Nanoparticle catalysis

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Supported Palladium Nanoparticles: An Efficient Catalyst for the Direct Formation of H_2O_2 from H_2 and O_2**

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Supported palladium nanoparticles have recently been studied as catalysts for such diverse reactions as the hydrogenation of olefins[1] and Heck or Suzuki coupling reactions.[2,3] Herein we report for the first time in the open literature the effectiveness of palladium nanoparticles, prepared ex situ and supported on carbon, in catalyzing the direct formation of hydrogen peroxide from H_2 and O_2. Among the various supported metal catalysts prepared by more conventional methods, palladium, either by itself or as a bimetallic with platinum or gold, is a superior catalyst with respect to activity and, importantly for commercial applications, selectivity.[4]The palladium nanoparticle catalyst is shown to exhibit exceptional selectivity for hydrogen utilization. In the overall reaction scheme, the formation of H_2O_2 competes with the direct formation of H_2O, as well as with the secondary reduction or decomposition of H_2O_2.[5] It has been argued that a selective catalyst must minimize the breaking of O–O bonds both in adsorbed O_2 and in H_2O_2.[5b] Small concentrations of halide anions (Cl^- or Br^-) are essential for achieving high selectivity, but other factors, such as the coordination of surface Pd atoms, may also play a role.[5,6]

A novel method of nanoparticle synthesis has been used, which results in a simplified approach for preparing the supported metal. Typically a liquid phase containing the metal nanoparticles is synthesized first, and this is followed by separation of the colloid, redispersion, and finally deposition of the nanoparticles on a suitable support, such as silica or carbon. Monodisperse particles cannot usually be obtained in one pot; therefore, a size selection step is necessary, which often results in considerably lower yields of the desired nanoparticles.[7] In the case of palladium, very few methods have been reported for achieving monodisperse nanoparticles.[8]

Herein we describe a simple and efficient approach for synthesizing supported monodisperse Pd in high yields. The Pd nanoparticles were obtained from the thermal decomposition of palladium acetate in the presence of trioctylphosphine (TOP), which served as a stabilizer to prevent the aggregation of particles. The liquid phase was 1-octadecene. After the decomposition/reduction of the palladium acetate, the resulting Pd nanoparticles were flocculated by adding a large amount of ethanol, centrifuged, and redispersed in toluene. This material was used to obtain the TEM image shown in Figure 1 A. Particle size distribution was determined from a sample of more than 400 particles, and the results (Figure 1 A, inset, bottom left) showed the particles to be nearly monodisperse, with a maximum in the histogram at 3.6 nm. It should be noted that this narrow distribution was obtained without any size-selective process.

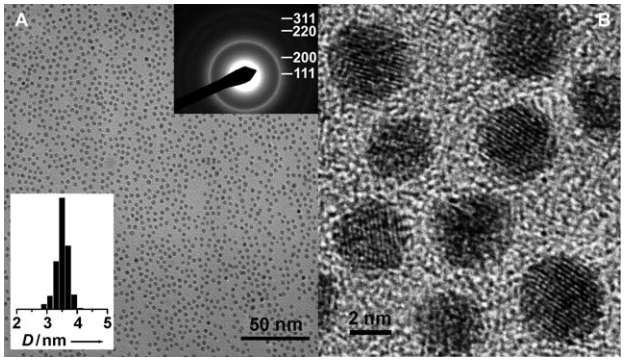

Figure 1. A) TEM image of Pd nanoparticles with electron diffraction pattern (inset, top right), and histogram showing the size distribution for the Pd colloid (inset, bottom left). B) HRTEM image of colloidal Pd nanoparticles.

The high resolution TEM (HRTEM) image shown in Figure 1 B confirms the highly crystalline nature of the Pd particles. The interplanar spacing of 0.23 nm, obtained from the fringes of the lattice, agrees well with the (111) lattice-spacing of face-centered cubic (fcc) Pd. The electron diffraction pattern (Figure 1 A, inset, top right), exhibits four diffuse rings that match well with the (111), (200), (220), and (311) reflections of the fcc metal.

