Supplementary Materials: On Metal Segregation of Bimetallic Nanocatalysts Prepared by a One-Pot Method in Microemulsions

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1. Simulation Model

The microemulsion technique to synthesize nanoparticles is a build-up (bottom-up) method by which a nanoparticle can be obtained starting from atoms. These first atoms form a nucleus, which grows by deposition of new atoms over the previous ones, building up new layers. In the case of bimetallic nanoparticles, the two metals are obtained by reduction of the corresponding metal salt. The whole process takes place inside the microemulsion droplets, i.e., water pools dispersed in a continuous oil phase (water-in-oil microemulsion) and stabilized interfacially by surface active molecules. Microemulsions perform as nanoreactors because they can exchange the content of their droplets through a collision event. Briefly, one prepares three similar microemulsions, one containing one of the metal salts, another containing the other metal salt, and the last one with the reducing agent. The three microemulsions are then mixed. The high mobility of the droplets in the oil phase and the flexibility of the surfactant film around them allows for an exchange of their content upon collision. Due to interdroplet exchange, one metal salt and the reduction agent can be located inside the same water pool, so the reduction reactions can take place. After some time the particles can be obtained by aggregation of metallic atoms in the water phase.

The prediction model recreates the assumed kinetic course of the reaction as follows.

1.1. Reaction Media

A set of 15,000 droplets randomly located in a three dimensional lattice are used to make a picture of the microemulsion. The one-pot method is simulated by mixing equal volumes of three sets of droplets: one carries the metal salt A^+, the second the metal salt B^+, and the third contains the reduction agent R. Each simulation run starts with a random location of these three droplet sets, in which a $\varphi = 10\%$ portion of the space is occupied by droplets.

1.2. Droplets Movement, Collisions and Time Unit Base.

The droplets motion is assumed to be governed by Brownian motion. When two droplets collide with a enough energetic collision, a interdroplet channel can be established between them [1], giving rise to a transient dimer [2] (fusion), which allows the material exchange (reactants, products, and/or growing particles). In each Monte Carlo step the collision events are simulated by selecting, at random, a 10% of droplets to collide, fuse, and redisperse. The exchange of material is only allowed between colliding droplets. One Monte Carlo step (mcs) is ended when the material inside the colliding droplets is recalculated after collision according to the material exchange criteria described below (see 1.4 and 1.9 sections).

1.3. Initial Reactant Distribution inside Droplets

It is assumed that all micelles do not contain the same number of reactants. So each type of reactant (metal salt A^+, metal salt B^+, and reduction agent R) is initially distributed throughout each droplet microemulsion using a Poisson distribution: the number of each reagent per droplet is referred to as n_i, where *i* represents metal salt A^+, metal salt B^+, or reducing agent R.

$$P(n_i) = \frac{\langle n_i \rangle^{n_i}}{n_i!} \exp\left(-\langle n_i \rangle\right) \qquad i = A^+, B^+ \text{ or } R \tag{1}$$

where $P\langle n_i \rangle$ is the probability that a droplet contains ni reactants (A^+, B^+, or R) whose average occupancy is $\langle n_i \rangle$. The reactant concentration inside droplets can be modified by changing the amount of reactant solved in the water phase for each microemulsion. In this study we present results using different initial averaged values of reactants: $\langle c_{A+salt} \rangle = \langle c_{B+salt} \rangle$ = 4, 16, and 64 metal ions in a droplet, which correspond to 0.02 M, 0.08 M, and 0.40 M, respectively. ($\langle c_{A+} \rangle = \langle c_{B+} \rangle$ = 2, 16, 32, and 64 metal ions in a droplet, which corresponds to 0.01 M, 0.08 M, 0.16 M, and 0.40 M, respectively).

1.4. Interdroplet Exchange of Non-Aggregated Material: the Exchange Parameter k_{ex}.

A priori, the exchange of material between two colliding droplets is assumed to obey the concentration gradient principle: ions/atoms will be transferred from the more to the less occupied droplet. To control the redistribution of material upon collision, the exchange parameter (k_{ex}) is introduced to quantify the maximum amount of non-aggregated material (reactants: A^+, B^+, R, and/or metallic atoms: A, B) to be exchanged during a interdroplet collision. Therefore, if the quantity of units of non-aggregated material carried by the more occupied droplet is greater than k_{ex}, only k_{ex} units could be transferred to the less occupied droplet. When the number of units to transfer is smaller than k_{ex}, the concentration inside colliding droplets will be the same after collision.

