

Wet organometallic chemistry for palladium nanoparticles synthesis performed in an organic media and under supercritical conditions in microreactors

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ABSTRACT

The synthesis of palladium nanoparticles was performed through an organometallic route in a microreactor. Two types of operating conditions have been experimented: a reactive two phase flow induced in an organic media and synthesis under supercritical conditions. A reactive two phase flow was specially developed for that purpose, in order to demonstrate the benefits of microreaction technology for the fast screening of chemistry synthesis conditions. We thus describe the possibility to continuously synthesize Pd nanoparticles in less than 120 s. The influence of the quantity of the stabilizing ligand and of the operating conditions on the nanoparticles properties was studied. Finally, we investigated the synthesis of Pd nanoparticles in supercritical conditions by using CO₂ as supercritical fluid. Preliminary studies in this work were carried out in a microreactor since this technology is a precise tool to control extreme operating conditions (pressure up to 105 bar and temperature set at 65 °C) in a safe way.

Keywords: Microreactor, Nanoparticles, Supercritical fluid, Organometallic Chemistry, Palladium

1 INTRODUCTION

Nanotechnology becomes more relevant, it is thus crucial to develop synthesis methods focusing on a precise control of the nanomaterials' characteristics. In literature, several synthesis methodologies, both "top-down" and "bottom-up" approaches, giving rise to a broad variety of nanomaterials of different size and shape have been reported [1]. As wet chemistry model, we choose the organometallic chemistry route for nanomaterials synthesis. This method is based on the use of metal organic precursors that are decomposed within a controlled atmosphere in a flask. An organic solution of the chosen organometallic complex and a stabilizing agent are mixed in a Fisher Porter reactor. The decomposition of the metal precursor is further accomplished under dihydrogen atmosphere in mild conditions of temperature and pressure (room temperature and 3 bar H₂). The effectiveness of this bottom up approach has been demonstrated for the control of size, shape, dispersion and the surface state of various nanoparticles of noble metals. It appeared to us as an interesting route to be

carried out continuously inside a microreactor. Furthermore, this method differs from the couple of papers describing the synthesis of palladium nanoparticles from a metal salt precursor in microreactors. In particular one process based on water in oil micro emulsion [2], and a second one based on single phase flow in a polymeric microreactor [3]. Very recently, the thermal decomposition of a Palladium acetate precursor in a glass capillary micro flow reactor was achieved [4].

As the organometallic chemistry route is in fact a two phase flow process, the use of CO₂ as supercritical fluid appears beneficial. Firstly, it eliminates the mass transfer limitation between the gas and the liquid and secondly it enhances the hydrogen solubility in the single supercritical phase within CO₂ as reaction solvent.

We describe in this paper our work to achieve the synthesis of palladium nanoparticles from an organometallic precursor inside a reactive two phase flow microreactor in an organic solvent, inspired from a previous work [5]. Moreover, different flow rate conditions were studied to observe the sensitivity of the microfluidic system for this synthesis and to reach a short reaction time for the nanoparticles production. Secondly, we present our preliminary results, showing the feasibility of the organometallic synthesis of nanoparticles under supercritical conditions.

2 EXPERIMENTAL

Hydrogen and CO₂ (Pangas) were used as supplied with a purity of 99.999% and 99.995% respectively. Pd₂(dba)₃ was purchased from Nanomeps, Hexadecylamine (HDA; 99%) from Sigma-aldrich. Tetrahydrofuran (THF) was purchased from Sigma-aldrich dried and distilled prior to use over sodium/benzophenone. THF and reagents were degassed under argon before use.

The Silicon/glass microreactors were manufactured with standard photolithography, dry etching and anodic bonding techniques. The channel height and width of the two phase flow microreactor are 200 μm ± 2 μm and its length is 2 m (Figure 1 top). For the adaptation of the established procedure described in [5] to a reactive two phase flow in a microreactor we proceeded as follows. A liquid phase was prepared that contains the metal precursor ((tris-dibenzylideneacetone dipalladium, Pd₂(dba)₃) and the stabilising ligand (hexadecylamine, HDA, 1 or 10 molar

equivalent regarding to the metal content) both dissolved in an organic solvent (THF). The liquid phase was delivered into the microreactor from a syringe pump (Harvard Apparatus), the volumetric flow rate is noted Q_l . The gas phase (pure dihydrogen) was stored in a bottle and its release was controlled by a gas flow controller (Bronkhorst), Q_g refers to its volumetric flow rate. Finally, the outlet PEEK capillary is immersed in 1 mL of THF to separate the gas from the liquid. The outlet solution was collected during 10 min and two droplets were deposited on a covered carbon copper grid for further TEM analysis. This procedure was applied for all the experiments. The solution was collected 10 min after changing the liquid and gas volumetric flowrate, in order to achieve stable operating conditions.

