

An Approach to Nanoscale Metals in Carbon Microflakes from Hexa-2,4-diyne-1,6-diol

Philippe Gerbier,* Christian Guérin,* and Bernard Henner

U.M.R. 5637 Chimie Moléculaire et Organisation du Solide, Université Montpellier II, Sciences et Techniques du Languedoc, Place Eugène Bataillon, Case 007, 34095 MONPELLIER Cedex 5-France

Received December 8, 1997

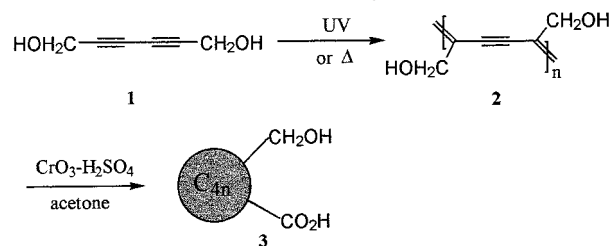
Revised Manuscript Received June 23, 1998

Currently, the synthesis of novel carbon modifications and their precursors is an area of interest.^{1–3} The low-temperature thermolysis of diacetylenic oligomers and polymers such as poly(arylenediacetylenes) is an alternative approach to new carbon-based surfaces and to modified carbon materials.^{4–7} Furthermore, related molecules are efficient precursors to new carbon allotropes.⁸

The easily available hexa-2,4-diyne-1,6-diol **1** itself could be a promising candidate. The triple bonds can function as efficient polymerizing sites (Scheme 1).^{9–11} Besides the carbon–carbon double and triple bonds, the polar hydroxymethyl side groups regularly attached to the related polymer **2** could be utilized to anchor transition metals in microdomains by adsorption or chemical interactions;¹² their transformation into an appropriate functionality such as a carboxylic acid or carboxylate salt would extend the range of metal sources. Finally, the prebinding of the metal to specific sites on the polymer backbone would prevent or slow the migration and agglomeration of the metal particles during a reductive thermal treatment; it would result in solids in which well-dispersed metal nanoclusters can be made in a controlled manner.^{13,14} Such materials are expected to have electrical, magnetic, or catalytic applications.^{15,16}

Because of its thermal instability above 140 °C,^{9,10} powdered hexa-2,4-diyne-1,6-diol (**1**) was first poly-

Scheme 1. Polymerization of **1** and Partial Oxidation of Polymer **2**



erized by exposure to UV light (Scheme 1).¹⁷ The resulting solid was washed with methanol to remove unreacted **1** and dried under vacuum to give a deep-red powder (25% yield).

IR and NMR spectroscopies and elemental analysis^{10,17} suggest a more complex framework than the one-dimensional enyne polymer **2** depicted in Scheme 1. The oxygen content is consistent with a substantial amount of cross-linked material involving ether-type bridges resulting from air-oxidation of transient radical species. Furthermore, a broad peak in the ¹³C CP-MAS spectrum at 143 ppm is indicative of the presence of aromatic subunits which may originate from either [2 + 2 + 2] or [4 + 2] cycloadditions.

Thermolysis¹⁸ of **2** in an argon flow at 600 °C resulted in a black powder in a 50% char yield, indicative of the conservation of 4.5 C per monomer unit (75% carbon yield). Mass spectrometry analysis reveals H₂O, CH₂O, and CO₂ as the main off-gases up to 500 °C; at higher temperatures, hydrogen, methane, and ethylene were essentially detected. Although X-ray diffraction (XRD) pattern of a sample prepared at 800 °C was indicative of an amorphous carbon matrix, the Raman scattering using the microprobe technique revealed the presence of disordered carbon (1336 cm⁻¹) and ordered graphitic structures (1593 cm⁻¹) in a 70:30 ratio. Scanning electron microscopy (SEM) images (Figure 1b) revealed a flaky structure similar to that obtained for **2** (Figure 1a).

