Electronic Supplementary Information (ESI).

Production of Pd Nanoparticles in Microemulsions. Effect of Reaction Rate on Particle Size.

Jhon F. Sánchez M.[1], Miguel D. Sánchez[1], R. Dario Falcone[2] and Hernán A. Ritacco[(*)1].

[1] Instituto de Física del Sur (IFISUR), Departamento de Física, Universidad Nacional del Sur (UNS), CONICET, Av. L. N. Alem 1253, *B8000CPB - Bahía Blanca, Argentina*.

[2] Departamento de Química, Universidad Nacional de Río Cuarto (UNRC). Instituto para el Desarrollo Agroindustrial y de la Salud (IDAS), CONICET–UNRC, *Agencia Postal No. 3, X5804BYA Río Cuarto, Argentina.*

(*) Corresponding author: hernan.ritacco@uns.edu.ar

1. DLS measurements.

The microemulsions were prepared from precisely measured amounts of n-Dodecyltrimethylammonium bromide [DTAB] = 0.1 M, n-octanol [$C_8H_{18}O$] = 0.7 M, Benzene (C_6H_6) and a water-surfactant molar ratio W_o=15. The microemulsions were characterized by Dynamic Light Scattering (DLS) to determine the size of the micelles that would contain the reagents ($PdCl_2$, $NaBH_4$). Microemulsions containing different amounts of the precursor and the reducing agent were analyzed. The preparation and measurements were carried out independently. The preparation and measurement temperatures were identical (25 ^oC). The results of the size distributions obtained are shown in Fig. ESI-1. There were no appreciable changes in the apparent average diameter of the micelles, which remained approximately constant and equal to 10 nm in all cases. The microemulsions were stable over time, retaining the same distribution for up to five days after preparation (Figs. ESI-1A). Regarding the microemulsions in which the content of the micelles was changed, there were no large size variations size reported (Figs. ESI-1B). DLS measurements were made of microemulsions with their micelles containing water (H_2O), reducing agent ($NaBH_4$) or palladium precursor (Pd^{+2}). Even those microemulsions containing the nanoparticles (NPs-Pd) that were already synthesized showed the same average size. A similar behavior was observed for microemulsions containing different amounts of $PdCl_2$ and $NABH_4$ (Figs. ESI-1C). However, the situation changed with a change in temperature. An inverse variation was observed, registering an increase in the average apparent diameter as the temperature was lowered during the measurement (Figs. ESI-1D).

2. Kinetic measurements of reactions

The reaction kinetics was determined from the variations in the concentration of the $[PdCl_4]^{-2}$ species. This variation was followed by UV-visible spectrophotometry. Initially, the typical spectra of different concentrations of aqueous solutions of $PdCl_2$ were determined (Figs. ESI-2). In each case, an accurately weighed amount of the palladium salt was dissolved in ultra pure MiliQ® water and the UV-visible absorption spectrum was determined. These solutions were prepared independently and in all cases the pH was regulated to 2.5 and the measurement temperature was 25 ^oC. The spectra obtained show two absorption peaks at 325 and 425 nm,

which are attributed to the presence of the $[PdCl_4]^{-2}$ species[1]. These same solutions were used as an aqueous phase in the preparation of the microemulsions.

