Synthesis, Characterization, and Highly Efficient Catalytic Reactivity of Suspended Palladium Nanoparticles

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The catalytic activities of suspended nano-sized palladium catalysts toward various olefin hydrogenation reactions are reported. The Pd nanoparticles were prepared by a laser ablation method followed by careful characterization. Two types of Pd nanoparticle systems were fabricated and subjected to a series of catalytic activity measurements: (i) Pd nanoparticles stabilized by tetraoctylammonium bromide (TC8ABr) ionic micelles with an average diameter of 2.4 ± 0.5 nm and (ii) bare-Pd nanoparticles with an average size of 12.7 ± 5.7 nm in diameter. The catalytic activities of both TC8ABr–Pd and bare-Pd nanoparticles were examined by measuring their turnover numbers (TON) in several target olefin hydrogenation reactions, such as the transformations of styrene to ethylbenzene, 2-methyl-2-butene to 2-methylbutane, 1-octene to n-octane, trans-stilbene to bibenzyl, and cyclohexene to cyclohexane. Data are compared to the hydrogenation results using a commercially available Pd/C catalyst system under similar reaction conditions. An exclusive selectivity of the catalytic styrene hydrogenation reaction on the C==C bond, rather than on the aromatic ring, was found among three systems, giving ethylbenzene as the only product. The catalyst stability was found to be on the order of TC8ABr–Pd > bare-Pd > 10% Pd/C.

Key Words: palladium nanoparticles; olefin hydrogenation; catalyst.

INTRODUCTION

The quantum size effect associated with nanoscale particles has been intensively studied during the past 2 decades. Nanoparticles with properties between bulk materials and molecules are potentially useful for the new generations of chemical, optical, magnetic, and electronic devices (1, 2). In addition, their feasible application in the field of catalysis has received considerable attention (3–5). Consequently, a wide range of synthetic approaches regarding the preparation of metal nanoparticles in various matrices, including reduction method (6), sol–gel process (7), solvent evaporation of hydrophobic colloids (8), cross-linking in colloidal aggregates (9), templates-directed methods (3d, 10), and bacterial superstructures (11), has been reported. We describe here an alternative synthetic route to prepare bare-Pd nanoparticle aggregates and surfactant-stabilized Pd nanoparticles using the laser ablation method (12) and the application of these Pd nanoparticles as potent hydrogenation catalysts for a series of olefins. In fact, the catalytic potential of noble-metal nanoparticles was first reported by Schmid (13) using Rn55 clusters. However, the liability of Rn55 clusters in solution did not allow any conclusive suggestion regarding its feasible application. The specific catalytic properties of nano-sized metal clusters are usually associated with a change in their electron properties relative to the bulk samples. This change is requisitioned by the quantum size effect and is usually prevailing with a great enhancement in catalytic activity (3–5). Recently, Pd nanoparticles protected by either micelles or organic polymers have been demonstrated to catalytically hydrogenate pyrene (14) and a selective double bond of dienes (15). In the present study, suspensions of Pd nanoparticles in ethyl acetate were prepared by a laser ablation method. The UV–Vis, EDX, and AA spectroscopic analyses and TEM image were used to characterize the palladium nanoparticles. The highly efficient activity of these nano-sized palladium catalysts were discussed within the framework of their catalytic performance in the olefin hydrogenation reactions.