After immobilization of the Pd nanoparticles onto Vulcan XC-72 carbon black, without a separation or rinsing process, the TEM image shown in Figure 2 A was obtained. This image reveals that the particles are uniformly dispersed, and particle size and morphology are nearly identical to those of the unsupported colloidal particles. The Pd loading was approximately 0.6 wt %, which corresponds to a Pd yield of about

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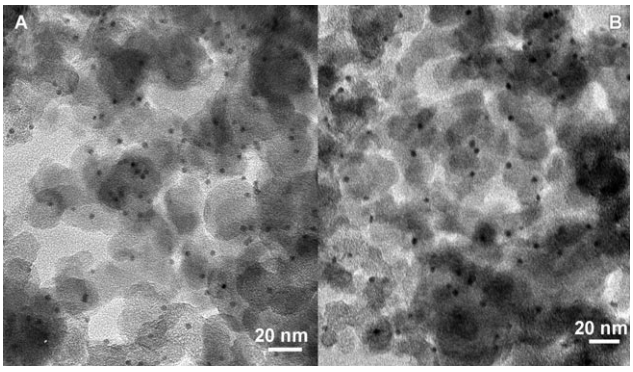

Figure 2. TEM images of Pd/XC-72 catalyst synthesized by colloidal method: A) fresh catalyst, and B) used catalyst after 4 h of reaction.

85%, based on the starting amount of palladium acetate. The Pd loading was kept small in order to avoid transport limitations during the catalytic reaction. The yield of 85% establishes this as a highly efficient method for the preparation of supported Pd nanoparticle catalysts. Moreover, with this method it is easy to vary the Pd loading without the varying particle size distribution or the morphology.

In order to compare catalytic results, a second catalyst was prepared using a conventional impregnation method with tetraammine palladium (II) chloride as the source of Pd. The loading was again 0.6 wt%. TEM results (not shown) indicated that the Pd particle size distribution was bimodal. Some particles were in the range of 6–10 nm, but most had a size in the range of 2–4 nm.

The catalytic behavior in the direct formation of H_2O_2 from H_2 and O_2 is shown in Figure 3. The catalyst prepared by the Pd colloid route was exceptionally active in the formation of H_2O_2: the specific rate was 48 $mmol_{H_2O_2}\, g_{Pd}^{-1}\, min^{-1}$, which is 2.5 times larger than that obtained over the catalyst prepared by the conventional impregnation method (see below). The rate was stable with respect to time on stream, indicating that the catalyst is stable and that secondary reactions are not important, at least up to H_2O_2 concentrations of ca. 0.3 wt%. In addition, selectivity for H_2O_2 was greater than 70% and remained nearly constant throughout the course of the reaction. The used catalyst was examined by TEM after 4 h of reaction, and the results (see Figure 2B) clearly show that the Pd particles remained homogeneously dispersed on the carbon, without any change in size or morphology.

To explore the possibility that a colloidal form of Pd in the liquid phase might be responsible for the catalytic activity, the solid catalyst was separated from the liquid phase after 2 h of reaction. A small aliquot of the liquid was analyzed for Pd and none was found to be present. In addition, the liquid was returned to a clean reactor and the H_2/O_2 gas mixture was reintroduced. This system was completely inactive for the formation of H_2O_2. These results confirm that a colloidal slurry of Pd (in contrast to supported Pd) was not responsible for the catalytic activity.

