The control of the growth of Pt clusters in solution: A way to prepare Pt particles of tailored size

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ABSTRACT

The growth of Pt particles in mesitylene-solvated metal atoms, obtained by metal vapour synthesis (MVS), has been followed at two temperatures (-40 and $25\,°C$) by NMR DOSY technique. The addition of 1,3-divinyltetramethyldisiloxane (DVS) at different time allows to quench the growth process and to make the resulting thermally stable solutions suitable for the evaluation of the Pt particles size at that moment. These solutions can be conveniently used to prepare supported Pt systems containing Pt particles of tailored size.

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1. Introduction

It is well known that the physical and chemical properties of metal nanoparticles are greatly dependent on particle size, not only because of change in surface area but also as result of the significantly different electronic structure of small clusters [1,2]. For metal particles with diameters in the range 1–5 nm, small changes in the size can be accompanied by significant morphological changes and effects on the distribution of valence bond density [3]. For this reason, the preparation of metal nanoparticles with a tailored final mean particle size and size distribution that is as narrow as possible is one of the most challenging tasks in nanoscience. Nowadays, in traditional synthetic routes, involving the reduction of metal complexes or salts, many efforts have been made to control the size empirically by changing the experimental conditions, such as temperature, solvent, precursors, reducing agents and ligand to metal ratio [4–8]. However, only few methods allow reproducible formation of uniform sizes. Recently, some studies on the controlled production of small ligand-stabilized metal clusters have appeared in the literature [9–13], but the methods described are suitable only in particular cases and generally do not allow the isolation of the particles during the growth process.

Metal vapour synthesis (MVS) provides a valuable synthetic route to weakly stabilized nanostructured metal particles [14]. Co-vapourization of platinum and mesitylene leads to solutions containing mesitylene-solvated platinum microclusters, which, at room temperature, undergoes in same hours a clustering process to insoluble platinum particles ranging 4 nm in diameter [15].

The addition of 1,3-divinyltetramethyldisiloxane (DVS) as stabilizing ligand allows to quench the growth processes of the platinum particles, making the resulting solutions thermally stable and suitable for NMR studies (Scheme 1) [16].

The nature of species present in solution can established by 1D and 2D NMR investigations [17], while the ^{1}H NMR DOSY technique proved to be a very powerful tool to probe the dimensions of Pt-aggregates [16,17].

In order to gain a better understanding of the factors affecting the clustering of Pt atoms, we reacted Pt and mesitylene vapour, at a defined Pt and mesitylene ratio, keeping the resulting mesitylene-solvated Pt atoms solution at the isolation temperature ($-40\,°C$) and room temperature ($25\,°C$). The growth process of platinum atoms has been quenched by addition of DVS, at different time, and the dimension of the Pt particles evaluated by ^{1}H NMR DOSY analysis. The DVS stabilized Pt/mesitylene solutions containing Pt particles of established dimensions have been conveniently used to support Pt clusters of tailored size on γ-alumina.

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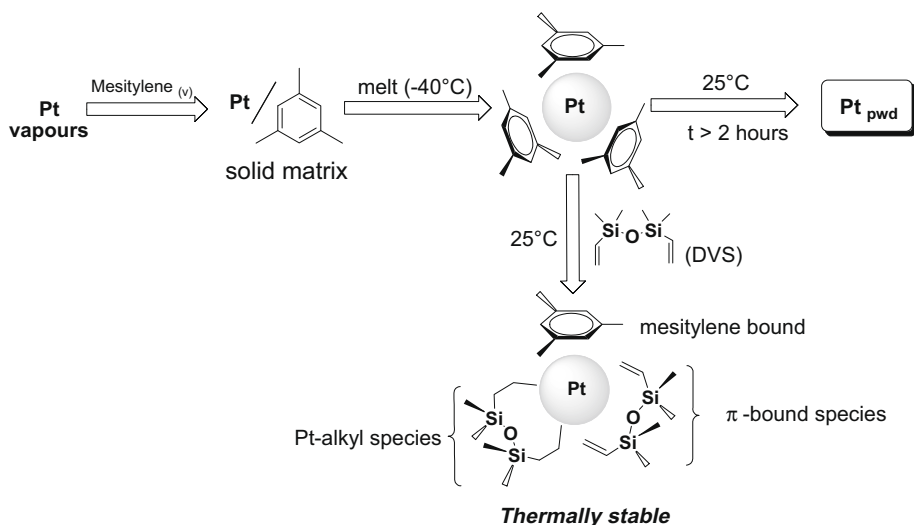
Scheme 1.