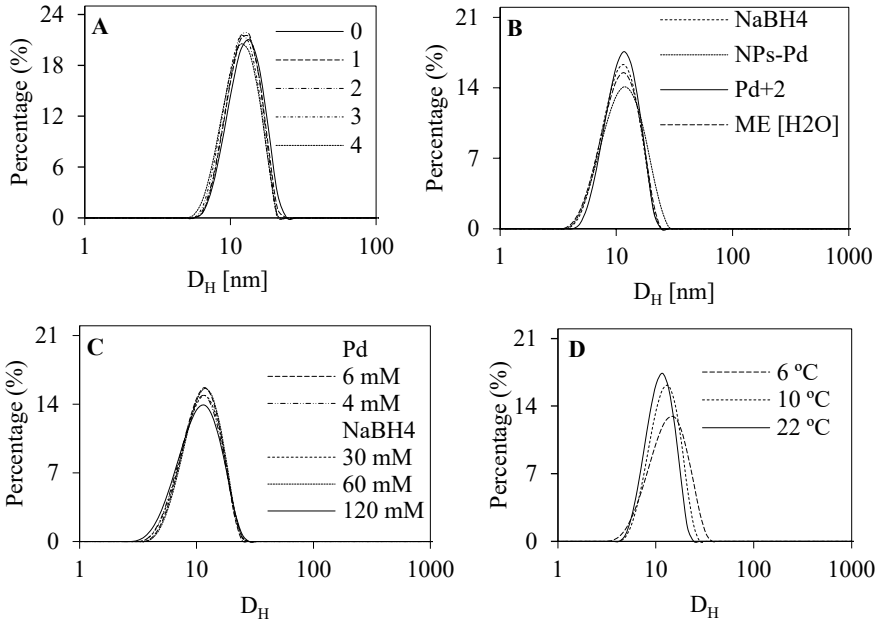

Figure ESI-1: Size distributions of the microemulsions using Dynamic Light Scattering (DLS): A) obtained up to 5 days after being prepared, B) containing solutions of the reagents sodium borohydride [60 mM], palladium precursor [6 mM] and the NPs-Pd nanoparticles that were obtained, C) containing different concentrations of the reagents, D) at different temperature values. All the intensity auto correlation functions were analyzed by cumulants.

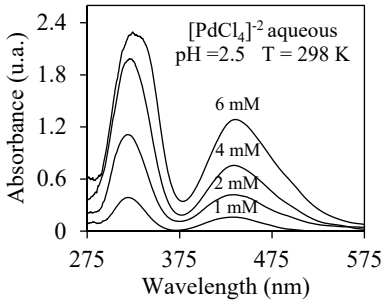

Figure ESI-2: UV-visible spectra of $[PdCl_4]^{-2}$ in aqueous solution at different concentrations.

An accurately measured volume of a $PdCl_2$ aqueous solution was added to a DTAB/octanol/Benzene mixture and the UV-visible absorption spectrum was measured. In this way, the absorbance value equivalent to the $[PdCl_4]^{-2}$ concentration in the micelle of the microemulsion could be determined. In order to determine the variation in concentrations during the reaction, measurements were made of the typical spectra of the microemulsions. Microemulsions containing different concentrations of aqueous solutions of $PdCl_2$ presented the spectra shown in Fig. ESI-3. In this case, the absorption peak attributed to the $[PdCl_4]^{-2}$ ions was detected at 340 nm. As benzene is the major component in the microemulsion, the analysis was

made only with the second peak. Additionally, using the peak at 340 nm we avoid the possibility of interference with a surface plasmon resonance from Pd nanoparticles.

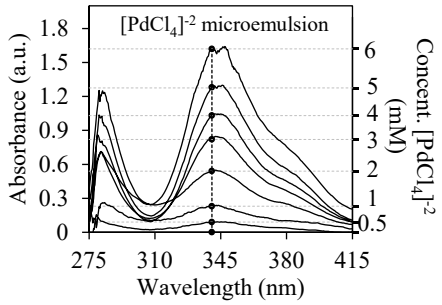

Figure ESI-3: UV-visible spectra of $[PdCl4]^{-2}$ in microemulsion at different concentrations.

The calibration curve shown in Fig. ESI-4 was obtained from the absorbance of each of the microemulsions that were measured at 340 nm. In this way, the variation in the concentration of the palladium species could be quantified during the synthesis of nanoparticles using the microemulsion method.

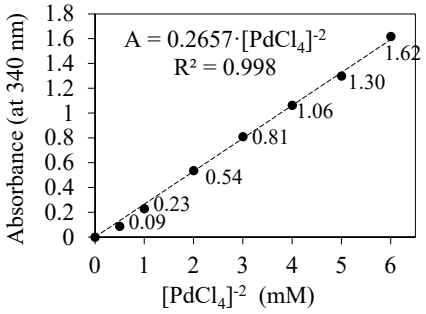

Figure ESI-4: Absorbance of $[PdCl4]^{-2}$ in microemulsion at different concentrations.

