Rapid Synthesis of Pt or Pd/Carbon Nanocomposites Using Microwave Irradiation

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Pt or Pd/Vulcan carbon nanocomposites containing metal nanoclusters highly dispersed on the carbon support are formed from precursor/Vulcan carbon composite materials in <1 min of total microwave irradiation. Metal halide salts or organometallic complexes can serve as metal precursors. A palladium−allyl complex affords nanoclusters of interstitial Pd−carbide compositions. Metal nanoclusters are formed with small average sizes and rather narrow particle size distributions, even at metal loadings as high as 20 wt %. The high surface area and electrical conductivity of Vulcan carbon powder is probably responsible for its rapid rate of heating by microwave irradiation. A quick and convenient method for preparing metal/carbon nanocomposites using readily available metal compounds is reported.

Introduction

Metal/carbon nanocomposites consisting of metal nanocrystals supported on a carbon powder of high surface area are commonly employed heterogeneous catalysts in both small- and large-scale chemical processes, particularly those involving hydrogenation/dehydrogenation reactions.[1,2] Commercial carbon-supported metal nanocomposites containing Pt or Pd are commonly prepared using various impregnation/reduction or chemical vapor deposition methods. A typical procedure involves impregnation of powdered carbon by solutions of Pt or Pd salts followed by drying and subsequent chemical reduction of the metal ions to the metal.[1,2] Mixtures of hydrogen and nitrogen gases, such as 10% hydrogen/90% nitrogen (known as “getter gas”) are commonly used as reducing agents. Metal/carbon nanocomposites have also been prepared by surface adsorption of preformed metal colloids, metal vapor deposition, and electrochemical deposition.[3]

We have recently communicated exceptionally rapid formation of metal/carbon nanocomposites using microwave irradiation when the carbon support is Vulcan carbon powder (XC-72R, Cabot Corp.).[4] Carbon blacks have been used as additives for the microwave processing of a variety of materials[5,6] including the preparation of metal oxide/carbon catalysts by calcination of precursor/carbon composites.[7] The rate of microwave heating of powdered carbon varies with carbon particle size and maximizes at ≈300 μm.[8] To our knowledge, however, the exceptionally rapid heating of Vulcan carbon powder XC-72R under microwave irradiation has neither been reported nor applied to the preparation of metal/carbon nanocomposites. This interesting property of Vulcan carbon XC-72R is probably related to its fine particle size (average particle diameter of 30 nm) and high electrical conductivity (≈100 S/cm). Polymer-stabilized Pt or Pd colloids have been prepared recently by microwave dielectric-loss heating of ethylene glycol/water solutions containing dissolved metal salts.[9,10]

We now report rapid syntheses of Pt or Pd/Vulcan carbon nanocomposite powders using molecular precursors as a source of the metals and microwave dielectric-loss heating as a thermal treatment. Metal precursors include the metal halide salts, K_2PtCl_4 and Na_2PdCl_4, and the organometallic complexes, $[(\eta\text{-}C_2H_4)PtCl_2]_2$ and $[(\eta\text{-allyl})PdCl]_2$. Precursor/carbon composite powders are converted to metal/carbon nanocomposites by microwave heating under sequential oxidizing and reducing atmospheres. Microwave irradiation periods of only 50 or 100 s are employed, and metal loading is arbitrarily varied from 2 to 20 wt %. While formation of metal nanocrystals is most commonly observed, the palladium−allyl precursor affords nanoclusters of interstitial Pd−carbide compositions, PdC_x. The rapid formation of metal/carbon nanocomposites using simple metal compounds as precursors, a highly conductive carbon powder support, and microwave irradiation for thermal treatment is demonstrated.

Experimental Section

General Methods. The precursor compounds, K_2PtCl_4, Na_2PdCl_4, $[(\eta\text{-}C_2H_4)PtCl_2]_2$, and $[(\eta\text{-allyl})PdCl]_2$ were purchased from Strem Chemicals, Inc., and were used as obtained. Vulcan carbon powder XC-72R was purchased from Cabot.