1.5 Chemical Reduction inside Droplets: the v_A and v_B Parameters

The reduction of the metal salts can take place when both reactants (metal salt and reduction agent) are located in the same droplet, due to redistribution of material upon collision. A bimetallic nanoparticle is composed of two different metals whose reduction rate can be different, so two reaction rate parameters must be included. To save computation time, the model assumes that chemical reduction of the fast metal precursor A is instantaneous, that is, 100% of metal A precursor inside the same droplet is reduced, whenever the reducing agent contained by the droplet would be enough. At this stage, A metal atoms are obtained. The reduction rate parameter v_A indicates the reduction rate of the fast reduction metal v_A =100% ($A^+ + R \rightarrow A$). Due to the reduction of metal B precursor is slower, only a small percentage v_B of the slow metal B precursor is reduced ($B^+ + R \rightarrow B$). In this paper we present results using v_B = 10% and v_B = 20%. The rest of the slow metal salt and reducing agent remains free in the micelle, so it can be exchanged or can react later.

Therefore, when both reactants (metal salt and reducing agent) are carried by a j droplet, a reduced metal atom (A or B) is obtained whenever the reaction rate parameter v_i (v_A or v_B) is smaller than ξ, where ξ is a random number between 0 and 1:

$$\begin{array}{lll} l = \min\left[n_j(i), n_j(R)\right] & & i = A^+, B^+ \\ if\ \xi \leq \mathrm{v}_i & n_j^a(k) = n_j^b(k) - l & k = A^+, B^+, R \\ & n_j^a(m) = n_j^b(m) + l & m = A, B \\ if\ \xi \geq \mathrm{v}_i & n_j^a(k) = n_j^b(k) & \\ & n_j^a(m) = n_j^b(m) & \end{array} \tag{2}$$

where the superscripts a and b characterize the material contents in the droplet after and before collision. The resulting reduced atoms are subject to the criteria defined in 1.7 and 1.8, whereas the remaining non-reacted reagents can be exchanged according to criterion 1.4.

1.6. Nucleation: the n^*_A, n^*_B, $n^*_{A\text{-}B}$ Parameters.

Atoms, initially free in a water pool, can come together to give rise to a thermodynamically stable cluster by means of a nucleation event. According to La Mer´s nucleation model [3], a characteristic of each specific material is the critical nucleus size, which depicts the minimum size of a stable nucleus. Aggregates that exceed a critical size for thermodynamic stability are made from a few atoms. These aggregates will continue to grow, leading to the following stage of the precipitation growth. On the contrary, if the aggregate is smaller than the critical size, it spontaneously becomes solved. To simulate a nucleation event the critical nucleus size parameter n^* is included. When the number of metal atoms carried by a droplet is equal or greater than n^*, they come together forming a nucleus. All atoms produced in a nucleated droplet will be considered to be aggregated forming a growing nanoparticle. The exchange of aggregates during a collision is discussed in section 1.9. Nevertheless, when the amount of atoms in a droplet is lower than n^*, they remain faraway and can be exchanged later, ruled by k_{ex} parameter.

Due to bimetallic particles are made up two metals, the different interactions metal-metal (A-A, B-B, and A-B) can cause that the critical nucleus size to be different depending on the composition. Thus, the model considers two different critical nucleation size (n_A^* and n_B^*). Likewise, the feasibility of a nucleus composed by two different metals (heterogeneous nucleation) is also taken into account by means a heterogeneous nucleus parameter n_{AB}^*. It quantifies the minimum number of atoms (equally A or B) in the same droplet required to produce a mixed nucleus capable of further growth. Therefore, in the absence of any pre-existing nuclei, the atoms come together forming a seed nuclei when the number of metal atoms inside a droplet verifies one of the following conditions:

$$\begin{aligned} n_j(A) &> n_A^* \\ n_j(B) &> n_B^* \\ n_j(A) + n_j(B) &> n_{AB}^* \end{aligned} \tag{3}$$

Once a droplet carries a nucleus (nucleated-droplet), all atoms exchanged or produced later will be considered to be aggregated, forming a growing nanoparticle.