For the supercritical CO_2 conditions the length of the glass/silicon microreactor is 9, 8 cm in order to decrease the residence time (Figure 1 bottom) and the channel height as well as the width is 400 microns. Inlet and outlet channels are etched on the same side of the silicon chip in order to connect the high pressure connections from the side. The high pressure connections, fused silica capillary from Polymicro (OD: 150 μm ID: 75 μm), are inserted within the inlets and the outlet and glued with an epoxy resin from Cotronics Ceramic adhesives. This technique allows to avoid any flow leakage under high pressure experiments. The solution of $\text{Pd}_2(\text{dba})_3$ in THF containing HDA and CO_2 were delivered from two high pressure pumps (Isco Apparatus). The gas phase was controlled by a mass flow controller (Bronkhorst). The pressure in the microreactor is controlled by a Back pressure regulator from Jasco. For the collection of the liquid at the outlet, the same procedure as in the two phase flow experiments was adopted.

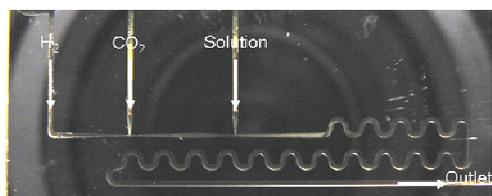


Figure 1: Pictures of the silicon/glass type microreactor used for the reactive two phase flow (top) and for supercritical conditions (bottom).

3 RESULTS

3.1. Synthesis of palladium nanoparticles in an organic media

Several operating conditions (Q_l and Q_g) have been applied to study their influence on the size and the shape of the palladium nanoparticles. In addition, two different liquid solutions were prepared, containing the same concentration of the organometallic compound (2.5 mmol.L^{-1}), varying only the ratio, R, of $[\text{HDA}]/[\text{Pd}]$ from 1 to 10, in order to compare the effect of the stabilizer quantity. The residence time (t_{res}) is defined as the ratio of the total microreactor volume and the total volumetric flowrate. The mean diameter (dm) and the standard deviation (s.d) of the nanoparticles were determined when only spherical ones were obtained, through a manual analysis of enlarged micrographs by measuring ca.150 particles on a given grid. The nature of the Palladium was revealed by EDX analysis under microscope. Table 1 summarizes the operating conditions and the characteristics of the nanoparticles.

| Entry | Synthesis conditions | | | | Nanoparticles characteristics | | |
|------------|--------------------------------------|--------------------------------------|----|------------------|-------------------------------|-------------|----------------------|
| | $^a Q_l$ $\mu\text{L}/\text{min}$ | $^a Q_g$ $\mu\text{L}/\text{min}$ | R | t_{res} | dm (nm) | s.d (nm) | Shape ^{c,d} |
| 1 Batch | - | - | 10 | 20 h | 6 | - | Sp. |
| 2 | 20 | 20 | 10 | 120 s | 3.84 | 0.78 | Sp. |
| 3 | 20 | 30 | 10 | 96 s | 3.6 | 0.77 | Sp. |
| 4 | 20 | 50 | 10 | 68 s | 3.08 | 0.55 | Sp. |
| 5 | 20 | 120 | 10 | 48 s | 2.57 | 0.52 | Sp. |
| 6 | 20 | 20 | 1 | 120 s | - | - | Sp. El. |

^cSp. for spherical. ^dEl. for elongated.

Table 1: Operating conditions and nanoparticles characteristics

In all the tested conditions, the TEM analysis of the samples revealed the presence of palladium nanoparticles (Fig.2). However, in comparison with the published results [5] some interesting differences were observed. First of all the reaction time could be decreased significantly compared to the batch process. For a $[\text{HDA}]/[\text{Pd}]$ ratio of 10 (Table 1, entries 1-5), we observed the formation of palladium nanoparticles as short as 120 s, while a reaction time of 20h is reported [5]. This process is thus less time consuming due to the enhancement of the mass transfer in the microreactors.

