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Novel carbon supported material: highly dispersed platinum particles on carbon nanospheres

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Highly dispersed 3–6 nm platinum nanoparticles have been deposited by low temperature chemical vapor deposition of [$PtMe_2(\eta^4\text{-}C_8H_{12})$] in a fluidized bed reactor on carbon nanospheres of low surface area.

Platinum deposited on carbon supports continues to attract great interest due to its versatility in catalysis, either for gas phase, liquid phase, or electrochemical reactions, particularly for fuel cells. Besides conventional activated carbon supports, new forms of carbon such as fullerenes and nanotubes have recently become available. These materials have been used as supports in heterogeneous catalysis,[1] and for the preparation of supported platinum or palladium derivatives,[2–7] some of which can be used as catalysts.[5–7] One way to graft palladium or platinum on fullerenes is through the use of organometallic complexes.[2,3] On carbon nanofibers of surface areas of *ca.* 40–50 m^2 g^{-1}, palladium nanoparticles of mean size 5 nm have been prepared.[5] On nanotube supports it is also possible to fill the internal volume to produce metallic nanorods.[4] Deposition of platinum and platinum oxide nanoparticles on low surface area polypyrrole/polystyrenesulfonate particles has also been reported.[8] It is worth mentioning that, in liquid phase catalysis, the absence of microporosity on such supports allows an efficient mass transfer.[5] We have recently developed a catalytic chemical vapor deposition (CVD) method to prepare new carbon nanospheres;[9] they present a significantly well organized structure that can induce electronic support effects in catalysis, and a very low porosity. We have investigated their behavior towards vapors of a platinum complex in order to see if, on a low surface area support, either a continuous film or metallic particles would be produced. We report here that, unexpectedly, a high metal dispersion can be easily obtained for this first noble metal deposit on carbon nanosized-spheres.

Carbon nanospheres have been produced from CH_4/H_2 mixtures by an iron catalytic process which is derived from that used to prepare vapor-grown carbon fibers.[9] The as-produced material was washed with acetone in a Soxhlet apparatus in order to remove heavy hydrocarbon contamination. Such a treatment induces the formation of a few surface carbonyl groups, as shown by temperature programmed desorption (TPD) measurements (Table 1). The carbon nanospheres, with diameters in the range 100–300 nm have a BET surface area of 16.4 m^2 g^{-1}. X-Ray powder diffractometry indicates a d_{002} average interplanar distance between the carbon layers of 0.352 nm, indicative of a relatively well organized structure (NanoC 1) which is comparible to those of pyrolytic carbons. In order to increase the concentration of grafting sites on the surface, further nitric acid oxidative treatment was carried out for 3 h at reflux with 5 M HNO_3. After several washing runs with distilled water until the pH value of the rinsing water reached a value of 5 (NanoC 2), TPD measurements show a significant increase in the concentration of surface oxygenated groups (Table 1), and particularly of carboxylic acid groups. This oxidative treatment has reduced the surface area (9.3 m^2 g^{-1}) and increased the microporous volume (Table 1). However, no alteration of the structure was noted by XRD ($d_{002} = 0.354$ nm).

The deposition experiments were performed in a hot wall fluidized bed CVD reactor previously described,[10] using [$PtMe_2(\eta^4\text{-}C_8H_{12})$] as precursor,[11] which presents a convenient vapor pressure.[12] The precursor was sublimed at 343 K and decomposed at 383 K in the presence of small amounts of hydrogen added to the helium carrier gas, at 1316 Pa. With 2 g of nanospheres, the runs were performed for 30 min. When the support is not previously treated with HNO_3 (NanoC 1), transmission electron microscopy (TEM) micrographs, recorded after deposition experiments at 383 K, do not show the presence of any deposited platinum particles. However, deposition on the glass walls of the reactor shows that the complex is decomposed. Such a phenomenon has already been observed by Kaesz and coworkers during the deposition of platinum by CVD on highly oriented pyrolytic graphite from [$PtMe_3(\eta^5\text{-}C_5H_4Me)$], and was proposed as resulting from the low amounts of anchoring sites on the support.[13] The present results support this assumption.