In an effort to improve selectivity, the chloride anion concentration was increased from 4×10^{-4} M to 5×10^{-4} M. Selectivity increased to greater than 80% while the rate of

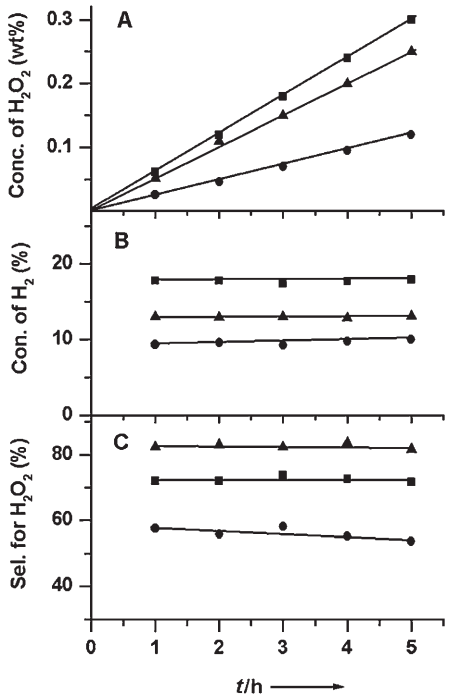

Figure 3. Formation of H_2O_2 with $O_2/H_2 = 15$ in the presence of chloride over Pd/XC-72: prepared by the colloidal process (■) 4×10^{-4} M HCl and (▲) 5×10^{-4} M HCl; prepared by the impregnation method (●) 4×10^{-4} M HCl. A) H_2O_2 concentration, B) conversion of H_2, and C) selectivity for H_2O_2.

H_2O_2 formation decreased by about 17%. Activity and selectivity again remained constant with respect to time. Selectivity was improved yet further by adding a combination of Cl^- and Br^- to the system,[9] but decreased with time as a result of an increase in H_2 conversion. For example, selectivity was 90% after 1 h in the presence of 4×10^{-4} M Cl^- and 2×10^{-6} M Br^-. When the Br^- ion concentration was increased further to 4×10^{-6} M the selectivity approached 100%, but the rate of peroxide formation decreased significantly. This exceptionally large selectivity has been reported in a patent,[10] for a reaction carried out at high pressures (approximately 95 atm).

Finally, in the absence of a halide (Cl^- or Br^-), selectivity for H_2O_2 was zero even though the conversion of H_2 was about 30% for the supported Pd nanoparticles that were prepared ex situ. This result indicates that any TOP retained on the surface did not have the same effect on selectivity as did the halide ions.

For comparison, the catalytic properties of supported Pd prepared by the conventional impregnation method were determined. The results are also reported in Figure 3. In 4×10^{-4} M HCl, the specific rate was 19 $mmol_{H_2O_2}\, g_{Pd}^{-1}\, min^{-1}$. Selectivity decreased slightly from 58% to 55% over 5 h. The selectivities and H_2O_2-formation rates are comparable to those obtained over a 0.5 wt% Pd/SiO_2 catalyst.[9]

The effect of residual TOP was further evaluated by adsorbing the phosphine from a toluene solution onto a reduced catalyst prepared by the conventional impregnation method, using the same TOP/Pd ratio. The catalytic results showed that the TOP-modified conventional catalyst was

25% less active for the formation of H_2O_2 and 10% less active for H_2 conversion than the conventional catalyst without TOP. Thus, the improved activity and selectivity described in Figure 3 for the monodisperse nanoparticles are not attributable to the presence of residual TOP.

Although the scope of this study did not include particle size effects, recent papers on this topic provide insight into possible reasons for the differences that were observed between the catalyst that contained monodisperse nanoparticles and that prepared by the traditional impregnation method.[11] Significant differences in activity and selectivity have been reported for several hydrogenation reactions catalyzed by palladium nanoparticles. There appears to be a consensus that so-called particle size effects, when observed, are a result of geometric, rather than electronic, factors for particle sizes >1 nm. The most thorough work has been carried out by Freund and co-workers, who studied the hydrogenation of 1,3-butadiene.[11d] They observed that, whereas the turnover frequency appears to increase linearly with respect to particle size, the effect is actually a result of an increasing number of Pd atoms associated with incomplete (111) terraces for particles >4 nm and Pd (110) planes for particles <4 nm. In our system, it is conceivable that monodisperse nanoparticles with a diameter of 3.6 nm have a preponderance of Pd atoms in the (110) plane, whereas the Pd particles on the conventional catalyst have a broader size distribution and, therefore, a less than optimum concentration of atoms in the (110) plane. Consistent with the conclusions of Freund and co-workers, we suggest that the dissociative adsorption of H_2 occurs most rapidly on these Pd (110) planes that are, of course, in equilibrium with the complex liquid phase. The conversion of H_2 was significantly larger on the monodisperse nanoparticles (Figure 3B). By contrast, the dissociation of O_2 may occur less rapidly on the halide-modified (110) planes, resulting in a higher selectivity for H_2O_2.