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Samples for transmission electron microscopy (TEM) imaging were prepared by placing a drop of a nanocomposite/CH_2Cl_2 suspension onto a holey carbon-coated, copper grid followed by evaporation of the solvent. Particle-size distributions for the nanocomposite materials were obtained by manually measuring particle diameters from bright-field micrographs recorded on a Philips CM20T TEM operating at 200 kV.

XRD scans were obtained using a Scintag X_1 θ/θ automated powder diffractometer with a Cu target, a Peltier-cooled solid-state detector, and a zero-background, Si(510) sample support. For particle size determinations, each XRD scan was corrected for background scattering and was stripped of the $K\alpha_2$ portion of the diffracted intensity using the DMSNT software (version 1.30c) provided by Scintag. Observed peaks were fitted with a profile function to extract the full-width-at-half-maximum (fwhm) values. The average crystallite size, L, was calculated from Scherrer's equation, $L = K\lambda/\beta \cos \theta_B$, assuming that peak broadening arises from size effects only (where β is the peak fwhm measured in radians on the 2θ scale, λ is the wavelength of X-rays used, θ_B is the Bragg angle for the measured *hkl* peak, and K is a constant equal to 0.90 for L taken as the volume-averaged crystallite dimension perpendicular to the *hkl* diffraction plane).[11]

X-ray photoelectron spectroscopic (XPS) analyses were performed at the University of Minnesota on a PHI 5400 XPS instrument using Mg Kα X-rays. Samples were mounted on copper high-vacuum tape (3M Corp.). XPS data were acquired from a 3×10 mm sample area. Samples were introduced into the main chamber at pressures $<1 \times 10^{-8}$ Torr. Base pressure in the chamber was 1.2×10^{-10} Torr. Operating pressure was 1×10^{-9} Torr.

General Preparation of the Metal/Vulcan Carbon Nanocomposites. Each precursor complex was deposited onto Vulcan carbon XC-72R by absorption/precipitation from acetone or aqueous solutions. Excess solvent was removed by rotoevaporation. Precursor loading was arbitrarily chosen to give final nanocomposites having metal contents of 2−20 wt %. Thermal treatment was accomplished by dielectric-loss heating of the Vulcan carbon powder support using a commercial microwave oven (Sharp Corp., model R-2M52B) operating at 2.45 GHz at a fixed power level of 600 W. A reaction assembly was constructed for these thermal treatments. Portions (≈70 mg) of the precursor/Vulcan carbon composite were placed into a one-half dram vial, filling the vial to a depth of ≈1 cm. This assembly was then embedded within a 1-cm deep layer of Vulcan carbon contained within a two-dram glass vial. The outer volume of carbon powder had a mass of ≈150 mg and served as a thermal bath for more uniform microwave heating. The reaction assembly was placed into a 100-mL glass beaker for mechanical stability during thermal treatment.

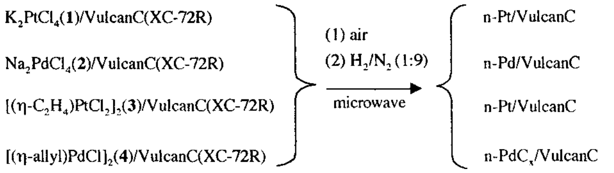
Control studies using untreated Vulcan carbon indicated that the temperature of the carbon powder in the reaction assembly (as measured by thermocouple immersion) increased rapidly upon microwave irradiation. Imprudently prolonged microwave irradiation readily led to softening of the glass vials, and caution is therefore recommended. A beaker of cold water is also placed with the microwave oven to protect the oven from irradiation damage. Two microwave heating protocols were used for nanocomposite syntheses: 30-s irradiation on, 45-s irradiation off, and 20-s irradiation on (heating protocol A), giving a final reaction temperature of ≈545 °C; 15-s irradiation on, 45-s irradiation off, and 10-s irradiation on (heating protocol B), giving a final reaction temperature of ≈390 °C. This observed rate of heating of Vulcan carbon powder is more than 2 times greater than that reported for other carbon powders when adjusted for comparable microwave power.[8]