When using NanoC 2 for deposition experiments, the platinum deposit is homogeneous on all the spheres and the

Table 1 Textural and surface characterization of the carbon nanospheres

NanoC *x*	S_{BET}/ m^2 g^{-1}	W_0/ 10^{-3} cm^3 g^{-1}	S_t/ m^2 g^{-1}	CO/ µmol g^{-1}	CO_2/ µmol g^{-1}	CO/ CO_2
NanoC 1	16.41	0.20	16.09	1187	136	8.72
NanoC 2	9.26	0.96	6.88	2817	2541	1.11

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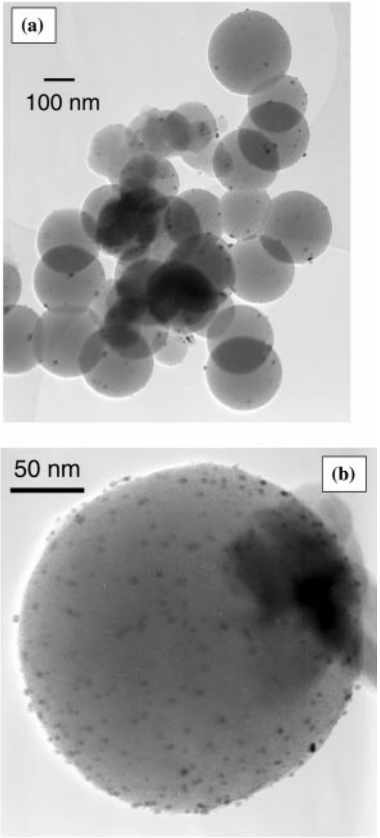

Fig. 1 TEM micrographs of the Pt/nanospheres: (a) an overview, (b) a single Pt/nanosphere.

particle size distribution is centered at *ca.* 5 nm. Fig. 1 shows two TEM† micrographs, the first being a general view of several Pt/nanospheres and the second one a single Pt/nanosphere. Moreover, high resolution TEM observations reveal the presence of external platinum particles, attached to the graphitic support, which are roughly spherical as shown on Fig. 2. Careful examination of the grafting shows a partial encapsulation resulting from the growth of the particle from a platinum germ located between graphene layers of the support, with simultaneous deformation of the external surface, and eventually exfoliation of part of the support. The intercalation of platinum nanosheets between graphite layers was recently described using more drastic conditions, starting from gaseous $PtCl_4$ under chlorine pressure, followed by hydrogen reduction.[14] It is worth noting that no structural modification of the Pt/nanospheres sample in the electron beam was noticed during TEM measurements.

Thus, the presence of carboxylic acid groups on the carbon nanospheres, a graphitic support of low surface area, allows the simple grafting of small sized platinum particles. This new material may be of interest for catalytic and electrochemical applications.

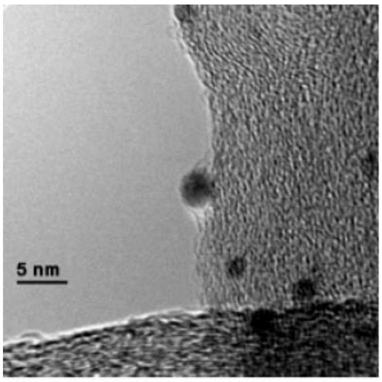

Fig. 2 High resolution TEM micrograph of a platinum nanoparticle partially encapsulated by the carbon nanosphere support.

Acknowledgements

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Notes and references

†TEM measurements were performed on a Philips CM12 instrument (120 keV) using carbon coated copper grids. HRTEM measurements were performed on a Philips CM30ST instrument (300 keV) equipped with a CCD "Slow Scan" Gatan 794 camera, using carbon coated copper grids.

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