Secondly, the shape of the nanoparticles is spherical as in the flask procedure, but the mean diameter measured for the nanoparticles is reduced from 6 nm to around 3 nm. At the same time, the standard deviation of the mean diameter was reduced by increasing the total volumetric flow rate. This effect is due to an increasing of the recirculation motion inside the liquid slug, enhancing the mixing efficiency. Same tendencies were previously observed and discussed for CdSe quantum dots synthesis in a gas-liquid segmented flow [6]. Another interesting result concerns the influence of the [HDA]/[Pd] ratio in the reactive solution (Table 1, entry 6 versus entry 2). As in the batch procedure we observed that the shape of the nanoparticles is influenced by the quantity of the stabilizer present in the reaction medium. A lower concentration ([HDA]/[Pd]=1) gives rise to a mixture of spherical and elongated nanoparticles (Fig.3). The elongated nanoparticles result from a coalescence phenomenon due to a lack of stability caused by the weak HDA ligand.

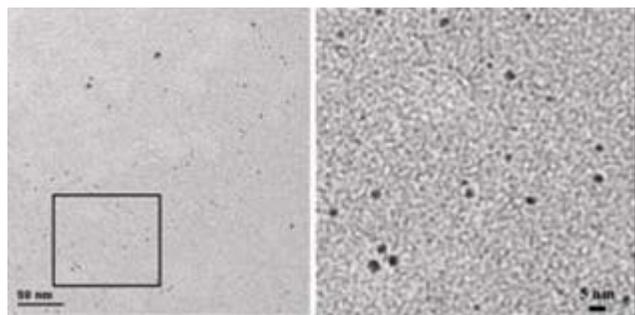


Figure 2: TEM images of Pd nanoparticles under two phase flow conditions in an organic media (reaction conditions: $Q_g = 30 \mu\text{L}/\text{min}$ and $Q_l = 20 \mu\text{L}/\text{min}$, [HDA]/[Pd]=10). The right picture corresponds to the numerical magnification of the defined area from the left picture.

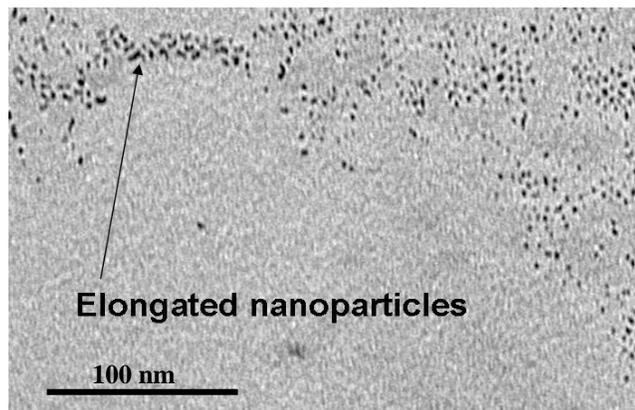


Figure 3: TEM images of Pd nanoparticles under two phase flow conditions in an organic media (reaction conditions: $Q_g = 30 \mu\text{L}/\text{min}$ and $Q_l = 20 \mu\text{L}/\text{min}$, [HDA]/[Pd]=1).

3.2. Synthesis of palladium nanoparticles under supercritical conditions

Experimental conditions were chosen in order to ensure the supercritical phase by using CO_2 on one hand and the solubility of the precursor and the stabilizing ligand on the other hand.

In order to determine reaction conditions (molar fraction, temperature and pressure), where all the compounds are miscible in each other, we refer to a study of the vapor-liquid equilibrium of the binary THF/ CO_2 mixture system [7, 8]. Nevertheless, the data cannot be transferred completely as we are facing a ternary mixture since hydrogen is involved in the reaction. Thus the molar ratio of hydrogen/precursor was set to 30, similar to the one in the batch procedure. Moreover for this value, the hydrogen dissolution within the supercritical THF/ CO_2 phase is full as we observed the one phase flow under a stereomicroscope.

Secondly, the solubility of hexadecylamine in the ternary mixture is one of the central parameters in order to avoid its crystallization and the clogging of the microchannel. In order to have a good compromise between temperature, pressure and molar composition, we set the temperature to 65°C . At this temperature, the supercritical phase for the binary mixture is obtained for a molar fraction of CO_2 above 95 % and pressures above 95 bars [8]. The molar excess of hydrogen, 30 times higher, compared to the precursor quantity is kept constant during all experiments and hydrogen is fully dissolved under supercritical conditions.

No precipitation of the hexadecylamine was observed at a concentration of 1.92 mg/ml solvent, corresponding to a dilution 10 times lower than for the two phase flow experiments. By consequence, the quantity of precursor was reduced in the same way keeping the [ligand]/[palladium] molar ratio constant to 10.

