied previously [20], so in this work we present results without restriction by droplet size.

Consistency between experimental and simulation results [8,9,13,20] show the validity of the simulation model.

Results and Discussion

Reduction Potential and Nanoparticle Structure

It is well-known that in homogeneous media, the higher reduction potential ions usually have the priority in reduction. Consequently, the difference in reduction potential of two metal ions may be the major factor to decide what structure the particles should be. It is assumed that a large difference in the reduction potential usually results in a core-shell structure, and a small difference in the reduction potential leads to an alloy one [21]. In order to study if this assumption can be used in a microheterogeneous media as a microemulsion, Figure 1 shows simulation results for two different reduction rate ratios v_A/v_B, being v_A and v_B the A and B metal reduction rates, and keeping constant the synthesis variables. The number of particles containing different percentage of one of the metals (A) is monitored from the nanoparticle core to the outside (layer by layer). When both reduction rates are equal (see Figure 1.A), an alloy structure of nanoparticle is observed from the core/beginning. Although the inner layers of some particles are mainly composed by only one of the metals, the composition shows a progressive improvement towards a perfect mix of both metals from the inner to the outer layers. At the end of the process, the composition of most of the particles is 50% in each metal. On increasing the difference between the chemical reaction rates, a progressive change from an alloy to a core-shell structure is observed, as in homogeneous media. Previous studies [9] allowed us to propose a detailed explanation of this result based on the interplay between the ripening contribution to nanoparticle growth (which is strongly dependent on intermicellar exchange) and the difference in reduction rate of both metals. The conclusion was that only for small differences in the reduction rates the
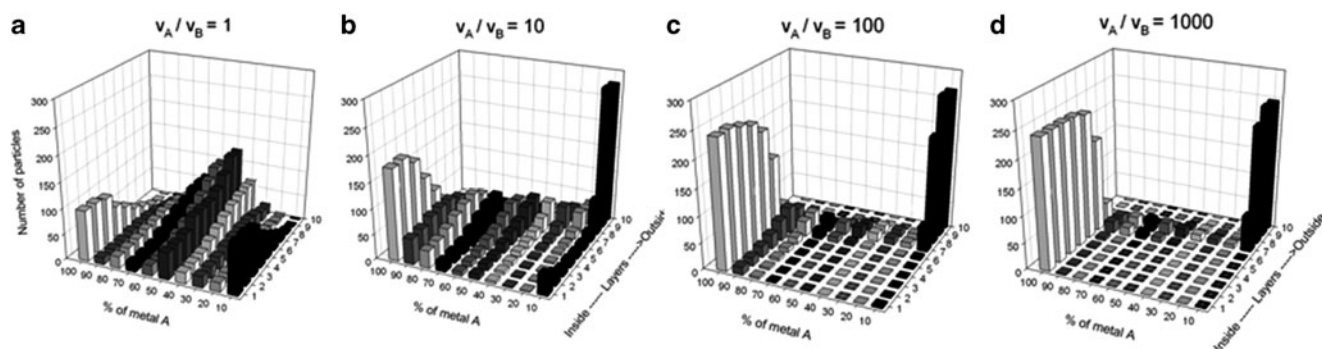
Figure 1 Number of particles versus the percentage of one of the products (a), from the nanoparticle core to the outside (layer by layer) for different reduction rate ratios. Synthesis conditions: reactant concentration $\langle c_A \rangle = \langle c_B \rangle = 32$, $f=30$, $k_{ex}=5$. A) $v_A/v_B=1$; b) $v_A/v_B=10$; c) $v_A/v_B=100$; d) $v_A/v_B=1000$

Table 1 Bimetallic nanoparticles prepared by simultaneous reduction in microemulsions

Metals	Structure	Microemulsionreductor agent; metal precursor	f	Ref
Au-Ag	Au core-enriched in Ag shell	water/AOT/isooctane N_2H_5OH; Ag^+, $AuCl_4^-$	rigid	[5]
	nanoalloy	water/TritonX-100/cyclohexane $NaBH_4$, Ag^+, $AuCl_4^-$	flexible	[4]
Au-Pt	core-shell	water/AOT/isooctane N_2H_5OH, $AuCl_4^-$, $PtCl_6^{2-}$	rigid	[11]
	nanoalloy	water/Tergitol 15-S-5/isooctane N_2H_5OH, $AuCl_4^-$, $PtCl_6^{2-}$	flexible	[10]

intermicellar exchange affects to nanoparticle structure. This conclusion was supported by a comparison study between experimental and simulation results, on the basis of electrochemical arguments [9].

## Microemulsion Composition and Nanoparticle Structure

Table 1 shows experimental data of Au-Ag [4,5] and Au-Pt [10,11] nanoparticles. It is observed that a given bimetallic nanoparticle can be obtained in alloy form if the surfactant film flexibility is high, or in a core-shell structure using a rigid film. In agreement with experimental results, our simulation model shows that the nanoparticle structure can be modified by changing the parameters which control the interdroplet channel size and the dimer stability, i.e. by changing the microemulsion composition. As the film flexibility increases the degree of alloying increases too, and a transition from core-shell to alloy structure is obtained for moderate differences in reduction rate ($v_A/v_B=10$). These results allow us to propose that it is possible, even when the chemical reaction rates are different, to obtain nanoal-

loyed nanoparticles just by changing the microemulsion composition. On the contrary, if both reduction rates take place at similar rates or if the difference between rates is large enough, the structure is not modified by changing the surfactant flexibility (see Ref. [9] for details).

