Microemulsions as reaction media for the synthesis of bimetallic nanoparticles

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Abstract

Bimetallic nanoparticles are particularly attractive due to their properties often differ markedly from either of the constituent metals. Nowadays it is well-known that the design and control of spatial arrangement of both metals in bimetallic nanoparticles are critical for exploiting their potential applications. The properties of bimetal nanoparticles strongly depend on their size, structure and morphology, so it is of the utmost importance to fully elucidate the mechanism underlying the nucleation and growth of nanoparticles. The fact that the nucleus evolves to a particle by accumulating new layers implies that the differences in nucleation rates of both metals would strongly affect the metals segregation and final nanoparticle sizes.

Because the synthetic route seems to be crucial to determine final sizes and structures of bimetallic nanoparticles, our study is focused on a concrete method: the reverse microemulsion route. This method 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 the dynamics of intermicellar exchange plays an important role in the kinetics [1, 2]. In line with our ongoing effort to study the formation of simple and bimetallic nanoparticles in microemulsions, we have aimed here to investigate the nucleation and growth of bimetallic nanoparticles and to provide a detailed insight into the factors affecting nanoparticle structure and size.

The main concept used to describe nucleation is related to the critical radius. Above this size, it is favorable for the new phase to form; below this size, the clusters will tend to dissolve rather than grow. Monte Carlo simulations were carried out to investigate the influence of critical nucleus sizes on the structure and sizes of final bimetallic nanoparticles. Because bimetallic particles are composed by two different metals (*A* and *B*), which can need a different minimum number of atoms to form a stable nucleus, the algorithm distinguish two critical nucleation numbers ($n_A{}^*$ and $n_B{}^*$). In addition, the possibility of heterogeneous nucleation (nucleus composed by different metals) has also been considered by including a new parameter ($n_{AB}{}^*$), defined as the minimum number of metal atoms (*A* or *B*) inside the same droplet needed to form a heterogeneous nucleus capable of further growth.

In relation to the nanoparticle structure, core-shell structures are expected when one metal reduces faster than the other [3]. The study reveals that, keeping equal the reduction rates of the two metals, the final structure is also sensitive to changes in the critical nucleus numbers, because these parameters determine the rate of nucleation. Figure 1A shows simulation results using equal reduction rates, a low value of concentration ($\langle c_A \rangle = \langle c_B \rangle = 4$ molecules of reactant per droplet), a rigid film ($f=5$, $k_{ex}=1$) and different critical nucleus sizes ($n^*_A=1$, $n^*_B=9$, $n^*_{AB}=4$). In this figure the number of particles containing different percentages of one of the metals (A: faster nucleation metal) is monitored from the nanoparticle core to the outside (layer by layer). One can observe that the inner layers are composed by the metal which nucleates faster, and composition shows a progressive improvement towards a mix of both metals as the process advances (from the inner to the outer layers). Finally, the outer layers show an enrichment in the slower nucleation metal. Therefore this kind of structure can be considered a core-shell, although it was obtained simulating two metals with the same reduction rate. An increase in the difference between nucleation rates of both metals gives rise to a better segregation of metals in the final nanoparticle. Likewise, as long as the formation of heterogeneous seeds is faster, the degree of alloying is greater. In addition, it is observed that the difference in nucleation rates of both metals is not the only parameter to determine the metals segregation, playing the interdroplet channel size a relevant role. In agreement with experimental observations, the results also suggest that the metal segregation can be avoid by using a more flexible surfactant (see figure 1). These results allow us to tune the experimental conditions for designing specific bimetallic structures.

In relation to the nanoparticle sizes, three different experimental behaviours have been found: bimetallic nanoparticles can be significatively smaller (negative deviation [4-7]), larger (positive deviation [8]) or equal than individual monometallic nanoparticles (no deviation [9, 10]). Because these results were ascribed to a difference in the nucleation process, we have carried out computer simulations to study how nanoparticle sizes change by using different combinations of the three critical nucleus numbers. Our results show that a negative deviation is obtained when heterogeneous critical size n^*_{AB} is

smaller than the two homogeneous ones (n^{*}_{A} and n^{*}_{B}), i.e., heterogeneous nucleation rate is the fastest nucleation. On the contrary, to obtain positive deviations the heterogeneous nucleation must be slower than the homogeneous ones. Both kind of deviations were obtained only if a rigid surfactant film was used. Also relevant to the discussion is the observation that no kind of deviation could be obtained when different reduction rates ratios were simulated. Therefore, the only factor affecting nucleation which can explain the sizes deviations is the different rate in heterogenous and homogeneous nucleation. Direct comparison between experimental and simulation results is not possible, because to the best of our knowledge, no experiment has ever directly measured the size of the critical nucleus.