1.7. Interdroplet Exchange of Non-Aggregated Material between a Nucleated and a Non-Mucleated Droplet

As the synthesis advances, a collision between a droplet containing reactants or free metal atoms and another containing a growing particle is more frequent. The droplet carrying a nucleus acts as nucleation point, so the reaction always proceeds on it. This means that the reactants exchange is towards the nucleated droplet, whenever the k_{ex} parameter allows the material flux. This situation also allows us to simulate an autocatalytic reaction on the nanoparticle surface: the growing particle plays as a nanocatalyst, so the reduction proceeds on it and the reduction rate is accelerated (v_B is double).

1.8. Interdroplet Exchange of Non-Aggregated Material between Two Nucleated Droplets

In case of both colliding droplets contain a growing particle, the flux of atoms and/or reactants takes place towards the droplet carrying the larger particle. In this way we consider that larger particle had a greater probability of performing as a nanocatalyst because of its larger surface. In addition, the reaction rate will be double.

1.9. Interdroplet Exchange of Particles (Aggregated Material): the Film Flexibility Parameter f

At later stages, collisions between two droplets both containing growing particles become more probable. As seen earlier, the material interdroplet exchange process requires the opening of the interfacial layer and the formation of a channel that communicates colliding droplets. The model assumes that the exchange of growing particles is restricted by the size of these channels. The ease with which channels can be established and the size of these channels, are mainly governed by the flexibility of the surfactant film around the droplets. Thus, surfactants are classified as flexible or rigid, depending on the strength of the interactions at both sides of the interface. The film flexibility depends not only on the surfactant but also on the length of the alkyl chain and the presence of additives [4–7].

The flexibility parameter (*f*) is directly related to the interdroplet channel size, and places a limit on the size of the growing particles traversing the droplet-droplet channels. That is, particles constituted by more than *f* atoms are forbidden to be exchanged from one droplet to another. In this way, the larger the film flexibility, the larger the channel size, and the larger the exchanged particles.

The criterion to dictate the direction of material flux between two droplets containing nanoparticles is based on Ostwald ripening. It supposes that the larger particles grow by condensation of material on their surface. This material arises from the smaller particles, which dissolve readily, and are redeposited on the surfaces of larger ones. Therefore, when the two colliding droplets contain a particle, the smaller particle is exchanged towards the droplet carrying the larger one, providing that the channel size is enough large.

1.10. Microemulsions Dynamics: the Flexibility f and the Exchange k_{ex} Parameters

The most complicated factor to understand microemulsions as nanoreactors is the interdroplet material exchange. In fact, the nanoparticle synthesis is not limited to the nanoreactors themselves, but it is a cooperative process which is, at least partly, controlled by the microemulsion composition [8]. The first requirement concerning material exchange is the formation of a transient dimer or encounter pair [1,9] during a collision. In order to simplify, this transient dimer must meet two conditions [10,11]: First, the dimer must be stable enough, because reactants (solved in the aqueous phase) can only traverse the channel while colliding droplets remain together. That is, the longer two water-droplets stay together as a dimer, the more species pass through the interdroplet channel. This characteristic is especially relevant when exchanged material are atoms/ions/molecules, which traverse the channel one by one. Second, the size of the channel connecting droplets must be sufficiently large to allow the material to cross. It will be very important when the transferred material is a growing nanoparticle, i.e. an aggregate of metal atoms which traverse the channel all together. Both features are directly related to the microemulsion composition, mainly due to the surfactant. Thus a highly flexible film is associated to a longer dimer stability, as well as a larger channel size. The surfactant film is included in the simulation model by means of the k_{ex} and the *f* parameters. The dimer stability is reflected by the k_{ex} parameter, which quantifies how many units of isolated material can traverse the channel during a collision. The flexibility parameter *f*, which limits the size of a material to be exchanged, represents the channel size. The two factors must be increased simultaneously. As a matter of fact, to compare experimental data obtained in an AOT/n-heptane/water microemulsion (which has a rigid film) with simulation results, the values $f = 5$ combined to $k_{ex} = 1$ was successfully used [12]. To simulate a more flexible microemulsion, such as isooctane/tergitol/water, higher values were required ($f = 30$, $k_{ex} = 5$).[13]

1.11. Nanoparticle Structure Description: Bar Diagrams and Calculated STEM Profiles

Each simulation run finishes when the metal precursors become exhausted and the interdroplet exchange no longer takes place, so that the material content within droplets does not vary. The result is a set of droplets, but not all of them contain a particle. In order to analyze nanoparticle composition, the sequence of metal deposition of each nanoparticle is stored step by step, and the results are averaged over 1000 runs.