Reactants Concentration and Nanoparticle Structure

A new set of computer experiments were carried out to study the influence of reactants concentration on the nanoparticle structure. Figure 2 shows the structures obtained using different number of atoms/molecules of reactants (two metal salts and reducing agent) initially contained inside a microemulsion droplet. When both reduction rates are equal a homogeneous alloy is obtained for all values of concentrations and flexibilities. Likewise, when the chemical reaction rates are very different ($v_A/v_B=1000$), concentration does not modify the structure, being always a core-shell. But the intermediate cases ($v_A/v_B=10,100$) show structural changes as increasing reactant concentration, as can be observed in Figure 2. In the left column ($v_A/v_B=10$) one can observe that the core enrichment in the faster product diminishes as increasing concentration (from the top to the bottom), giving rise to a higher degree of mixture in the inner layers. In addition the shell is enriched in the slower product with the increase of concentration. Right column shows results using a higher reduction rate ratio ($v_A/v_B=100$), which presents a better separation of both metals in the middle layers as increasing concentration. Qualitatively similar results are obtained using lower or higher values of the flexibility parameters. It seems that when the reduction rates are not very different the nanoparticle structure is also affected by changing reactants concentration.

Figure 2 Number of particles versus the percentage of one of the products (*A*), from the nanoparticle core to the outside for different concentrations and keeping constant the film flexibility (*f*=30, k_{ex}=5). Left column: v_A/v_B =10; right column: v_A/v_B=100. Reactant concentration: a) and d) $\langle c_A \rangle$= $\langle c_B \rangle$ = 4; b) and e) $\langle c_A \rangle$= $\langle c_B \rangle$ = 32; c) and f) $\langle c_A \rangle$= $\langle c_B \rangle$ = 128 reactants per droplet
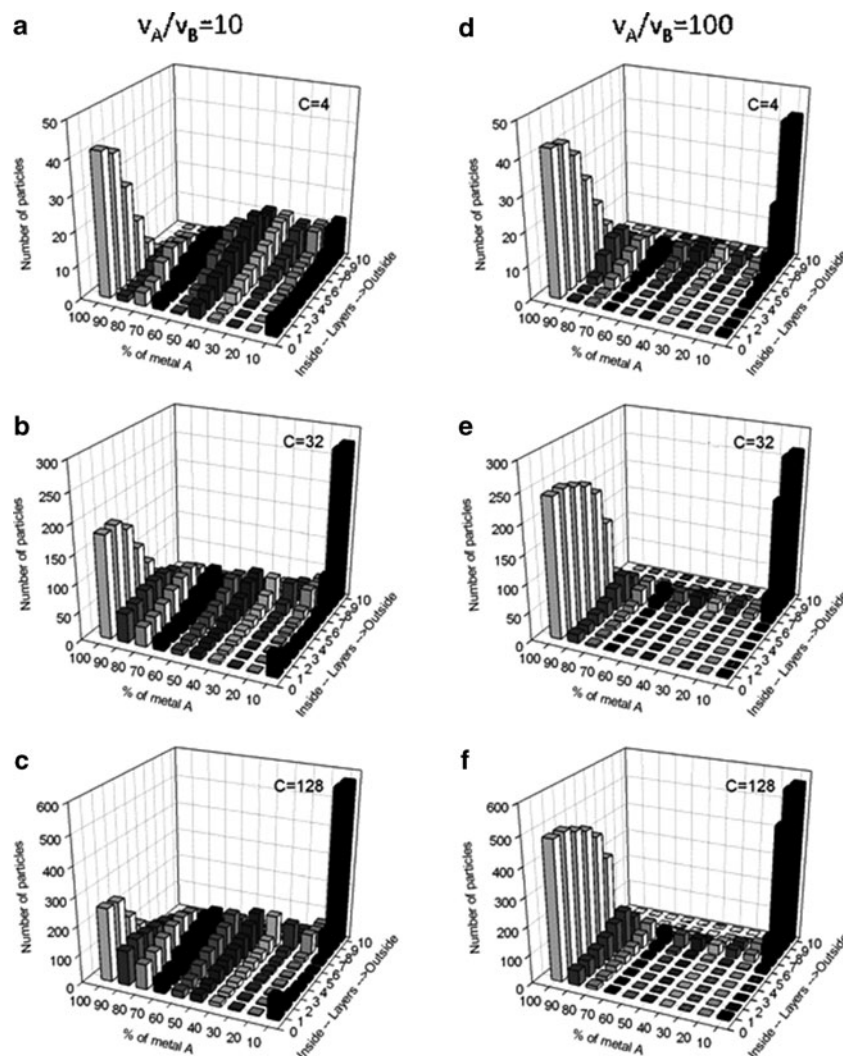
Conclusions

The main conclusion is that nanoparticle structure is determined by the chemical reaction rates ratio, as in homogeneous media, only if both reactions take place at the same rate and if the reaction rates are very different. The first case leads to a nanoalloy and the second one to a core-shell structure. But in the common case of a nanoparticle composed by two metals with a moderate difference in reduction potentials, the dynamics of the intermicellar exchange causes that the synthesis variables, such as surfactant film flexibility or initial reactants concentrations, become more relevant, modifying the nanoparticle structure: An increase of flexibility gives rise to alloys, and an increase of concentration implies a higher degree of mixture in the inner layers and an enrichment in the slower product in the outer layers.

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