The nitrogen adsorption–desorption isotherms (Figure 2) are typical of microporous substances.¹⁹ The micropore volume is estimated to be 0.16 cm³/g and the BET specific surface area is calculated at 450 m²/g. The hysteresis observed for low N₂ relative pressures (*P*/*P*₀ < 0.3) is often encountered with highly microporous carbon-based materials.²⁰

(17) Polymer **2**: Crystals from toluene of **1** (5 g, 45.5 mmol) are suspended in heptane (300 mL) and irradiated for 2 h (UV, Hg low-pressure lamp, 400 W) in a quartz reactor under Ar. IR (Nujol, cm⁻¹): ν 3550, 3475, 3410 (s, OH), 1638, 1616 (s, C=C) 1150–1020 (br, C–O–C, C–O–H). ¹³C CP/MAS NMR (resonance frequency = 50.30 MHz, spinning rate = 4.015 kHz, ppm): δ 64, 51 (CH₂), 102 (C≡C), 133, 143 (C=C). Anal. Calcd for C₆H₆O₂: C, 66.45; H, 5.49; O, 29.06. Found: C, 61.19; H, 4.90; O, 33.63.

(18) Pyrolysis experiments were carried out in a gas flow (Ar or N₂, 60 mL/min) on weighted samples (0.1–0.5 g) in glass vessel up to 500 °C or in alumina boats for higher temperatures. The samples were heated at 10 °C/min to the final temperature and held for 0.5 h before cooling.

(19) N₂ adsorption–desorption isotherms were measured on a Micromeritics Gemini apparatus.

(20) Gregg, S. J.; Sing, K. S. W. *Adsorption, Surface Area and Porosity*; Academic Press: London, New York, 1982.

- (1) Chang, P. H.; Labes, M. M. *Chem. Mater.* **1989**, *1*, 523.
- (2) Suh, M. C.; Shim, S. C. *Macromolecules* **1995**, *28*, 8707.
- (3) Suh, M. C.; Shim, S. C. *Chem. Mater.* **1997**, *9*, 192.
- (4) Yasuda, H.; Hiwara, A.; Nakamura, A.; Sakai, H. *J. Inorg. Organomet. Polym.* **1991**, *1*, 239.
- (5) Pocard, N. L.; Alsmeyer, D. C.; McCreery, R. L.; Neenan, T. X.; Callstrom, M. R. *J. Mater. Chem.* **1992**, *2*, 771 and references therein.
- (6) Hutton, H. D.; Pocard, N. L.; Alsmeyer, D. C.; Schueller, O. J. A.; Spontak, R. J.; Huston, M. E.; Huang, W.; McCreery, R. L.; Neenan, T. X.; Callstrom, M. R. *Chem. Mater.* **1993**, *5*, 1727.
- (7) Schueller, O. J. A.; Brittain, S. T.; Whitesides, G. M. *Adv. Mater.* **1997**, *9*, 477.
- (8) Boese, R.; Matzger, A. J.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1997**, *119*, 2052.
- (9) Park, S. W.; Kim, J. S. *Bull. Korean Chem. Soc.* **1996**, *17*, 1077.
- (10) Baughman, R. H. *J. Appl. Phys.* **1972**, *43*, 4362.
- (11) Bloor, D.; Stevens, G. C. *J. Polym. Sci.: Polym. Phys. Ed.* **1977**, *15*, 703.
- (12) Bachand, B.; Wuest, D. *Organometallics* **1991**, *10*, 2015.
- (13) Nandi, M.; Conklin, J. A.; Salvati, L., Jr.; Sen, A. *Chem. Mater.* **1990**, *2*, 772.
- (14) Sohn, B. H.; Cohen, R. E. *Chem. Mater.* **1997**, *9*, 264.
- (15) Henglein, A. *Chem. Rev.* **1989**, *89*, 1861.
- (16) Schmid, G. *Chem. Rev.* **1992**, *92*, 1709.