2. Results and discussion

As previously demonstrated [16], addition of DVS to the solution of mesitylene-solvated platinum atoms, gives stable aggregates (Scheme 1) which can be handled by conventional techniques and characterized by NMR analysis, after removal of the solvent and dissolution of the resulting brown solid in C_6D_6. By ^1H NMR analyses [16–18] the presence of Pt species bound to mesitylene, Pt-containing π-bound DVS and Pt-alkyls derived from insertion of DVS vinyl groups into Pt–H species [18] was confirmed [16,17] (Scheme 1) and NMR features did not undergo significant changes in the samples prepared at −40 and 25 °C.

Even though the nature of the species involved at the different stage of growth process of platinum nanoparticles did not change over the time, a variation of the metal particle sizes of the different samples occurred. The variation in the metal particle sizes was effectively detected by the NMR DOSY technique, which enabled measurement of the diffusion coefficients of the platinum aggregates. Above said parameters can be correlated with molecular sizes on the basis of Eq. (1), which strictly holds for medium to high spherical molecules [21,22],

$$D = \frac{kT}{6\pi\eta r} \tag{1}$$

where k is the Boltzmann constant, T the temperature, η the viscosity and r the hydrodynamic radius. Diffusion coefficients were measured in solutions containing 0.1% of TMS in order to take account of changes in the viscosity of the solutions and compared to the diffusion coefficients of pure mesitylene and DVS [22].

DOSY analysis of Pt samples pointed out sizes of different species present in solution. Average diffusion coefficients of 7.0×10^{-10} m^2/s were measured for π-bound or chelated DVS species. This value did not change in all the samples stabilized at different times and, on the basis of Eq. (1), corresponds to very small platinum particles with hydrodynamic diameter of 1.0 nm. For Pt-alkyl species the average value of the diffusion coefficient changed over time, indicative of a size-evolution of the platinum particles (Table 1, Fig. 1).

The quenching of metal aggregation at $T = -40$ °C and $t = 0$, which was caused by addition of DVS to a just isolated Pt/mesitylene solution, produced very small platinum particles with a distribution of diffusion coefficients ranging from 5.3×10^{-10} m^2 s^{-1} to 6.9×10^{-10} m^2 s^{-1}, corresponding to a very narrow distribution

Table 1
Time evolution of hydrodynamic diameter of Pt-alkyl aggregates at 25 °C calculated from diffusion coefficients (Eq. (1)) measured by NMR DOSY.

Time	Diffusion coefficient (m^2/s) ($\times 10^{10}$)	Hydrodynamic diameter (nm) (±0.1 nm)
0	3.9–5.3	1.3–1.8
30	3.6–5.0	1.4–1.9
60	3.5–4.6	1.5–2.0
90	3.2–4.2	1.7–2.2
120	2.5–4.2	1.7–2.8

of hydrodynamic diameters in the range 1.0–1.3 nm. DOSY data registered on Pt samples kept at −40 °C for longer times showed very similar values of diffusion coefficient indicating that a very slow aggregation process takes place under above conditions (Fig. 1).

In order to evaluate the role of the temperature on platinum aggregation process, the stabilization of a Pt/mesitylene solution by addition of DVS at different times was repeated at 25 °C. The ^1H NMR spectra of these samples were very similar to those obtained at −40 °C. In contrast, NMR DOSY analyses showed the hydrodynamic diameters to be significantly larger; in particular, the platinum particles formed from samples at longer times have smaller diffusion coefficients (Table 1), indicative of a growth of particle size over time.

A plot vs. time of the hydrodynamic diameter, which was obtained from the minimum diffusion coefficient of the Pt-aggregates for each sample (Fig. 1), showed that the Pt particles grow to a maximum hydrodynamic diameter of 2.8 nm in 2 h.

After 2 h partial precipitation began and diffusion coefficients could no longer be measured because of the presence of insoluble particles, which obviously could not be detected by solution NMR. HRTEM analyses on the insoluble platinum powder showed the presence of spongy aggregates with a diameter less than 1 μm formed by closely packed Pt particles of 3.8 nm in diameter [15]. This proves that after about 2 h the nucleation stage is completed, and a fast autocatalytic stage then follows, as is customarily assumed for such systems [10,19].

