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SHORT COMMUNICATIONS

Solvent Effect on the Size of Platinum Nanoparticle Synthesized in Microemulsion Systems[1]

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Abstract—In this research work, the effect of solvent on the size of paltinum nanoparticles synthesized by microemulsion method was investigated. Platinum nanoparticles have been prepared by the reduction of H_2PtCl_6 with hydrazine in water-in-oil (w/o) microemulsions consisting of sodium bis(2-ethylhexyl) sulfosuccinate (AOT) and solvents *n*-hexane, cyclohexane and *n*-nonane. The size of the platinum nanoparticles was measured using transmission electron microscopy (TEM). It was verified that, for reduction of H_2PtCl_6 by hydrazine in microemulsion with different organic solvents, the solvents are arranged by their influence on nanoparticle sizes as follows: *n*-nonane > cyclohexane > *n*-hexane.

Keywords: nanoparticles, platinum nanoparticles, microemulsion, AOT, hexachloroplatinic acid.

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INTRODUCTION

Nanoparticle synthesis within the aqueous cores of water-in-oil microemulsion systems is a viable method, which allows control over the size and shape of the particles. Microemulsion systems are isotropic, macroscopically homogeneous, and thermodynamically stable solutions containing at least three components, namely a polar phase (usually water), a nonpolar phase (usually oil), and a surfactant. On a microscopic level the surfactant molecules form an interfacial film separating the polar and non-polar domains. This interfacial layer forms different microstructures ranging from droplets of oil dispersed in a continuous water phase (o/w-microemulsion) over a bicontinuous "sponge" phase to water droplets dispersed in a continuous oil phase (w/o-microemulsion). The latter can be used as nano-reactors for the synthesis of metal nanoparticles leading to nanoparticles with a low polydispersity [1–5]. The size of the aqueous droplets in a water-in-oil microemulsion can be varied by the choice of the solvent [6], and so affecting the size of the nanoparticles obtained, particularly in anionic microemulsion systems.

Considerable research has been done in order to better understand the factors controlling the synthesis of nanomaterials through aqueous phase reduction reactions within the reverse micelle core, particularly stability and the intermicellar exchange of the contents [7–9].

The intermicellar exchange rate may be affected by the bulk solvent type, the contents dissolved within the core, and the size of the reverse micelle or the water content, referred to as the W value, where W is the molar ratio of the water to surfactant concentrations. Fletcher and co-workers [10] presented a comprehensive study on the water/alkane/AOT system where the rate of micellar exchange k_{ex} was measured as a function of W, the AOT concentration, temperature, and the bulk solvent type. The results from their study reveal that k_{ex} decreases with increasing water content for $W = 10$, 15, 20, and 30; k_{ex} is independent of AOT and reactant concentration; k_{ex} increases with an increase in temperature; and k_{ex} increases slightly with carbon atoms number for pentane through dodecane in addition to a significant decrease in k_{ex} for the corresponding cyclic compounds, particularly cyclohexane. The dependency of k_{ex} on the bulk solvent can be explained by the solvent interactions with the AOT tails where a more favorable interaction will allow for the solvent to insert itself within the surfactant tails, thus creating a more rigid micelle. Binks et al. [11] discuss the extent of oil penetration into the surfactant chain region, showing an increase in micelle rigidity with decreasing solvent chain length from C_{14} to C_7.

In the present work we have synthesized platinum nanoparticles in w/o microemulsion system. The effect of solvent (*n*-hexane, cyclohexane, and *n*-nonane) on the size of the synthesized platinum nanoparticles was investigated. These nanoparticles are very important as a catalysts for a range of reactions, including the evolution of hydrogen, reduction of oxygen, oxidation of hydrogen and methanol and hydrogenation reactions [12–14].

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[1] The article is published in the original.