Thermal treatment of precursor/Vulcan carbon composites by microwave irradiation was conducted initially under air to permit oxidative degradation of the precursor followed by microwave irradiation under getter gas (10% H_2:90% N_2) to ensure reduction of any oxidized metal. Between repetitive oxidative thermal treatments, the air atmosphere above the inner sample was replenished by mild flushing with a stream of air. The reaction assembly was then evacuated to ≈0.01 mmHg and was back-filled with nitrogen gas between oxidative and reductive thermal treatments to preclude formation of potentially explosive air/hydrogen mixtures. Getter gas was supplied using a partially filled helium-grade balloon at a pressure slightly above 1 atm. The filled balloon was taped to the mouth of the two-dram outer vial. Repetition of the above synthesis procedure afforded substantial masses of metal/carbon nanocomposite. Control studies indicated that heating Vulcan carbon in air for a microwave irradiation time of 2 min gave a mass loss of only 6.1 wt %. Therefore, the microwave heating periods of 10−30 s used in the preparation of the reported nanocomposites result in only minimal mass loss due to oxidation of the carbon powder support.

Nanocomposites prepared from the metal halide salt precursors contained residues of NaCl or KCl, as determined by powder XRD and energy-dispersive spectroscopy (EDS). These alkali metal salts were removed by washing the nanocomposites with several portions of deionized water.

Results and Discussion

The nanocomposite syntheses reported in this study are shown in eq 1. Precursors **1−4** are absorbed or precipitated onto Vulcan carbon powder (Cabot; XC-72R), giving the corresponding precursor/carbon composite materials. Precursor loading is arbitrarily varied to give final metal/carbon nanocomposites with metal loading ranging from 2 to 20 wt %. Highly dispersed nanocomposites are obtained using a single deposition of precursor on the carbon support at all metal loadings examined.



(1)

Conversion of the precursor/carbon composites to metal/carbon nanocomposites is affected using two heating protocols (see Experimental Section) to determine any dependence of nanocomposite properties on the duration of microwave heating. With heating protocol A, a precursor/carbon composite is subjected to microwave irradiation for a total of 50 s each under an atmosphere of air and of getter gas (90:10 N_2:H_2) for a total of 100 s of microwave heating. The attained reaction temperature is ≈545 °C. Heating protocol B follows an identical procedure with irradiation periods of only 25 s, giving a reaction temperature of ≈390 °C for a total of 50 s of total microwave heating. The identity of precursor decomposition products formed during these thermal treatments was not investigated.

Experimental results obtained from this study are summarized in Table 1. The two metal salt precursors **1** and **2** form Pt or Pd/carbon nanocomposites, respectively. The organometallic Pt precursor **3** likewise affords Pt/carbon nanocomposites; however, the organometallic Pd precursor **4** forms interstitial Pd−carbide/carbon nanocomposites. Thermal treatment conditions that might inhibit the formation of such Pd−carbide phases were not determined.

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(11) Klug, H. P.; Alexander, L. E. *X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials*, 2nd ed.; Wiley: New York, 1974.

Table 1. Experimental Results Obtained for M or MC$_x$/Vulcan Carbon Nanocomposites Prepared from Precursor/Carbon Composites by Microwave Dielectric-Loss Heating