3. Experimental results

3.1 Spectra as a function of time for each concentration

The palladium nanoparticles were synthesized using the microemulsion method. The variation in time of the UV-visible absorption spectrum of the reagent mixture allowed us to study the kinetics of nanoparticle formation in microemulsion media. The freshly prepared microemulsions containing the precursor solutions in their micelles were mixed rapidly and carefully. The reaction temperature was held constant by using a constant-temperature thermal bath and the UV-visible spectra were recorded during the process. Some of the spectra obtained at intervals of 0.2 s are shown in Fig. ESI-5. In all cases, the preparation and composition of the microemulsions were identical, [DTAB] = 0.1 M, [n-octanol] = 0.7 M in benzene. Likewise, the volume (54 µL) of the aqueous solutions that were added was the same in each case. A water-surfactant molar ratio W_0=15 was maintained. Tests were conducted while varying the concentration of palladium precursor (2-8 mM) and the concentration of reductant (30-120 mM). The variations in the absorption spectrum were rapid and the peak at 340 nm disappeared

within a time period of less than 5 s. The final microemulsion was translucent but a slight change in color could be observed which became slightly dark. This would be a visual indication of the reduction of Pd^{+2} and the formation of the nanoparticles.

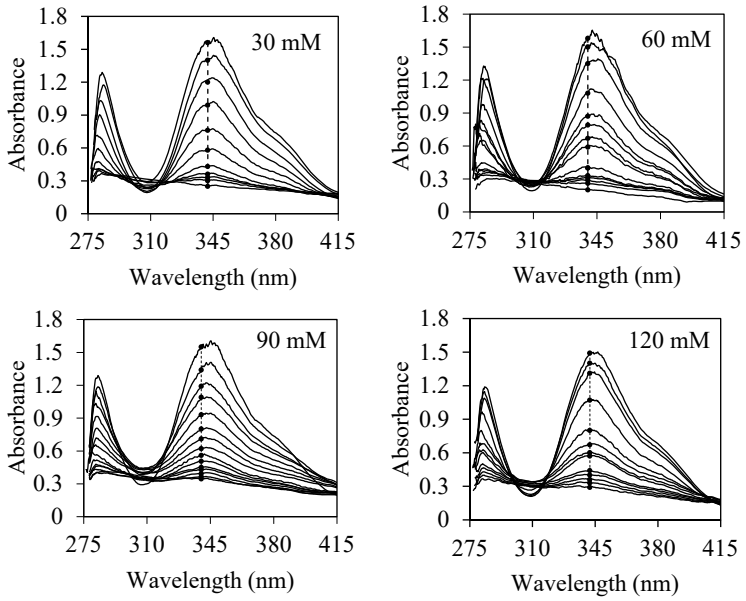

Figure ESI-5: Successive UV-visible spectra (time interval 0.2 s) for the reduction of palladium with different concentrations of [$NaBH_4$] in microemulsion. Conditions: $[PdCl4]^{-2}$ = 6 mM, [DTAB] = 0.1 M, [n-octanol] = 0.7 M. T = 25 °C.

3.2 Reaction kinetics

From the variation of the UV-visible spectra, for each reaction the decrease in concentration of the species $[PdCl_4]^{-2}$ was determined as a function of time. Some the typical variation of the absorption signal at 340 nm during the synthesis of the palladium nanoparticles is shown in Fig. ESI-6. The absorption intensity at 340 nm decreased over time until it approached a minimum value that remained constant. This variation was used for the study of the kinetics of the nanoparticle synthesis via the microemulsion method and the time for the formation of the NPs-Pd can be obtained. It was found that this time period was typically 3 s. The initial reaction rate was obtained from the palladium concentration data as a function of time. It was found that the palladium reduction rate was higher as the $NaBH_4$ concentration increased.