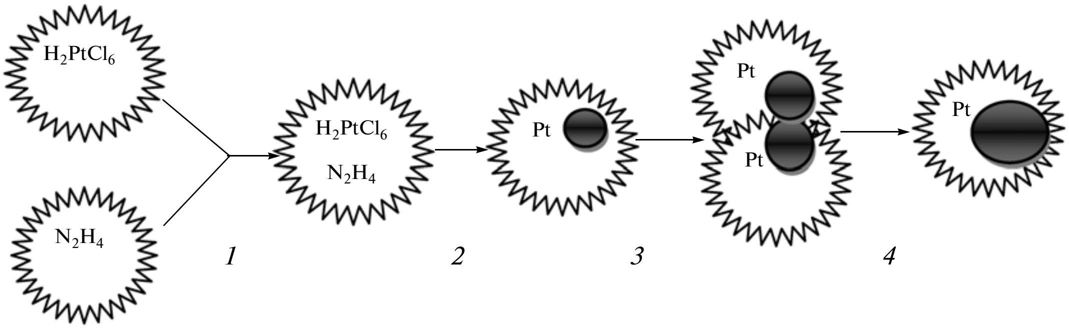

Fig. 1. Model for the micelles served as a nanoreactor for fabricating of platinum nanoparticles; (*1*) collision and exchange, (*2*) reaction, (*3*) aggregation, (*4*) growth.

EXPERIMENTAL

Materials. The anionic surfactant sodium bis(2-ethylhexyl) sulfosuccinate (AOT) was purchased from Acros Organics and used without further purification. Hexachloroplatinic acid hexahydrate ($H_2PtCl_6 \cdot 6H_2O$), hydrazine hydrate ($N_2H_4 \cdot H_2O$), *n*-hexane, cyclohexane and *n*-nonane were purchased from Merck.

Method. Microemulsions were prepared by mixing the same volume of aqueous solution of H_2PtCl_6 (0.01 M) and hydrazine hydrate (0.05 M) to the 0.12 M AOT/*n*-hexane, AOT/*n*-nonane, or AOT/cyclohexane solution. The water-to-AOT molar ratio, W, was kept the same in all cases and was equal to 5. The microemulsion containing hydrazine hydrate was added into the microemulsion containing H_2PtCl_6 drop by drop. After the microemulsion was added, the vigorous magnetic stirring was maintained for 2 h. Morphology and size of the platinum nanoparticles were determined by transmission electron microscopy (Philips CM 200) operating at 200 kV. Samples for the electron microscopy were prepared by placing a drop of the microemulsion containing the platinum nanoparticles onto a carbon-copper grid and evaporating the organic solvent at room temperature.

RESULTS AND DISCUSSION

After mixing of two microemulsions, the interchange of the reactants takes place during the collisions of the water droplets. For the formation of platinum nanoparticles, a model can be given to illustrate the template role of the reverse micelles in the AOT microemulsions for fabricating nanoparticles. This model is illustrated in Fig. 1 schematically. At the beginning of the process, the attractive van der Waals forces and the repulsive osmotic and elastic forces between reverse micelles lead to collisions of micelles and result in exchange of the compounds (H_2PtCl_6 and N_2H_4) solubilized within the water cores in two different reverse micelles [15]. In result, the initial monomeric platinum nuclei will form and further grow. Owing to the fast exchange between the water cores, the initially formed platinum nuclei grow to reach a certain size, which corresponds to the thermodynamically best stabilized species in the presence of microemulsion.