precursor	nanophase formed	metal loading (wt %)	lattice constant in Å (esd)	ave. diameter by XRD in nm (esd)	ave. diameter by TEM in nm (esd)
		Microwave Protocol A^a			
K_2PtCl_4 (**1**)	n-Pt	20	3.932(6)	44 (13)	large range
	n-Pt	10	3.921(5)	29 (5)	9 (6)
	n-Pt	2	3.932(7)	30 (10)	8 (2)
Na_2PdCl_4 (**2**)	n-Pd	10	3.888(4)	50 (20)	71 (31)
$[Pt(C_2H_4)Cl_2]_2$ (**3**)	n-Pt	20	3.930(8)	6 (1)	4 (1)
$[Pd(C_3H_5)Cl]_2$ (**4**)	n-$PdC_{0.14}$	20	3.971(5)	13 (3)	9 (5)
		Microwave Protocol B^a			
K_2PtCl_4 (**1**)	n-Pt	20	3.934(4)	30 (3)	8 (8)
	n-Pt	10	3.920(3)	10 (2)	5 (3)
	n-Pt	2	3.939(8)	21 (5)	4 (2)
Na_2PdCl_4 (**2**)	n-Pd	10	3.892(4)	8 (2)	7 (3)
$[Pt(C_2H_4)Cl_2]_2$ (**3**)	n-Pt	20	3.903(9)	6 (7)	3 (1)
$[Pd(C_3H_5)Cl]_2$ (**4**)	n-$PdC_{0.12}$	20	3.956(11)	10 (3)	5 (2)

[a] Protocol A, 100 s of total microwave irradiation. Protocol B, 50 s of total microwave irradiation.

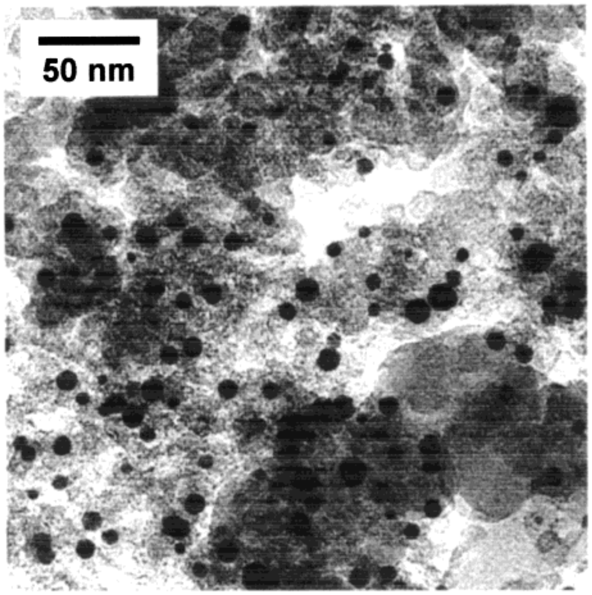

Figure 1. TEM micrograph of a Pt/Vulcan carbon nanocomposite prepared from precursor **1** by protocol A (metal loading = 2 wt %).

Transmission electron micrographs of the nanocomposite products reveal nanoclusters of high contrast and widely dispersed on the carbon powder support. A TEM micrograph typical of a Pt/Vulcan carbon nanocomposite is shown in Figure 1. Representative TEM micrographs for the Pd/carbon or PdC$_x$/carbon nanocomposites are available as Supporting Information. Average nanocluster diameters (with standard deviation) provided in Table 1 are obtained from histograms of nanoparticle sizes constructed from individually measured particle diameters. Nanocluster size distributions are typically monomodal in appearance but of varying breadth. A histogram of Pt nanocluster diameters observed for the Pt/carbon nanocomposite prepared from **1** using protocol B at a metal loading of 20 wt % is shown in Figure 2. The average diameter is 8 nm with particle diameters ranging from ≈1.5−18 nm. The log-normal shape of this distribution indicates metal nanoparticle growth by a liquidlike coalescence process rather than by Ostwald ripening.[12]