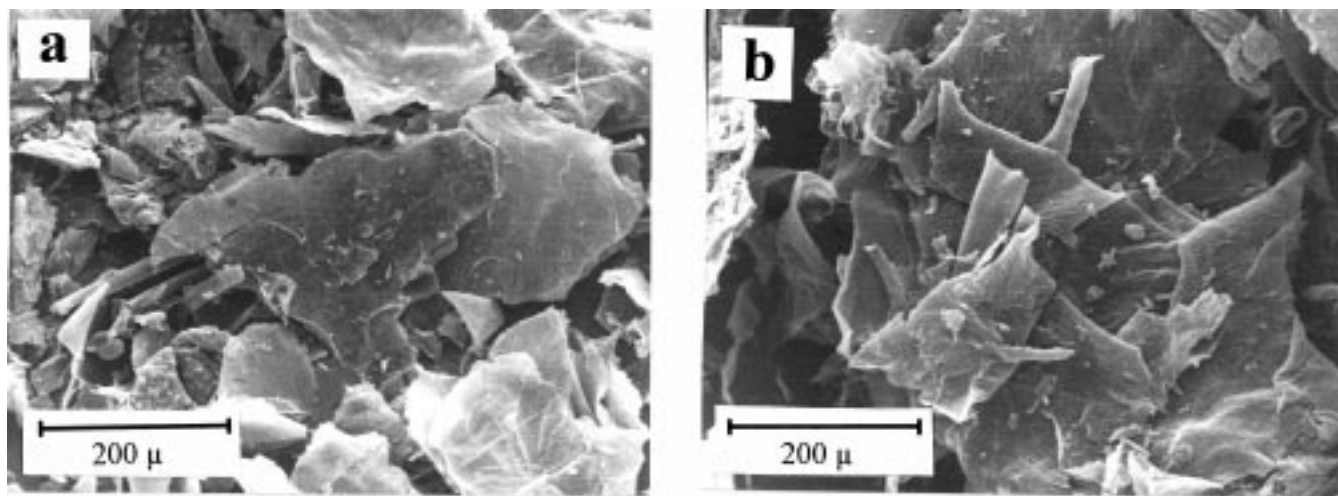


Figure 1. SEM images of (a) polymer **2** and (b) polymer **2** fired at 800 °C under Ar.

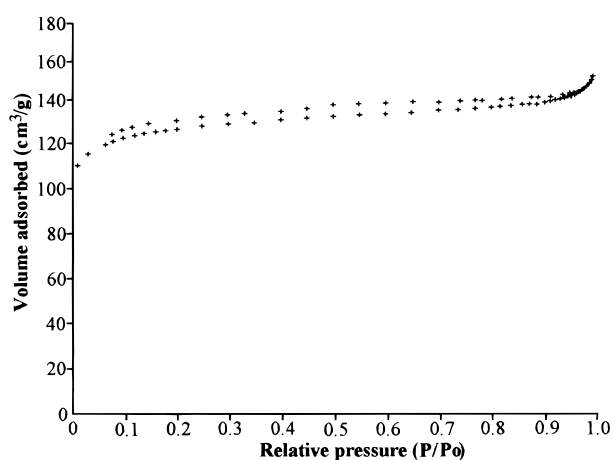


Figure 2. N₂ adsorption–desorption isotherm plot of carbon microflakes obtained by pyrolysis of **2** at 800 °C under Ar.

In an attempt to oxidize partially the hydroxy groups (1 group out of 2 in the following example) and to elaborate a polyfunctional structure (Scheme 1), a solution of chromic acid (CrO₃, 0.133 g, 1.33 mmol in 3 mL of 12 N H₂SO₄) was added to a suspension of **2** (0.220 g, 2.00 mmol) in 30 mL of acetone. The mixture was stirred at 30 °C for 30 min, giving a color change to deep green. The crude product was filtered off, washed successively with aqueous HCl (3 M) and H₂O, and dried to yield a brown powder (0.24 g, 89% yield) formulated as **3** (Scheme 1) on the basis of the titration of the carboxylic acid groups (5.9×10^{21} sites/g), IR, and thermogravimetric analysis.²¹ Heat treatment at 750 °C affords carbon flakes in a reasonable yield (42%). The specific surface area of the solid reached 600 m²/g and the micropore volume was estimated to 0.25 cm³/g.

Taking into account the facile manner in which highly electrophilic Pd(II) complexes undergo reduction in methanol,²² **2** (0.20 g, 1.8 mmol) was reacted with [Pd(CH₃CN)₄](BF₄)₂²³ (0.05 g, 0.1 mmol) in acetonitrile to yield a brown powder. The Pd(II) salt was converted into palladium metal in the presence of the polymer, as