It is noteworthy to note that these solutions can be conveniently used to prepare supported catalysts containing platinum nanoparticles of tailored sizes. As example, supported platinum catalysts containing particles with a mean diameter of 1.7 nm with a very narrow size distribution (1.0–2.0 nm) (Fig. 2A) were ob-
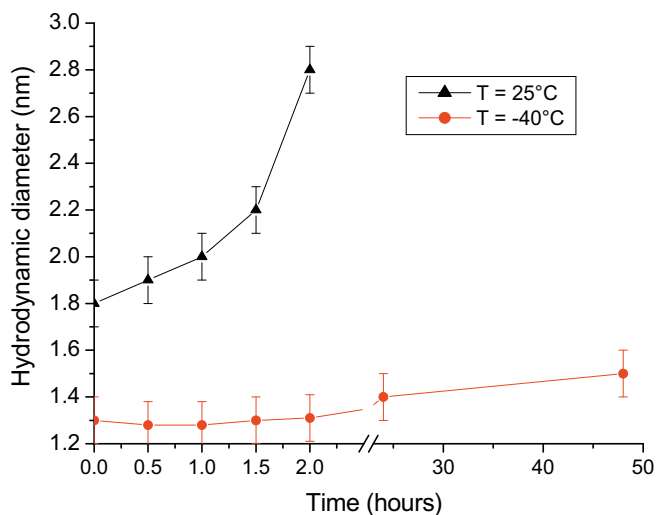
Fig. 1. Time evolution of the maximum hydrodynamic diameter of Pt-alkyl aggregates at −40 °C (●) and 25 °C (▲) calculated from diffusion coefficients (Eq. (1)) measured by NMR DOSY.

tained by deposition on γ-alumina of Pt particles deriving from the quenching of metal particles in solution by addition of DVS at $T = 25$ °C and $t = 0$. Differently, the analogous sample prepared

from the quenching of metal aggregation at $T = 25$ °C and $t = 2$ h provided platinum catalysts containing particles with a larger mean diameter (2.9 nm) and a less narrow size distribution (1.5–4.5 nm) (Fig. 2B).