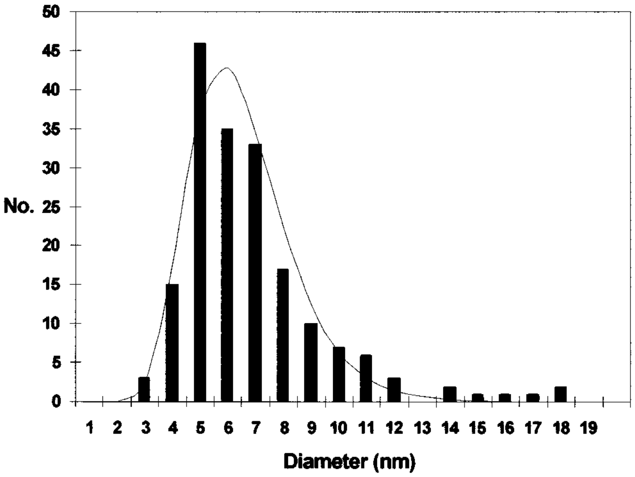

Figure 2. Histogram of Pt nanocluster diameters of a Pt/Vulcan carbon nanocomposite prepared from precursor **1** by protocol B (metal loading = 20 wt %).

EDS spectra confirm the presence of metal in each nanocomposite and the absence of residual chlorine, as shown in Figure 3 for a Pt/carbon nanocomposite prepared from **1** using protocol B at a metal loading of 20 wt %. Nanocomposites prepared from precursors **1** and **2** contain either KCl or NaCl as formed, but these salts are readily removed by aqueous washing. Copper emission from the Cu grid of the sample holder is also observed. Weak Si emission is observed because of the presence of trace amounts of inorganic minerals in commercial-grade Vulcan carbon powder.[13]

Representative XRD scans for the reported nanocomposites are shown in Figure 4 along with standard line patterns for Pt and Pd metal. As expected, each nanocomposite gives an XRD pattern consistent with a face-centered-cubic (fcc) unit cell. Cell constants (with standard deviations) determined from XRD peak positions are provided in Table 1. Volume-weighted average nanocluster diameters calculated from XRD peak widths using Scherrer's equation are also listed in Table 1 along with computed standard deviations. Samples containing exceptionally large nanoclusters usually give larger average nanocluster sizes as determined by XRD than those measured directly from TEM micrographs.

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(13) Private communication, Cabot Corp.

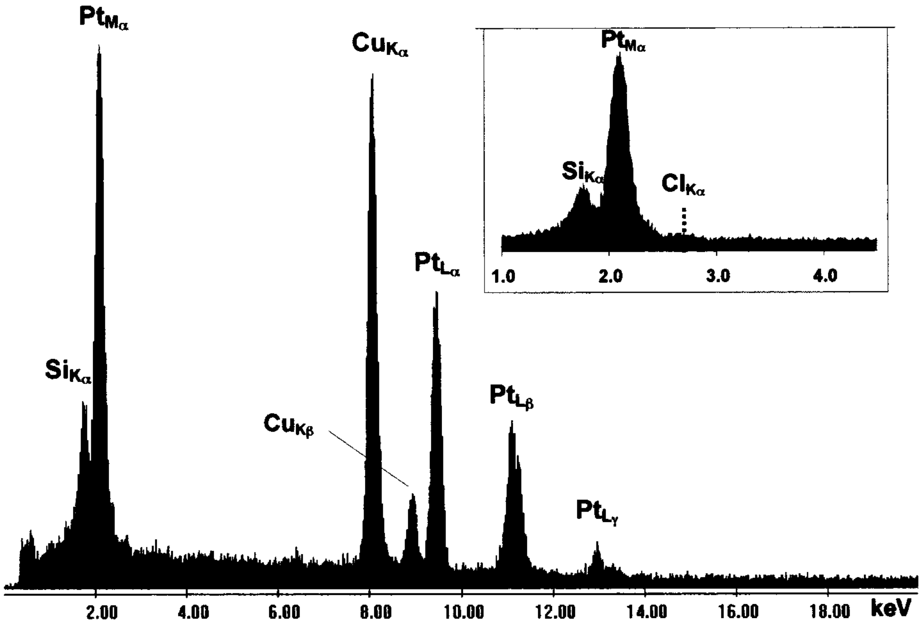

Figure 3. EDS spectrum of a Pt/Vulcan carbon nanocomposite prepared from precursor **1** by protocol B (metal loading = 2 wt %). Absence of chlorine Kα_1 emission at 2.62 keV is evident from the expanded region shown as an insert.