The process of the exchange of solubilizates and subsequent reaction can be followed by the five main steps [16]: (1) Brownian diffusion of reverse micelles leading to collisions; (2) surfactant layer opening through effective collisions and a coalescence of the micelles happening; (3) diffusion of solubilizate molecules resulting in exchange of materials between micelles; (4) reaction among solubilizate molecules resulting in formation of metallic nuclei; (5) the aggregates splitting to return as reverse micelles. The aggregation step is essential for nanoparticles growth and depend on interaction between microemulsion droplets [16]. Figure 1 shows TEM micrographs of platinum nanoparticles in microemulsion systems containing H_2PtCl_6 as platinum source and *n*-hexane, cyclohexane and *n*-nonane solvents. As can be seen from the micrographs, the size of nanoparticles formed in microemulsion containing *n*-hexane as the solvent is less than for cyclohexane and both are less than for *n*-nonane. The reason for this phenomenon can be related to the interaction of the microemulsion droplets in different solvents, which is related to the solvent interactions with the AOT tails. The extent of solvent penetration into the surfactant chain region creates more rigid micelle and then decreasing the k_{ex}. Obviously, the solvent penetration decrease with increasing the chain length of the solvents from *n*-hexane to *n*-nonane. Then, the repulsive interaction in the systems with *n*-hexane or cyclohexane solvents, which have rigid microemulsion droplets, is more than in systems containing *n*-nonane. It means that the attractive interaction or aggregation step for systems containing nonane is domain, and then produces greater nanoparticle size. On the other hand, comparing the *n*-hexane and cyclohexane solvents, it can be said that *n*-hexane has more penetration into the surfactant chain region, because of its shape and volume. It causes more rigidity of microemulsion droplets and then more repulsive interaction between microemul-

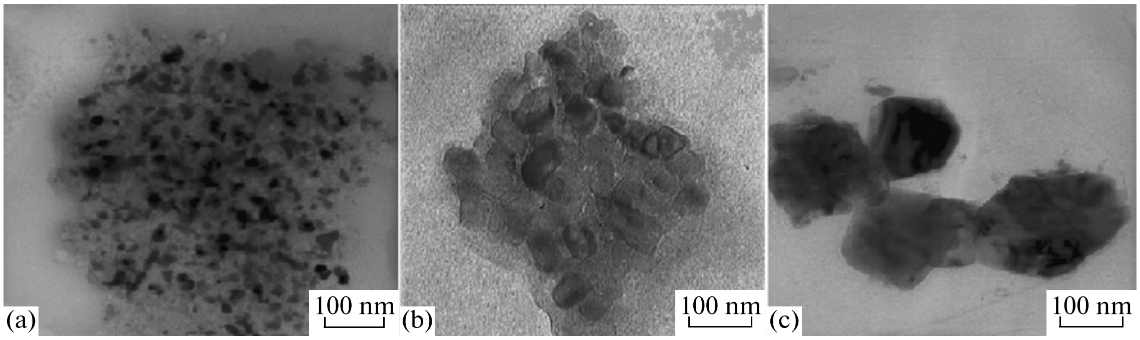

Fig. 2. TEM micrograph of platinum nanoparticles synthesized in microemulsion systems containing (a) *n*-hexane, (b) cyclohexane, and (c) *n*-nonane solvents.

sion droplets and decreasing of particle size. Previous investigations by other researchers on the effects of the bulk alkane solvent on the AOT reverse micelle system have produced results that support these findings [10, 11, 16]. Considerable work has been done to gain a better understanding of CdS nanocrystal growth where Towey states that particle formation is controlled to an extent by the nature of the continuous phase, where the growth rate increases from cyclohexane to *n*-heptane to *n*-decane [17]. Bagwe demonstrated with the production of silver and silver chloride particles that an increased intermicellar exchange rate has the effect to increase the growth rate and more importantly decrease the final particle size [16]. These results are explained by the solvent–tail interactions or more generally, a decrease in the rigidity of the micelle.

CONCLUSION

This research demonstrates that, for the synthesis of platinum nanoparticles within the AOT reverse micelle system, the bulk organic phase influences the particle size. It was found that, reduction of H_2PtCl_6 by hydrazine in microemulsion system with three different organic solvents, give the platinum nanoparticles with different size. The final nanoparticles size in different solvents can be arranged as *n*-nonane > cyclohexane > *n*-hexane.

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