3. Conclusions

Among various preparative routes, metal vapourization chemistry provides a valuable synthetic route to weakly stabilized nanostructured metal particles. Recently we discussed the catalytic performances of platinum nanoparticles prepared by metal vapour synthesis in the industrially relevant curing of silicones via hydrosilylation reaction: the catalytic activity is higher than that commercially available platinum catalysts [17,20]. Vapourization processes of platinum led to small-sized nanoparticles which underwent growth phenomena during the time, and, hence, in principle, constitute a very interesting starting material for the study of factors affecting the growth of platinum nanoparticles in solution and to prepare supported catalysts containing platinum nanoparticles of tailored size. We evidenced here, starting from above said solutions, that the temperature plays a crucial role in the clustering process, as, at 25 °C, particle sizes increase over a period of 2 h from a maximum hydrodynamic diameter of 1.8 nm ($t = 0$) to a maximum hydrodynamic diameter of 2.8 nm and, after that critical value, precipitation occurs.
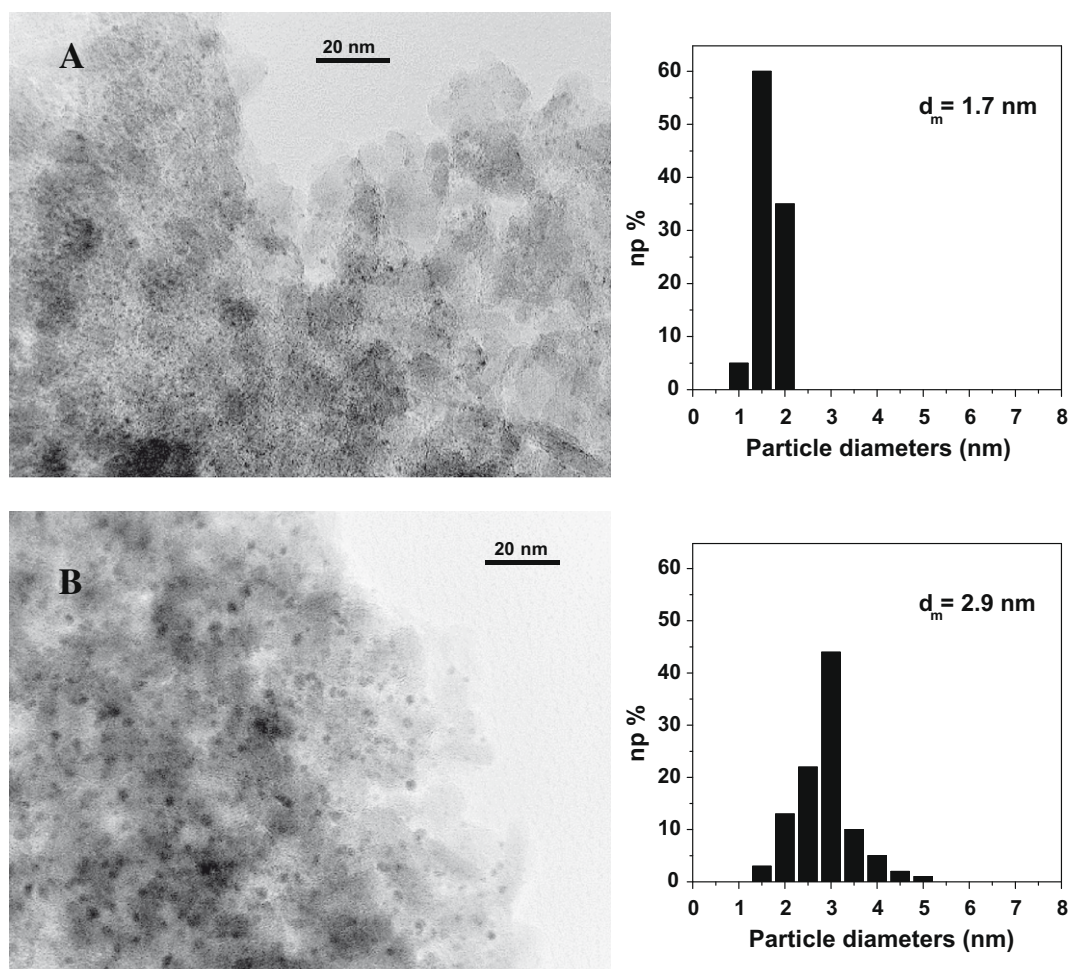

Fig. 2. HRTEM micrographs and particle size distributions of Pt/γ-alumina 5 w/w % prepared from Pt solutions obtained by addition of DVS at $T = 25$ °C and $t = 0$ (A) and by addition of DVS at $T = 25$ °C and $t = 2$ h (B), respectively.

The deposition of the platinum particles on γ-alumina, starting from the above mentioned solutions, allows to obtain supported systems containing metal particles of tailored size (1.7 nm in mean diameter starting from an hydrodynamic diameter in solution ranging 1.3–1.8 nm and 2.9 nm in mean diameter starting from hydrodynamic diameter in solution ranging 1.7–2.8 nm). At $-40\,^{\circ}\mathrm{C}$, the size of Pt particles in solution do not change significantly over the same time (maximum hydrodynamic diameter = 1.5 nm after 48 h). As a final remark, great usefulness of NMR spectroscopy for investigations involving nanostructured material must be stressed: both information regarding the molecular structure of nanoparticles and their sizes can be gathered together.

4. Experimental

4.1. General

All operations involving the metal vapour synthesis (MVS) products were performed under a dry argon atmosphere. The co-condensation of platinum and mesitylene was carried out in a static reactor. The mesitylene-solvated Pt atom solutions were worked up under argon with use of standard Schlenk techniques. The amount of platinum in these solutions was determined by atomic absorption spectrometry (AAS) in an electrochemically heated graphite furnace with a Perkin–Elmer 4100ZL instrument. Mesitylene was distilled (Na) and stored under argon. 1,3-Divinyltetramethyldisiloxane (DVS) was degassed and stored under argon before use. Commercial γ-Al$_2$O$_3$ (Chimet product, type 49, surface area 110 m^2 g^{-1}, mean particle diameter 31 mm) was dried in a static oven before use. Electron micrographs were obtained with a JEOL 2000EX microscope equipped with polar piece and top entry stage. Before introduction in the instrument, the samples were ultrasonically dispersed in isopropyl alcohol and a drop of the suspension was deposited on a copper grid covered with a lacey carbon film. The histograms of the metal particle size distribution for the Cu samples were obtained by counting at least 300 particles onto the micrographs. The mean particle diameter (d_{m}) was calculated by using the formula $d_{\mathrm{m}} = \sum d_i n_i / \sum n_i$, where n_i is the number of particles with diameter d_i.