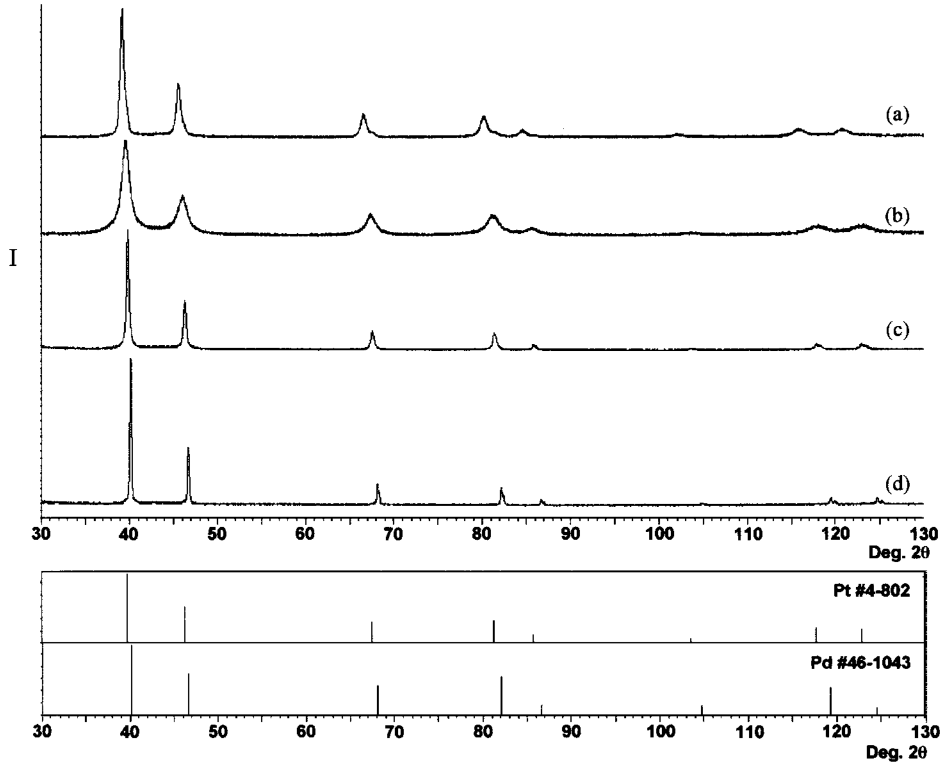

Figure 4. Representative XRD scans (Cu radiation) for the reported nanocomposites [(scan), nanophase, precursor, metal wt %] prepared by protocol A along with standard line patterns for Pt and Pd: (a) $PdC_{0.14}$, **4**, 20 wt %; (b) Pt, **3**, 20 wt %; (c) Pt, **1** 10 wt %; (d) Pd, **2**, 10 wt %.

Lattice constants for nanocomposites prepared from precursors **1**–**3** have values consistent with those known for the pure metal. Lattice constants slightly larger than those expected for pure Pd are observed for those nanocomposites prepared from precursor **4**. Interstitial Pd–carbide phases of stoichiometry PdC_x ($0 < x < 0.15$) are known[14] and have been formed in the solution reduction of $[PdCl_4]^{2-}$ ion by various organic radicals.[15] We speculate that the allyl ligand in precursor **4** encourages the formation of Pd–carbide nanoclusters. The lattice parameter of PdC_x materials increases linearly with increasing values of x. From this correlation, we infer that Pd–carbide nanocrystals of composition $PdC_{0.12}$ and $PdC_{0.14}$ are formed from precursor **4** in these carbon-supported nanocomposites. Pd–carbide phases are not formed from precursor **2**, so the

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[14] Ziemechi, S. B.; Jones, G. A.; Swartzfager, D. G.; Harlow, R. L. *J. Am. Chem. Soc.* **1985**, *107*, 4547.