The effect of the reaction temperature was also studied. Experiments at different temperatures were conducted and the initial rate of reaction was determined. The temperature was controlled and held constant during the reaction. Some results of the changes in palladium concentration as a function of time are presented in Fig. ESI-6. The preparation conditions of the microemulsions were the same for all measurements, [DTAB] = 0.1 M, [n-octanol] = 0.7 M, W_o = 15. The initial concentrations of the reagents were $[NaBH_4]_o$ = 60 mM, $[PdCl_4]^{-2}{}_o$ = 5 mM, and the temperature was varied between 10 and 25 ^oC. It was observed that the rate of reduction of the palladium species increased as the temperature increased.

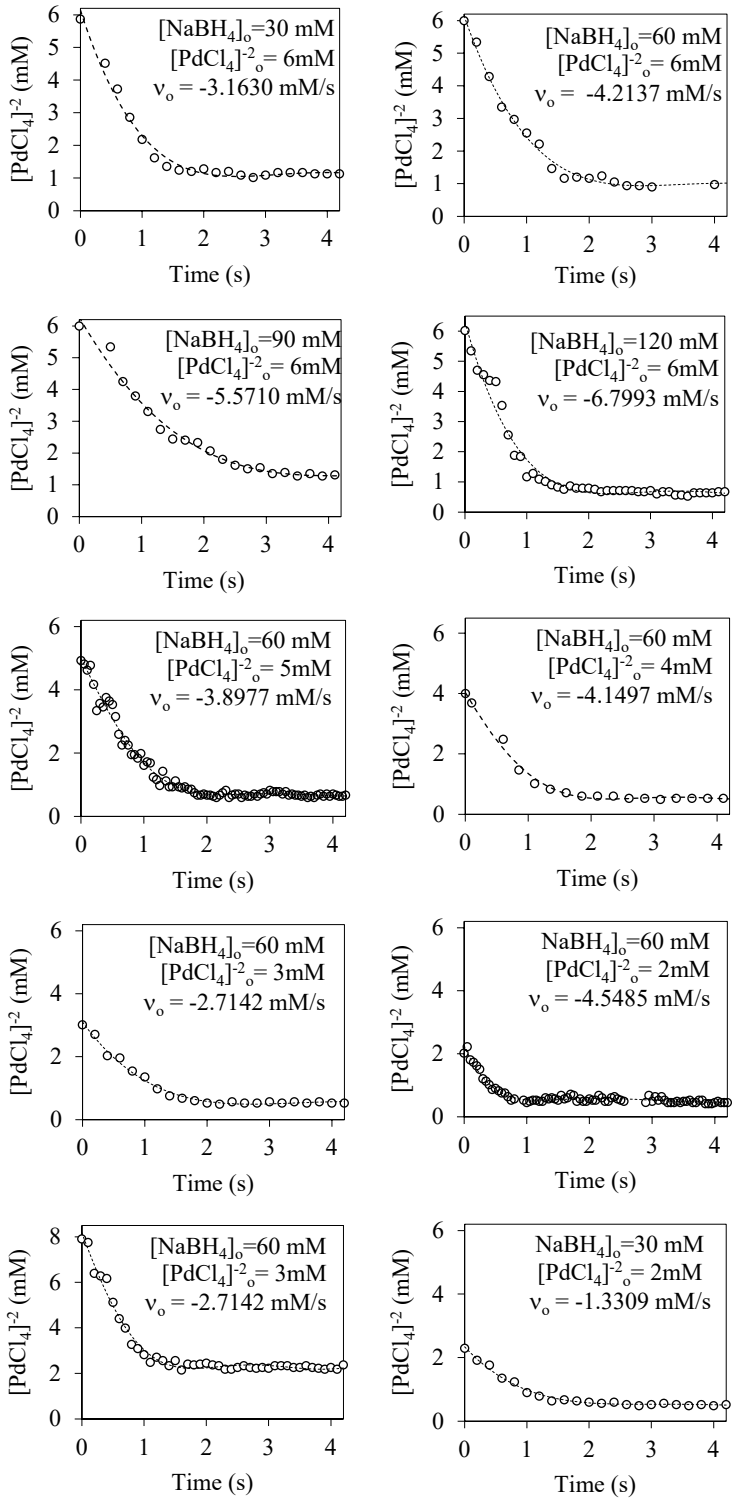

Figure ESI-6: Variation in time of the concentration of Pd (II) chloride complex ions by the reduction with $NaBH_4$ in microemulsion. Conditions: Absorbance at λ = 340 nm, [DTAB] = 0.1 M, [octanol] = 0.7 M, W_o = 15, T= 25°C.