EXPERIMENTAL

Catalyst Preparation

The laser ablation method was employed to fabricate both bare-Pd nanoparticles and TC8ABr-stabilized Pd nanoparticles suspensions. A Pd metal plate was first cleaned by a regular cleaning procedure, which incorporates an ultrasonication by immersing the Pd plate into acetone and then dried ethyl acetate in sequence. While it is needed, fine sandpaper was employed to polish the surface before the ultrasonication. The Pd metal plate after regular cleaning was then fixed onto a Teflon disc placed at the...
A typical 3 ml of dried ethyl acetate solution was then added into the glass vessel. In the case of preparing the TC$_8$ABr-stabilized Pd nanoparticles suspension, 3 ml of 0.01 M tetraoctylammonium bromide (TC$_8$ABr) in the ethylacetate solution was employed at this stage. The TC$_8$ABr was used to form a micellar system, which serves as the stabilizers for the Pd nanoparticles. The ablation was then conducted by irradiating an unfocused Nd: YAG laser beam (2$^{nd}$ harmonic, 532 nm and 10 Hz, Continum Model Surlite II) from the top onto the Pd metal plate perpendicularly. The laser power of 3.2 W, corresponding to the fluence of $8.6 \times 10^{17}$ photons/pulse/cm$^2$, was employed throughout the study. The laser beam diameter and the pulse duration is 6 ns. The ablation time was typically set to 3 min. The suspended Pd nanoparticles formed during the ablation were then ready for the material characterization and catalytic studies.

Catalyst Characterization

UV-Vis spectroscopy. The absorption spectra were recorded on a HP 8453 photodiode array spectrophotometer. The UV-Vis spectra of both bare- and TC$_8$ABr-Pd nanoparticles exhibit similar absorption spectral features, which are consistent with the electrostatic model (16) on the collective dipolar oscillation (the surface plasmon) of free electrons of the Pd nanoparticles. The resonance of the surface plasmon for Pd nanoparticles suspended in water is predicted to be located at ca. 210 nm. To avoid the spectral cut-off region due to the absorption of ethyl acetate, the long-wavelength side of the surface plasmon band can be used routinely to roughly check the concentration of the Pd nanoparticles and the correctness of the experimental conditions.

Transmission electron microscope (TEM) and energy-dispersive X-ray (EDS). The size distributions of thus prepared Pd nanoparticles were determined from the TEM (JEOL JEM-1200EX) measurements. The TEM images for both TC$_8$ABr-Pd and bare-Pd nanoparticles are shown in Fig. 1. The size of TC$_8$ABr-Pd nanoparticles (ca. 2.4 ± 0.5 nm in diameter, Fig. 1A) is more as evenly distributed as that of bare-Pd nanoparticles (ca. 12.7 ± 5.7 nm in diameter, Fig. 1B). The results can be best rationalized by the micellar stabilization effect, which prevents Pd particles from self aggregation. As a result, the TC$_8$ABr-Pd nanoparticles system shows much smaller and higher uniformity in sizes. EDS analyses on individual Pd nanoparticles indicate that no detectable oxygen and other metallic impurities were present in the suspended Pd nanoparticles.

Atomic absorption (AA). The weight percentages of Pd in the Pd/ethyl acetate suspensions were quantified by atomic absorption (AA) (Perkin-Elmer model 3110) analyses. The AA analysis was conducted in parallel with the catalytic measurement for every freshly prepared Pd nanoparticle suspension. The content of Pd obtained from a typical preparation condition is ca. 20 μg in 3 ml of ethyl acetate.

Olefin hydrogenation and catalytic activity measurements. Catalytic olefin hydrogenation reactions were carried out under various H$_2$ gas pressures in a Parr high-pressure minireactor (Model 4560 series) at ambient temperature. A representative procedure for catalytic styrene hydrogenation reaction follows: To a glass sample vial was added 3 ml of a dry ethyl acetate suspension containing either the 10% Pd/C (5 mg) or one of the TC$_8$ABr-stabilized Pd nanoparticles and bare-Pd nanoparticles. To this solution was then transferred 0.3 ml of styrene (2.6 mmol). The reactor was flushed with H$_2$ gas before being charged with...


Results and Discussion

Table 1 shows the results of various olefin hydrogenation reactions catalyzed by TC₈ABr–Pd nanoparticles at ambient temperature. The commercially available Pd/C is often used as a catalyst for the hydrogenation of unsaturated organic molecules (17). In a comparative study, the control experiments were performed at various H₂ gas pressures containing 5 mg of 10% Pd/C at similar reaction conditions. The results listed in Table 1 indicate that values of gross-TON obtained from TC₈ABr–Pd nanoparticles were significantly higher than those obtained from 10% