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## Recommended Citation

Park, S. J.; Bhargava, S.; Bender, E. T.; Chase, George G.; and Ramsier, R. D., "Palladium Nanoparticles Supported by Alumina Nanofibers Synthesized by Electrospinning" (2008). *Chemical and Biomolecular Engineering Faculty Research*. 4.

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### Palladium nanoparticles supported by alumina nanofibers synthesized by electrospinning

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(Received 11 July 2007; accepted 5 February 2008)

Palladium nanoparticles supported by alumina nanofibers have been successfully synthesized by electrospinning using palladium chloride incorporated into a solution of polyvinyl pyrrolidone and aluminum acetate. Palladium agglomerate sizes and the surface morphology of the electrospun nanofibers were determined by transmission electron microscopy. Palladium nanoparticles appeared to be well dispersed within the electrospun nanofiber structure. X-ray diffraction, x-ray photoelectron spectroscopy, and Raman scattering spectroscopy techniques were used to identify the crystalline form and distinguish between oxidized and metallic palladium particles after heating and hydrogenation.

Metal oxide nanofibers are promising candidates as catalyst supports in heterogeneous catalytic reactions.<sup>1–5</sup> Such fibers can be fabricated by electrospinning with polymer solutions followed by heating to produce composite fibers with diameters ranging from nanometers to micrometers.<sup>6–11</sup> As a catalyst-support structure these materials can provide a means of constructing catalytic systems that are lightweight, efficient, thermally and chemically stable, and with large surface area.<sup>10</sup>

One of the noble metals, palladium, has strong catalytic activity for hydrogenation,<sup>3,11</sup> oxidation,<sup>12,13</sup> and hydrogenolysis reactions.<sup>14,15</sup> For example, alumina-supported palladium catalysts have been used for simultaneous NO reduction and CO oxidation.<sup>16–18</sup> The most commonly used method for preparation of supported palladium catalysts is by wet impregnation of commercial alumina particles.<sup>3,18</sup> It has been shown that noble metal

nanoparticles can be deposited directly on carbon nanofibers by physical deposition from solutions,<sup>3</sup> or they can be added to the polymer solution prior to electrospinning.<sup>10,11</sup> For example, Pham-Huu et al.<sup>3</sup> grew carbon nanofibers and coated them with palladium by wet impregnation. These composite materials show higher activity and chemoselectivity compared with commercial high surface area activated charcoal supported palladium catalysts for the hydrogenation of C=C bonds.

The work reported here demonstrates a method by which palladium particles are directly incorporated into composite alumina nanofibers during electrospinning without the need for physical deposition or wet impregnation steps. Nanoparticles have properties between bulk materials and molecules and are potentially useful for new generations of chemical, optical, magnetic, and electronic devices.<sup>11,19</sup> Well-distributed nanosized noble metal particles show better potential for catalyst than bulk materials. However, nanomaterials are difficult to handle and difficult to recover if suspended in reaction fluids.<sup>20</sup> Our method of putting catalysts on surfaces of nanofibers gives good surface area exposure of

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DOI: 10.1557/JMR.2008.0173

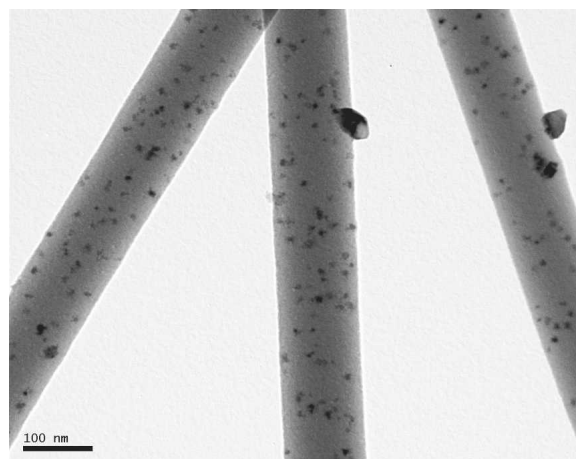
the catalyst particles to the surrounding fluid phase, and the nanofiber mats are easily handled. The use of nanofibers for catalyst structure support is relatively new, and patents are pending.

A 7 wt% solution of polyvinyl pyrrolidone [PVP; Aldrich, St. Louis, MO, molecular weight (MW) 1,300,000] was made in ethanol (AAPER alcohol). Aluminum acetate (Alfa Aesar, Ward Hill, MA, basic hydrate) was dissolved with water and formic acid in the weight ratio 1:2.5:1. This PVP and aluminum acetate solutions were mixed with weight ratio 3:1, respectively. Palladium chloride (Sigma-Aldrich, Gillingham, UK, 60% Pd) was dissolved in the resulting mixture in the ratio of 5 wt% PdCl<sub>2</sub> with respect to aluminum acetate and mixed overnight at 40 °C using a magnetic stirrer.

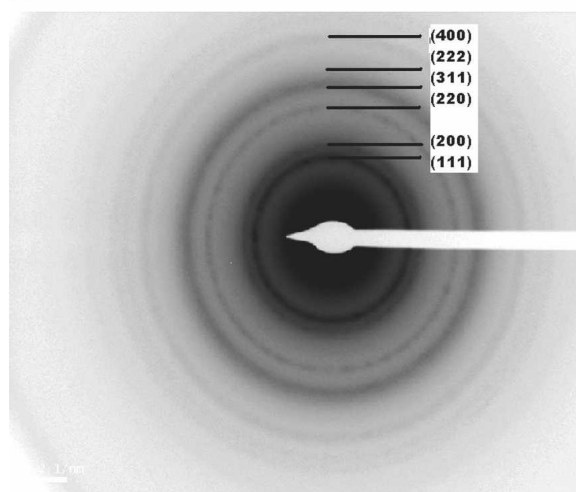
Nonwoven mats were electrospun by applying 20 kV (Gamma High Voltage Research Inc., Ormond Beach, FL) to the polymer solution in a 3 mL glass syringe with a stainless steel needle at the end. The solution was pumped at 3.0 μL/min using a syringe pump (World Precision Instruments, Sarasota, FL; SP1011). The needle was positioned about 20 cm above a grounded aluminum foil collector.

The nanofiber mat was calcined at 600 °C for 2 h and reduced under flowing hydrogen (50 mL/min) at 400 °C for 4 h. Morphology of nanofibers with particle agglomerates was observed using transmission electron microscopy (TEM; FEI Tecnai 12), and selected-area electron diffraction (SAED) was also taken to identify the structure of particle agglomerates on the nanofibers. Furthermore, phase structures of fibers were confirmed by wide-angle x-ray diffraction (WAXD; Rigaku Co., Ltd., Tokyo, Japan) in the reflection mode. The chemical nature of the palladium-incorporated alumina nanofibers was determined by x-ray photoelectron spectroscopy (XPS; VG ESCALAB MK II) (VG Scientific, West Sussex, UK) using an aluminum anode x-ray source operating at 180 W. Experiments were done at a typical operating pressure below  $3 \times 10^{-8}$  mbar, and the hemispherical analyzer had a pass energy of 50 eV. Raman scattering spectra (Jobin Yvon T64000 triple monochromator) (Horiba Jobin Yvon, Edison, NJ) of the palladium-doped alumina nanofibers were measured in backscattering geometry. A krypton laser with a wavelength of 647 nm and power of 20 mW was used as an excitation source.

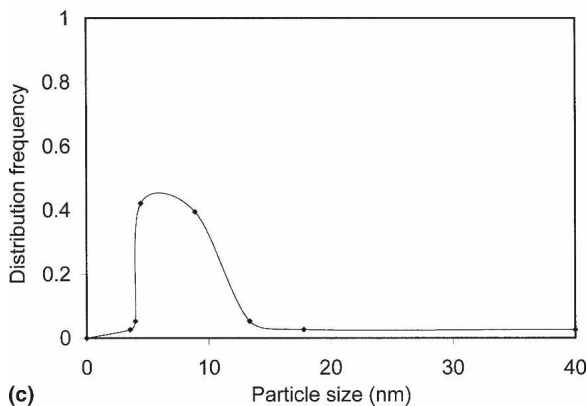
The bright-field TEM image shows a good dispersion of palladium particles, with an average particle size distribution around 7 nm after calcination at 600 °C and hydrogenation (Fig. 1). The alumina nanofibers had diameters of about 100 nm. In the present work, no attempt was made to control the palladium particle sizes, but this will be considered in future work. Figure 1(b) shows a corresponding SAED pattern for palladium nanoparticles on the amorphous alumina nanofibers. Several diffused



(a)



(b)



(c)

FIG. 1. (a) Bright-field TEM image, (b) corresponding SAED pattern, and (c) particle size distribution of palladium on alumina nanofibers.

diffraction rings appeared with different  $d$ -spacings: 0.225, 0.195, 0.138, 0.117, 0.112, and 0.097 nm, which indexed with (111), (200), (220), (311), (222), and (400) of the palladium metal with face-centered cubic unit cell dimensions.<sup>21</sup> From the diffraction data a lattice constant of  $a = 0.389$  nm is calculated, which is in excellent agreement with literature data for palladium.<sup>22</sup>

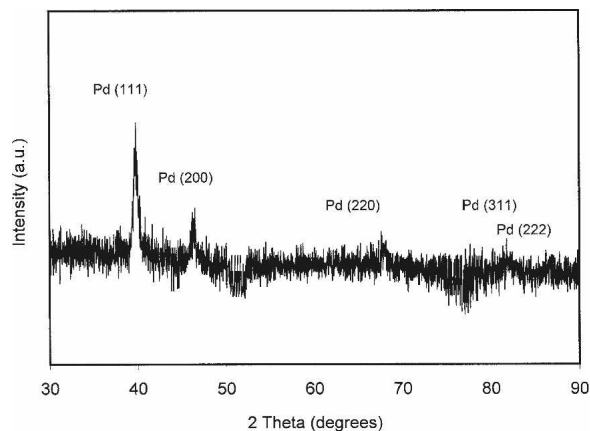


FIG. 2. XRD data from palladium-doped alumina nanofibers after calcination at 600 °C and hydrogenation.

The SAED results confirm that the palladium nanoparticles in TEM morphology are the randomly oriented palladium crystals and the diffused diffractions come from the relatively lower crystallinity in the palladium nanosized particles. Diffraction peaks for alumina are not observed because alumina fiber is in amorphous state, which will be supported by the following x-ray diffraction (XRD) results. Figure 2 shows an XRD pattern of the composites. Crystalline peaks of palladium after hydrogenation appear at angles of 40° (111), 47° (200), 68° (220), 81.5° (311), and 86° (222); these results agree well with those of SAED.<sup>11</sup>

XPS results are shown in Fig. 3. These demonstrate that the palladium is no longer in its chloride form after annealing at 600 °C. The chemical state of palladium was inferred from the chemical shift of the Pd (3d<sub>5/2</sub>) and Pd (3d<sub>3/2</sub>) peaks. It was located at 336.8 and 342 eV before

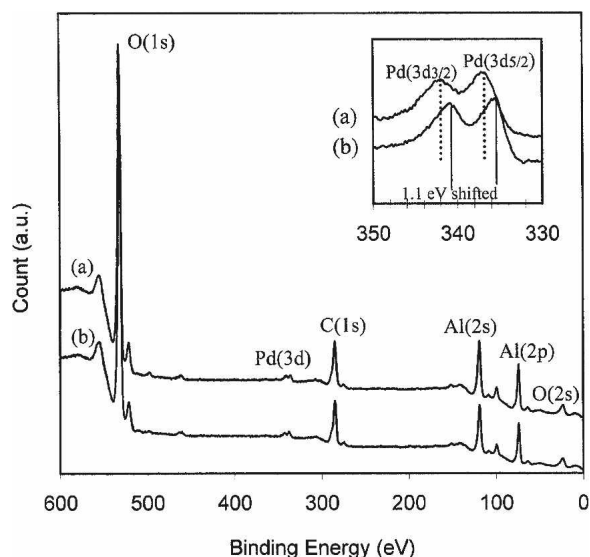


FIG. 3. XPS data from alumina nanofibers doped with palladium and calcined at 600 °C. (a) Before hydrogenation. (b) After hydrogenation.

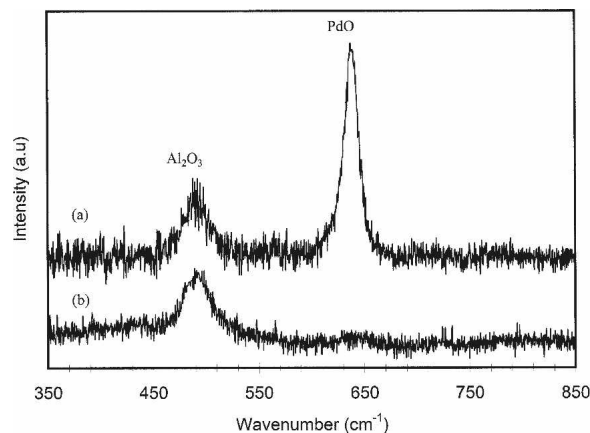


FIG. 4. Raman scattering spectra from palladium-doped alumina nanofibers calcined at 600 °C. (a) Before hydrogenation. (b) After hydrogenation.

hydrogenation, which shifted 1.1 eV toward lower binding energies after hydrogenation.<sup>23–25</sup> This suggests that the palladium is in its oxide form before hydrogenation and in a metallic form after hydrogenation. The relatively large signature from carbon in the spectra in Fig. 3 is likely caused by contamination that is frequently detected independent of sample composition. Carbon contamination is a common issue in XPS; for instance, Rotole and Sherwood recorded XPS spectra of pure gamma alumina,<sup>26</sup> and their survey spectrum shows carbon in an amount comparable to what is seen here in Fig. 3. Raman scattering spectra of the palladium and palladium oxide doped alumina nanofibers are presented in Fig. 4. After calcination at 600 °C, a strong peak appears at 639 cm<sup>-1</sup> corresponding to palladium oxide. There is also another peak at 490 cm<sup>-1</sup> corresponding to alumina. The peak at 639 cm<sup>-1</sup> is not present after hydrogenation and indicates the reduction of palladium oxide to palladium.<sup>27–29</sup>

Composite nanofibers of Pd/Al<sub>2</sub>O<sub>3</sub> have been synthesized using electrospinning followed by calcination and hydrogen reduction techniques. Palladium nanoparticles were observed to be well dispersed, roughly spherical in shape, and with a narrow size distribution. Palladium oxide incorporated into the alumina nanofiber mats was reduced to metallic palladium by heating and hydrogenation. High-resolution transmission electron microscopy will be used in the future for imaging and determination of crystal structure.

## ACKNOWLEDGMENTS

This work was supported by the MemPro Ceramics Corporation (MEMPRO) and National Science Foundation (NSF) grants IIP 0637539 and DMI-0403835. We especially thank our colleagues, Professor A.P. Sokolov, Dr. T.E. Chang, and Professor E.A. Evans, for their assistance with the Raman spectroscopy.

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