By assuming a spherical arrangement, the structure of each nanoparticle is built from atoms, which are placed in ten concentric layers according to the metal sequence. Then the averaged composition (in %A, fast reduction metal) and the dispersion are estimated layer by layer. A color code is used to represent the averaged percentage of each metal in each layer, so when the proportion of metal A increases, the bar color changes from blue (0%–10% fast metal A) to red (90%–100% fast metal A). A mixture (50% of each metal) is represented by grey, and the color turns towards lighter tonalities when the proportion of pure metal in the layer is higher. In this way, the nanoparticle structure is depicted by concentric colored spheres, which display a high thickness as the number of layers with the same composition is greater.

A more detailed information about structure is shown by histograms, which show how many particles contain a fixed percentage of the fast metal A, monitored from the beginning of the synthesis (inner layer, nanoparticle core) to the end (outer layer, nanoparticle shell), keeping the same color scheme. With this in mind, one can observe the gradual change of the averaged nanoparticle composition as the synthesis advances.

From the averaged nanoparticle structure, the theoretical STEM profile was calculated by monitoring how many atoms of each metal are detected as the nanoparticle is crossed by a beam of 2 Å (approximate size of the energy dispersive X-ray spectroscopy EDX beam).

2. Materials

Metal salts, HAuCl4.3H2O (≥99.9% trace metals basis) and $H_2PtCl_6.6H_2O$ (≥37.50% Pt basis), isooctane (2,2,4-trimethylpentane, ≥99%), tergitol (Type 15-S-5), tetrahydrofuran (≥99%) and hydrazine monohydrate (98%) were purchased from Sigma Aldrich. Carbon Vulcan 72 XR was supplied by Cabot. All aqueous solutions were prepared with deionized water from a Milli-Q system (Millipore).

3. Bimetallic Nanoparticles Preparation

The metal precursor microemulsions were prepared by adding aqueous solutions (5 wt%) of the appropriate amounts of the metals (0.01 M, 0.08 M, 0.16 M, and 0.40 M, corresponding to $\langle c_{A+} \rangle = \langle c_{B+} \rangle$ = 2, 16, 32, and 64 atoms per droplet in the final microemulsion, respectively) to a mixture of isooctane (75 wt %) and Tergitol (20 wt %) under stirring to obtain a transparent mixture. Simultaneously, a similar micromulsion (isooctane 75%, Tergitol 20%, and water 5%) was prepared by using a hydrazine aqueous solution (10 equivalents with respect to the metal concentration) as the water phase. The radius of the microemulsion droplets was 7.3 ± 0.1 nm (calculated by dynamic light scattering, DLS). Both microemulsions (the one with metal precursors and the one with hydrazine) were mixed and stirred at room temperature for 5 h. Afterwards, in order to remove particles from the microemulsion and remove the surfactant, Carbon Vulcan was added (calculated to be a 20 wt % loading of Pt in the final product) and stirred overnight. Tetrahydrofuran was then added to break the microemulsion and, after decantation, a solid was obtained by filtration and centrifugation, washed thoroughly with a water/ethanol mixture, and dried at 100 °C for 12 h."

4. Nanoparticles Characterization

High-resolution scanning transmission electron microscopy (HR-STEM) and energy dispersive X-ray spectroscopy (EDX) characterization were conducted. Electron microscopy analysis was carried out with a FEI-TITAN X-FEG transmission electron microscope used in STEM mode and operated at 300 kV. The images were acquired using a high angle annular dark field (HAADF) detector. The spherical aberration corrector (CEOS) for the electron probe, allowing an effective spatial resolution of 0.08 nm. The column is also fitted with EDX which was employed for carrying out the compositional analysis. The Au/Pt nanoparticles were prepared on a carbon-coated Cu TEM grid.

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