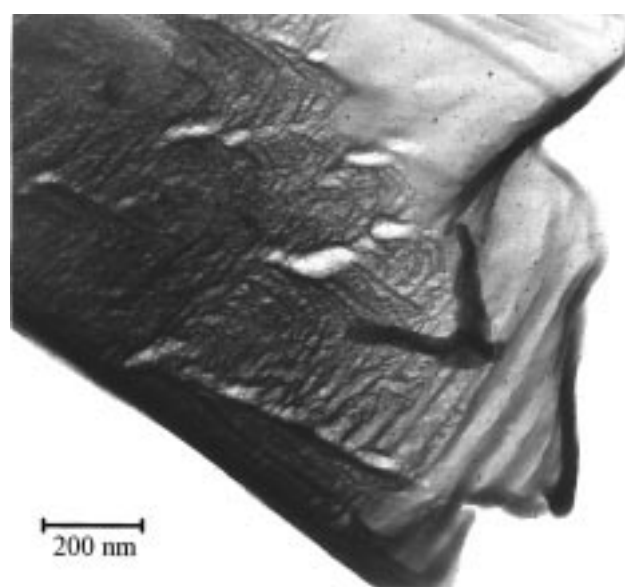


Figure 3. TEM image of a Pd/C sample obtained by pyrolysis of a **2**/[Pd(CH₃CN)₄]²⁺ precursor.

shown by X-ray photoelectron spectroscopy (XPS) analysis.²⁴ Thermolysis at 500 °C (1 h) in a N₂ flow produced palladium-doped carbon (4.5 wt % Pd). Transmission electron microscopy (TEM) analysis (Figure 3) reveals the presence of palladium nanoparticles homogeneously dispersed throughout the carbon flakes as clusters possessing a narrow size distribution of ca. 1–5 nm. The BET surface area is 508 m²/g, whereas the number of accessible metallic atoms was estimated at 6% from H₂ chemisorption measurement.²⁵

Either the polar hydroxy groups or the carbon–carbon double and triple bonds would allow the immobilization of transition metal halides or complexes. Typically, **2** (0.500 g, 4.54 mmol) was impregnated with a THF solution of hexachloroplatinic acid (0.060 g). After evaporation of the solvent, the solid residue was fired at 500 °C in a N₂ flow. The off-gases (H₂, CH₄, C₂H₄)

(21) IR (Fluorolub, cm⁻¹): ν 3350 (br, OH), 1620 (br, C=O, C=C). TGA (Ar flow, T_{max} = 800 °C; heating rate, 10 °C/min): weight loss = 58%, expected value for **3** → **4** C: 57%.

(22) Crocker, M.; Buglass, J. G.; Herold, R. H. M. *Chem. Mater.* **1993**, *5*, 105.

(23) Schramm, R. F.; Wayland, B. B. *Chem. Commun.* **1968**, 898.

(24) The XPS analysis was conducted on a VGS ESCALAB MKII spectrometer using a Mg K α X-ray source. The position of the Pd (3d_{5/2}) peak is 336.1 eV, which is in agreement with the value reported for palladium(0) in the literature (ref 22).

(25) H₂ chemisorption analyses were performed on a Micromeritics Pulse Chemisorb 2700 apparatus at 298 K.