In summary, a simple, high-yield process has been used to synthesize a Pd/carbon catalyst that is effective for the direct formation of H_2O_2. The monodisperse particles had a narrow size range with a maximum at 3.6 nm. In this form the Pd exhibited a 2.5-fold larger specific activity and a 15% higher selectivity than was observed over a conventionally prepared catalyst. These results were obtained with Cl^- as the halide ion. With a combination of Cl^- and Br^- ions even higher selectivities, approaching 100%, could be achieved.

Experimental Section

A colloidal suspension of palladium was synthesized by thermal decomposition of palladium acetate (trimer, 99.9%, Alfa Aesar) in the presence of trioctylphosphine (TOP, 90%, Alfa Aesar) and 1-octadecene (ODE, 90%, Alfa Aesar). In a typical synthesis, palladium acetate (0.0225 g), ODE (5 mL), and TOP (0.5 mL) were mixed in a 50 mL, three-necked flask (equipped with a condenser and a Teflon-coated magnetic stirring bar) under an argon atmosphere at room temperature. After 40 min the orange solution was heated, with vigorous stirring, to 260 °C over 10 min and held at that temperature for another 20 min, affording a black solution. The heating source was removed, and the resulting mixture was allowed to cool to room temperature without further treatment.

The Pd nanoparticles were subsequently immobilized on Vulcan XC-72 carbon black (Cabot). Typically, the colloidal suspension of Pd was taken up in toluene (35 mL), and the resulting solution was slowly added to a slurry consisting of toluene (500 mL) and XC-72 powder (1.5 g) in a 1000 mL beaker. The slurry was stirred in air at room temperature. After 1 day the solid phase was separated by centrifuge, and dried in an oven at 60 °C for another 1 day to obtain the supported catalyst. For the purpose of comparison, another Vulcan XC-72-supported Pd catalyst was prepared by a conventional impregnation method. In this case, tetraamminepalladium (II) chloride (98%, Aldrich, 0.017 g) was dissolved in water and added to XC-72 powder (1.13 g) using the incipient wetness method. After drying overnight at 60 °C, the sample was oxidized for 3 h at 300 °C in O_2 (100 mL min^{-1}) and reduced for 2 h at 300 °C in H_2/He (20/80 mL min^{-1}).

Catalytic reactions were carried out at atmospheric pressure and 10 °C in the glass reactor described in Ref. [5a]. The reactor had a vent that exited to a gas chromatograph (HP 5890 with a 5 Å molecular sieve column operating at 30 °C) to analyze the H_2 and O_2 composition. The O_2/H_2 ratio was 15:1; an H_2/N_2 mixture was used which contained 80% N_2 and the oxygen used in experiments was 99.99% in purity. Gases were introduced at a total flow rate of 50 mL min^{-1} through a glass frit (Ace Glass, 4–8 μm) at the bottom of the reactor. Usually 50 mg of catalyst was used in each reaction, and the liquid phase consisted of 60 mL of ethanol acidified with sulfuric acid to 0.12 M. The halide concentration for each experiment was attained by adding appropriate amounts of aqueous HCl or HBr to provide the Cl^- or Br^- concentrations indicated above. **Caution**: because the O_2/H_2 ratio is within the explosive region, the dry catalyst should not be added to O_2/H_2 gas mixture. Moreover, precautions should be taken to contain the system in the event of an explosion. At appropriate times an aliquot of the liquid phase (ca. 0.2 g) was removed and analyzed for H_2O_2 using a colorimetric method with a $TiOSO_4/H_2SO_4$ reagent.[12] The selectivity for H_2O_2 was determined using the ratio of H_2O_2 formation to the rate of H_2 conversion.