[15] Okitsu, K.; Mizukoshi, Y.; Bandow, H.; Yamamoto, T. A.; Nagata, Y.; Maeda, Y. *J. Phys. Chem. B* **1997**, *101*, 5470.

carbide carbon is presumably obtained from the allyl ligand and not from the Vulcan carbon support.

XPS spectra of the PdC_x/Vulcan carbon nanocomposite **4** show a Pd $3d_{5/2}$ peak at a binding energy of 335.2 eV. Pd $3d_{5/2}$ binding energies for a Pd(0)/carbon composite[16] and a putative PdC_x/Al_2O_3 composite[17] are 334.3 and 336.7 eV, respectively. The Pd $3d_{5/2}$ binding energy observed for nanocomposite **4** is nearly 1 eV higher than that expected for Pd(0)/carbon composites and is, therefore, consistent with PdC_x phase formation. However, the relatively small differences expected for Pd $3d_{5/2}$ binding energies between Pd(0) and PdC_x phases diminishes the diagnostic value of XPS data for phase identification. In addition, a $PdC_{0.12}$ composition has a low carbon atomic percent, and the degree of charge separation between Pd and C atoms in these interstitial phases is apparently not great.

Some noteworthy conclusions derived from these results include the following:

(1) Carbon-supported simple salts of Pt or Pd and organoplatinum complexes can serve as precursor materials for Pt or Pd/Vulcan carbon nanocomposites. These nanocomposites are formed rapidly using microwave heating due to the high electrical conductivity and very small particle size of the Vulcan carbon support. Allylpalladium precursors form interstitial palladium carbide phases under the conditions investigated.

(2) At a metal loading of 20 wt %, the platinum salt precursor **1** forms Pt nanoclusters significantly larger than those obtained from the neutral, organoplatinum precursor **3**. This trend is relatively independent of microwave heating protocol. Salt precursors might be more likely to deposit as small crystallites, whereas neutral precursors might absorb more diffusely onto the carbon support.

(3) Rapid formation of metal/carbon nanocomposites using microwave irradiation provides some control over the metal nanoparticle average size and the breadth of nanoparticle size distributions. In general, doubling the period of microwave irradiation increases both the average size of the resulting metal nanoclusters and the breadth of the metal nanoparticle size distribution. These trends are more dramatic for metal/carbon nanocomposites prepared from salt-like precursors. Even so, at a metal loading of 20 wt %, a Pt/carbon nanocomposite prepared from precursor **1** under protocol B contains Pt nanoclusters of only 8-nm average diameter (by TEM).

(4) Increased metal loading generally leads to an increase in the average diameter of the resulting metal nanocluster. For example, Pt/carbon nanocomposites prepared using precursor **1** under protocol B at metal loadings of 2 and 20 wt % have Pt nanoparticle average diameters of 4 and 8 nm, respectively. A similar effect is observed for Pt/carbon nanocomposites prepared under protocol A with a much broader particle size distribution being observed for the nanocomposite of higher metal loading.

While metal agglomeration is a significant problem encountered in the synthesis of metal/carbon catalysts using conventional heating methods, the use of Vulcan carbon as a support and microwave dielectric-loss heating lead to rapid formation of metal/carbon nanocomposites from simple precursor/carbon composite materials. Metal nanoclusters having an average size as small as 3 nm are formed within 50 s of heating at metal loadings as high as 20 wt % using this method. We speculate that this synthetic strategy could be applied to the synthesis of other metal/carbon nanocomposites and thus extend the use of microwave processing for materials preparation.[18−21]

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Supporting Information Available: TEM micrographs of typical Pd/C and PdC_x/C nanocomposites, representative histograms of metal nanoparticle size distributions, and representative EDS spectra (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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