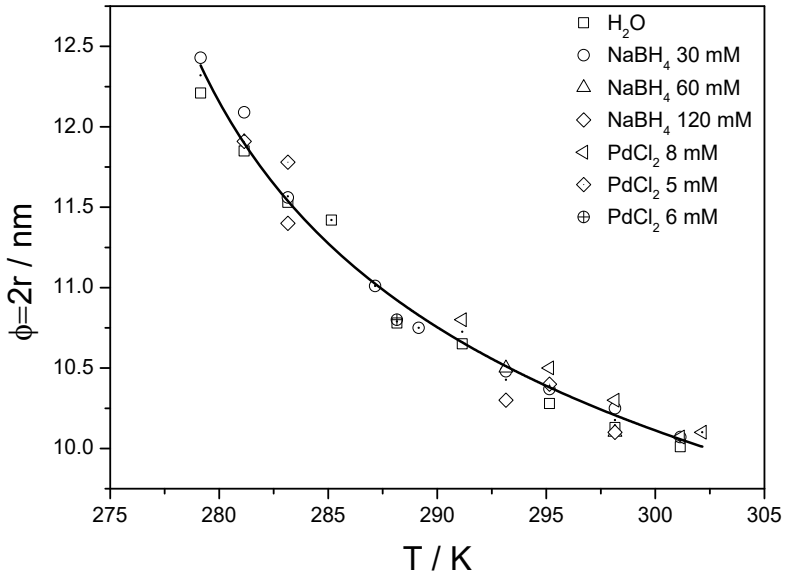

Figure ESI-7: Hydrodynamic diameter (2r) of micelles as a function of temperature for microemulsions containing different amounts of reactants (before mixing and reacting). The line is a fitting curve with a power law: $2r \sim (T-273.15)^{-018}$. W_0=15.

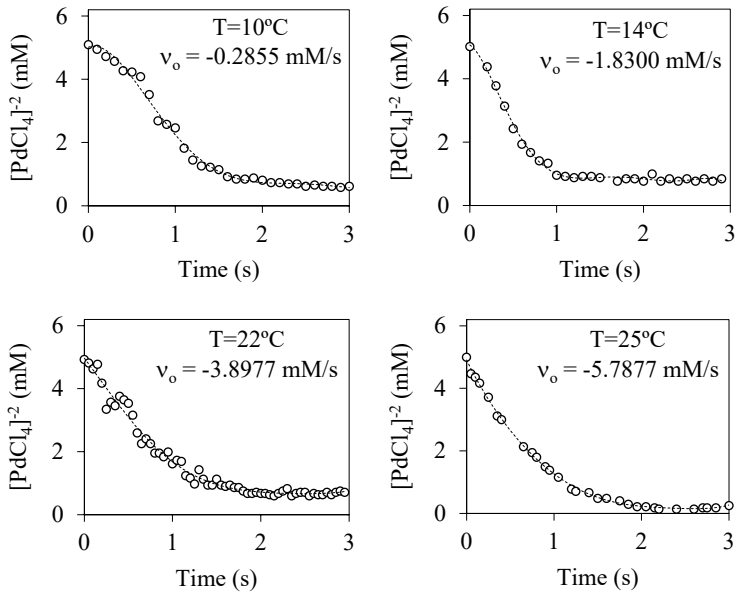

Figure ESI-8. Some examples of the effect of the temperature on the kinetic of reaction in the microemulsion. Conditions: $NaBH_4]_o$=60 mM, $[PdCl4]^{-2}{}_o$ = 5 mM. [DTAB]= 0.1 M, [n-octanol]=0.7 M. W_o=15.