Transmission electron microscopy (TEM) images were taken on a JEOL JEM-2010 TEM. The TEM samples were prepared by placing one drop of the suspended solution onto a carbon-coated Ni grid and allowing it to dry in air.

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[1] X. Ma, T. Jiang, B. Han, J. Zhang, S. Miao, K. Ding, G. An, Y. Xie, Y. Zhou, A. Zhu, *Catal. Commun.* **2008**, *9*, 70–77.
[2] Z. Zhang, Z. Wang, *J. Org. Chem.* **2006**, *71*, 7485–7487.
[3] J. K. Cho, R. Najman, T. W. Dean, O. Ichihara, C. Muller, M. Bradley, *J. Am. Chem. Soc.* **2006**, *128*, 6276–6277.
[4] a) P. Landon, P. J. Collier, A. F. Carley, D. Chadwick, A. J. Papworth, A. Burrows, C. J. Kiely, G. J. Hutchings, *Phys. Chem. Chem. Phys.* **2003**, *5*, 1917–1923; b) J. K. Edwards, B. E. Solsona, P. Landon, A. F. Carley, A. Herzing, C. J. Kiely, G. J. Hutchings, *J. Catal.* **2005**, *236*, 69–79; c) V. R. Choudhary, C. Samanta, T. V. Choudhary, *Appl. Catal. A* **2006**, *308*, 128–133.
[5] a) S. Chinta, J. H. Lunsford, *J. Catal.* **2004**, *225*, 249–255; b) Q. Liu, J. H. Lunsord, *J. Catal.* **2006**, *239*, 237–243.
[6] S. Abate, S. Melada, G. Centi, S. Perathoner, F. Pinna, G. Strukul, *Catal. Today* **2006**, *117*, 193–198.
[7] C. B. Murray, C. R. Kagan, M. G. Bawendi, *Annu. Rev. Mater. Sci.* **2000**, *30*, 545–610.
[8] a) S.-W. Kim, J. Park, Y. Jang, Y. Chung, S. Hwang, T. Hyeon, Y. W. Kim, *Nano Lett.* **2003**, *3*, 1290–1291; b) M. Ganesan, R. G. Freemantle, S. O. Obare, *Chem. Mater.* **2007**, *19*, 3464–3471;

c) N. Zheng, J. Fan, G. D. Stucky, *J. Am. Chem. Soc.* **2006**, *128*, 6550 – 6551.
[9] Q. Liu, J. H. Lunsford, *Appl. Catal. A* **2006**, *314*, 94 – 100.
[10] M. A. Rueter, S. Parasher, C. Zhang, B. Zhou, Pat. Appl.No.US 393,334, **2006**, Headwaters Nanokinetix.
[11] a) Y. Sun, L. Zhuang, J. Lu, X. Hong, P. Liu, *J. Am. Chem. Soc.* **2007**, *129*, 15465 – 15467; b) N. Semagina, A. Renken, L. Kiwi-Minsker, *J. Phys. Chem. C* **2007**, *111*, 13933 – 13937; c) M. G. Musolino, G. Apa, A. Donato, R. Pietropaolo, F. Frusteri, *Appl. Catal. A* **2007**, *325*, 112 – 120; d) J. Silvestre-Albero, G. Rupprechter, H.-J. Freund, *J. Catal.* **2006**, *240*, 58 – 65.
[12] I. R. Cohen, T. C. Purcell, A. P. Altshuller, *Environ. Sci. Technol.* **1967**, *1*, 247 – 252.