4.2. NMR analyses

NMR measurements were performed on a Varian INOVA-600 spectrometer operating at 600 MHz and 150 MHz for ^{1}H and ^{13}C, respectively. The temperature was controlled to ±0.1 $^{\circ}$C. ^{1}H and ^{13}C NMR chemical shifts are referenced to TMS as internal standard. Nanoparticles solution were characterized [16,17] by 2D ROESY (Rotating-frame Overhauser Enhancement SpectroscopY), TOCSY (TOtal Correlation SpectroscopY), HSQC (Heteronuclear Single Quantum Correlation) and HMBC (Heteronuclear Multiple Bond Correlation) experiments. DOSY (Diffusion Ordered SpectroscopY) experiments were carried out by using a stimulated echo sequence with self-compensating gradient schemes, a spectral width of 8000 Hz and 64 K data points. Typically, a value ranging from 50 to 190 ms was used for Δ, 1.0 ms for δ, and g was varied in 30 steps (16 transients each) to obtain an approximately 90–95% decrease in the resonance intensity at the largest gradient amplitudes. The baselines of all arrayed spectra were corrected before the data were processed. After data acquisition, each FID was apodized with 1.0 Hz line broadening and Fourier transformed. The data were processed with the DOSY macro (VNMR software) (involving the determination of the resonance heights of all the signals above a pre-established threshold and the fitting of the decay curve for each resonance to a Gaussian function) to obtain pseudo two-dimensional spectra with NMR chemical shifts along one axis and calculated diffusion coefficients along the other.

4.3. Preparation of mesitylene-solvated Pt atoms

Pt vapour, generated by resistive heating of a tungsten wire surface coated with electrodeposited Pt (40 mg), was co-condensed with mesitylene (80 ml) in a glass reactor described elsewhere [14]. The reactor chamber was warmed at the melting point of the solid matrix ($\approx$40 $^{\circ}$C), and the resulting yellow-brown solution was siphoned and handled by Schlenk techniques. The content of the metal, evaluated by AAS, was 0.35 mg/ml of solution.

4.4. Stabilization of mesitylene-solvated Pt atoms solutions by 1,3-divinyltetramethyldisiloxane (DVS)

In a typical experiment, the Pt/mesitylene solution, obtained by co-vapourization, was kept at -40 and 25 $^{\circ}$C, respectively, by a thermostat bath. When the temperature reached the selected value, 5 ml portions of the solution (1.75 mg of Pt, 8.97×10^{-3} mmol) were taken at different times (0, 30′, 90′, 120′, 6 h, 24 h, 48 h for the sample at $-40\,^{\circ}$C and 0, 30′, 90′, 120′, 240′ for the sample kept at 25 $^{\circ}$C), and added to 2 ml of DVS (8.68 mmol) in a Schlenk tube. The resulting thermally stable solutions were stirred at 25 $^{\circ}$C for 15 min. The solvent was removed under vacuum by keeping the solution at 5×10^{-5} mbar for 30 min at 25 $^{\circ}$C.

4.5. Preparation of NMR samples

NMR samples were dissolved in C$_6$D$_6$ (0.7 ml) containing 0.1% of TMS and solutions transferred into a NMR tube under argon atmosphere. TMS was used as internal standard both for ^{1}H NMR analyses and for NMR-DOSY analyses [21,22].

4.6. Preparation of Pt/γ-Al$_2$O$_3$ systems

The Pt/DVS-mesitylene solution (28.6 ml, 10 mg Pt) was added to a suspension of γ-Al$_2$O$_3$ (200 mg) in mesitylene (5 ml). The mixture was stirred for 1 h at room temperature. The colourless mesitylene and DVS were removed and the light-brown solid, containing 5 wt.% Pt, was washed with n-pentane and dried under reduced pressure.

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