3.3 Microscopy results

The particle size distribution of the obtained NPs-Pd was generated using Transmission Electron Microscopy (TEM) image analysis (TEM Jeol-100-CX-II microscope, 100 kV). Several grids were analyzed per sample and particles from different locations on each grid were counted. The average apparent diameter was determined by analyzing no less than 250 particles per grid (Fig. ESI-9). The results were confirmed using HAADF-STEM and digital HRTEM image analysis.
The images showed high-quality particles in terms of shape and dispersion (Fig. ESI-10). The effectiveness of the confined medium in the synthesis of nanoparticles was compared with the material obtained with no microemulsion.

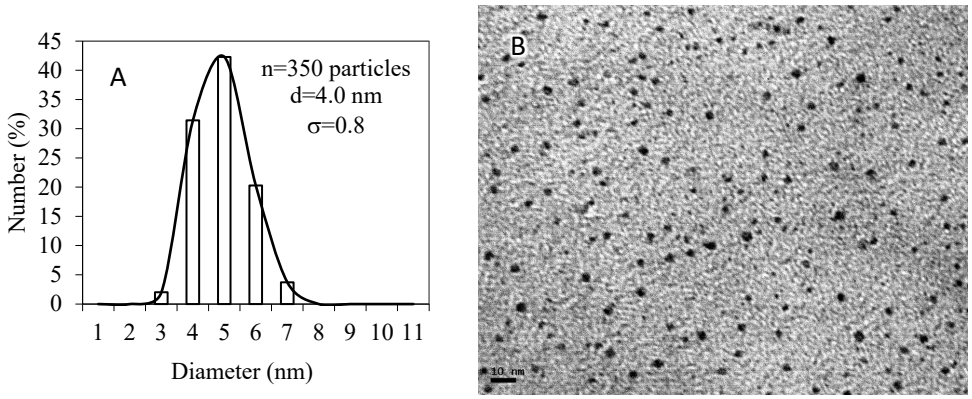

Figure ESI-9: Size distribution (A) and TEM image (B) of the nanoparticles obtained with $[PdCl4]^{-2}_o$ = 6 mM, $[NaBH4]_o$ = 60 mM in microemulsion. W_0 = 15.

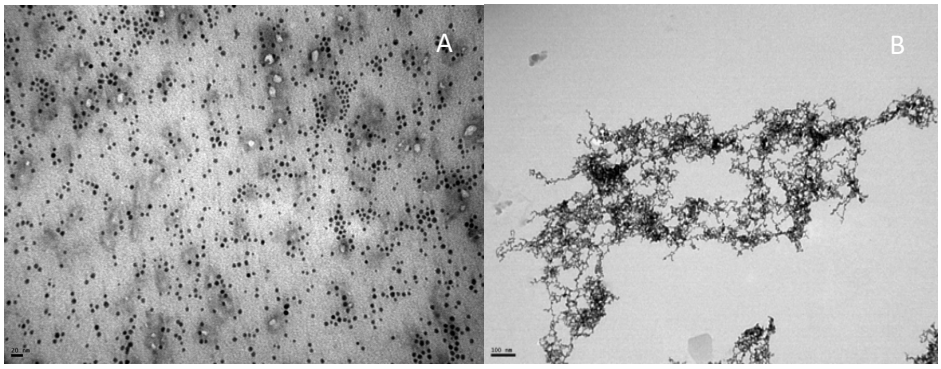

Figure ESI-10: TEM images of the palladium material obtained (A) with microemulsion and (B) without microemulsion at identical concentrations of the reactants. $[PdCl4]^{-2}_o$ = 6 mM, $[NaBH_4]_o$ = 60 mM. Room temperature. Jeol 100 CX-II transmission electron microscope, operating at 100 kV.

[1] Wojnicki, M.; Fitzner, K.; Luty-Błocho, M. Kinetic Studies of Nucleation and Growth of Palladium Nanoparticles. *J. Colloid Interface Sci.* **2016**, *465*, 190–199.