The simulation results are expected to contribute to developing advanced strategies for the design nanostructured particles.

References
[1] R.P. Bagwe, K.C. Khilar, Langmuir, **16** (2000) 905.
[2] M.A. López-Quintela, C. Tojo, M.C. Blanco, L. García-Río, J.R. Leis, Curr. Opin. Colloid Interface. Sci., **9** (2004) 264.
[3] C. Tojo, M. de Dios, M.A. López-Quintela, J. Phys. Chem. C, **113** (2009) 19145.
[4] M. Wu, D. Chen, T. Huang, Langmuir, **17** (2001) 3877.
[5] A. Habrioux, W. Vogel, M. Guinel, L. Guetaz, K. Servat, B. Kokoh, N. Alonso-Vante, Phys. Chem. Chem. Phys., **11** (2009) 3573.
[6] M. Wu, D. Chen, T. Huang, Chem. Mater., **13** (2001) 599.
[7] M. Wu, L. Lai, Coll. Surf.A, **244** (2004) 149.
[8] J. Santhanalakshmi, P. Venkatesan, J. Nanopart. Res., **13** (2011) 479.
[9] L.M. Magno, W. Sigle, P.A.v. Aken, D.G. Angelescu, C. Stubenrauch, Chem. Mater., **22** (2010) 6263.
[10] F.J. Vidal-Iglesias, J. Solla-Gullón, V. Montiel, J.M. Feliu, A. Aldaz, J. Power Sources, **171** (2007) 448.
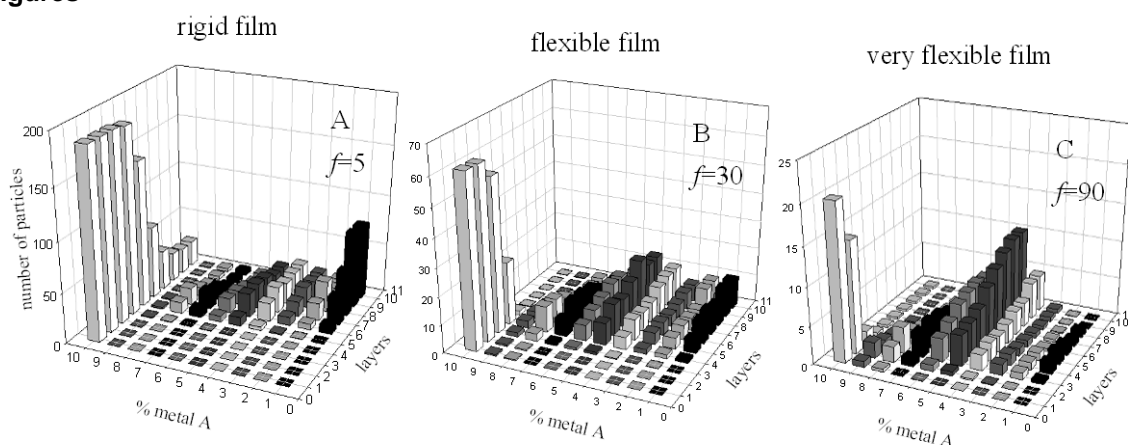
Figures

Figure 1.- Number of particles versus the percentage of one of the products (A), from the nanoparticle core to the outside (layer by layer) using different surfactant flexibilities, and remaining constant critical sizes (n^{*}_{A}=1, n^{*}_{B}=9, n^{*}_{AB}=4), concentration $\langle c_{A} \rangle$=$\langle c_{B} \rangle$=4, $\langle c_{R} \rangle$=8, and reduction rates v_{A}=v_{B}.