The pressure was the main parameter studied within this preliminary study on the synthesis of palladium nanoparticles under supercritical conditions. For each experiment, we adjusted the volumetric flow rate in order to achieve a constant residence time of 5 s. Table 2 summarizes the operating conditions.

| Entry | ^a Q_{CO_2} | ^a Q_l | ^a Q_g | P (bar) |
|-------|--------------------------------|--------------------|--------------------|---------|
| 7 | 200 | 10 | 2000 | 75 |
| 8 | 300 | 15 | 3000 | 95 |
| 9 | 400 | 20 | 4000 | 105 |

^a Volumetric flow rate in $\mu\text{L}/\text{min}$ at standard conditions.

Table 2: Synthesis conditions in supercritical conditions.

Figure 4 reports TEM pictures of samples obtained at 75

bar, 95 bar and 105 bar respectively from the left to the right.

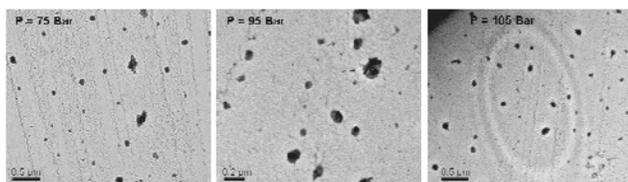


Figure 4: TEM images of Pd nanoparticles obtained at different pressure conditions as mentioned on the pictures.

Two different types of morphologies are observed for all the experiments performed both at subcritical conditions (below 95 bar) and at supercritical conditions ($P = 105$ bar) as following: large ones above 60 nm in size, and smaller ones around 50 nm in size made of small Pd nanoparticles. It is thus difficult to determine an influence of the pressure on the morphology of the particles.

Figure 5 presents images of the two kinds of nano-objects observed. At first, we observed (Fig. 5 left) a mixture of organic compounds, as confirmed by EDX analysis under microscopy. At this stage, the origin of these large superstructures is difficult to explain. They could correspond to interaction between HDA or other organic products resulting from the organometallic precursor decomposition with the solvent (THF). Secondly, smaller nano-objects are present (Fig. 5 right) which are made of palladium nanoparticles as revealed by EDX. These nano-objects are thus agglomerates of individual very small nanoparticles of around 3 nm in size. The formation of agglomerates made of small palladium nanoparticles could be attributed to the non polarity of CO_2 . In addition, this agglomeration could be favored by the stabilizing agent, which is not fully soluble in the supercritical phase and thus could form organic pockets in the reaction mixture in which the Pd nanoparticles are assembled.

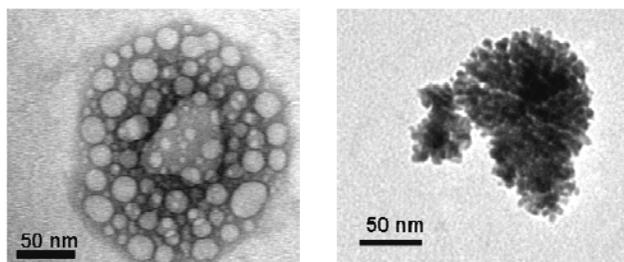


Figure 5: TEM images of large organic superstructures (left) and Pd agglomerates (right).

4 CONCLUSION

The continuous synthesis of palladium nanoparticles following an organometallic chemistry route was successfully performed inside a reactive two phase flow in

an organic solvent in microreactor specially developed for this purpose. The obtained results evidenced that this procedure displays some advantages in comparison to the classical organometallic methodology carried out in a flask reactor: 1) it allows a continuous synthesis of metal nanoparticles, 2) it consumes less time as metal nanoparticles are produced in a time which is 2-3 orders of magnitude shorter and 3) the nanoparticles characteristics, as their size or their shape, can be controlled by adjusting the working conditions. The microreactor developed has thus demonstrated its benefit as an analytical tool for the organometallic synthesis of metal nanoparticles. This process opens thus some perspective to study the synthesis of metal nanoparticles from organometallic precursors by a screening of the reaction conditions (ligand nature and quantity, precursor, solvent, pressure, temperature) in a much faster way than in the flask procedure and with reduced cost. Such a screening may shed some light on both the nucleation and growth steps that are involved in nanoparticles synthesis.

Finally, preliminary results obtained from experiments performed under supercritical conditions in CO_2 show that palladium nanoparticles can be prepared in reaction times as short as 5 s. Nevertheless, the supercritical conditions need to be improved to better understand the particular morphologies observed. One challenge in the near future is to understand the mechanism of formation of the nanoparticles in CO_2 as reaction solvent.

Acknowledgments

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