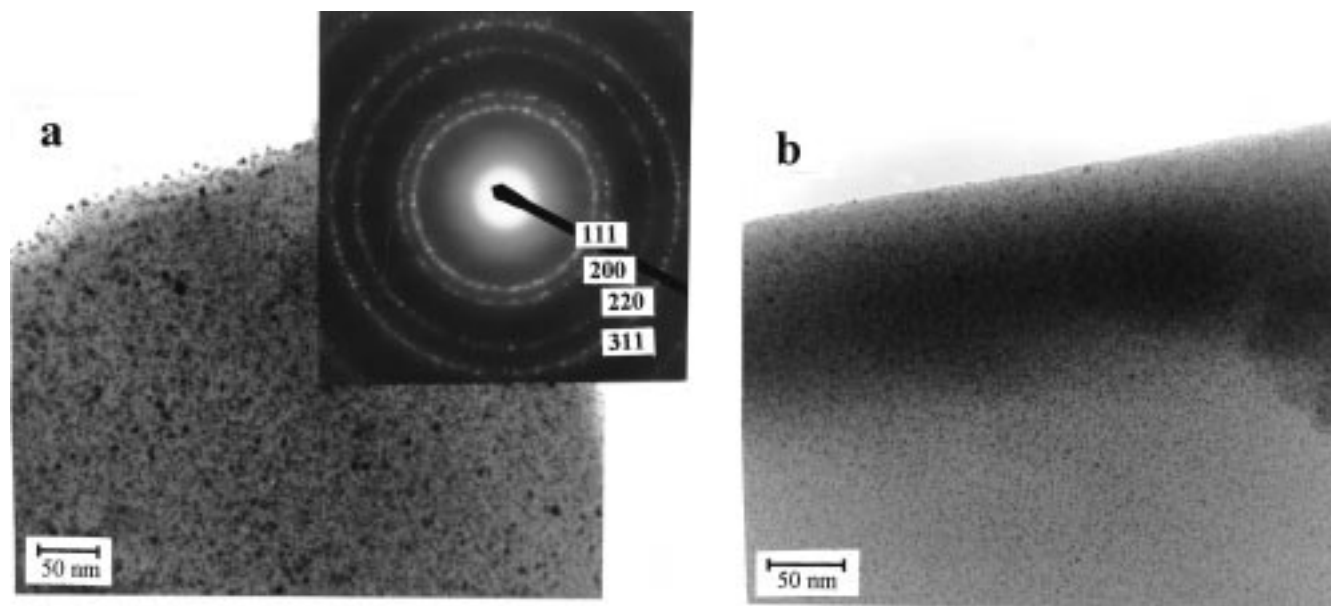


Figure 4. TEM micrographs of Pt/C samples obtained by pyrolysis of a $2/H_2PtCl_6$ precursor (a) under N_2 and (b) under H_2 flow.

formed in the latest steps of the thermal degradation of **2** (vide supra) enabled the reduction of the encapsulated Pt(IV) species to Pt(0) phase, as identified by indexation of their electron diffraction pattern (Figure 4a). The TG analysis of the residue indicated a Pt content of 11 wt % (calcd value 10%). The BET surface area reached $580\text{ m}^2/\text{g}$, whereas the number of accessible metallic atoms was estimated to 12%. As observed by TEM (Figure 4a), nanoclusters are uniformly distributed throughout the carbon matrix, which shows a sharp particle size distribution spread in a narrow range around 5 nm. Subsequent heating of the sample at $500\text{ }^\circ\text{C}$ (1 h) under H_2 (20 mL/min) led to a significant increase of platinum accessible to the gas phase, ca. 20%. Finally, the reduction of a $2/Pt(IV)$ sample in H_2 flow clearly favors the formation of smaller platinum particles ($\leq 1\text{ nm}$, Figure 4b) and results in a substantial increase of accessible platinum atoms, ca. 42% versus 12% (vide supra). In comparison, a commercial sample (5% Pt)²⁶ treated under identical conditions showed a smaller number of active metal sites exposed, ca. 30%.

As transition metal carbides are known to exhibit interesting catalytic properties,^{27,28} we extended this approach to the synthesis of tungsten carbide/C materials. Mixing **2** (0.500 g, 4.54 mmol) with WCl_6 (0.7 g, 1.77 mmol) in toluene generated a deep brown solid of

composition $C_{6.0}H_{5.5}O_{1.9}W_{0.2}Cl_{0.5}$, which was further pyrolyzed at $1330\text{ }^\circ\text{C}$ under argon. Elemental analysis of the residue gives 37.21% W and 56.66% C in weight percent, i.e., a 1/23 W/C stoichiometry. The XRD pattern indicates WC and W_2C as the only crystalline phases in a ratio 70:30.

In summary, our observations suggest that the hexa-2,4-diyne-1,6-diol (**1**) is a promising candidate on the route to transition metal-containing carbon phases. Its photolysis affords a highly functionalized polymeric framework. Besides the alkene and alkyne functionalities, the hydroxy groups appear as binding or reactive sites toward transition metal complexes, enabling the metal deposition to be controlled. Their conversion into carboxy substituents is easily achieved and other functionalities can be envisaged in order to widen the variety of metal sources which could be introduced. At last, the carbonization takes place at relatively low temperature ($<600\text{ }^\circ\text{C}$) and leads to carbon matrixes containing homogeneously dispersed nanoscale metallic particles with narrow size distribution. One can expect heterometallic systems of defined compositions to be prepared in a similar way. Further studies are currently under progress.

Acknowledgment. The authors thank Pr. R. Corriu for fruitful discussions and Dr. Sylvain Dutremez for CP-MAS NMR characterization.

(26) Platinum on activated carbon, not reduced (5% Pt), was purchased from Acros.

(27) Keller, V.; Wehrer, P.; Garin, F.; Ducros, R.; Maire, G. *J. Catal.* **1997**, *166*, 125.

(28) Nashner, M. S.; Frenkel, A. I.; Adler, D. L.; Shapley, J. R.; Nuzzo, R. G. *J. Am. Chem. Soc.* **1997**, *119*, 7760.

CM970790K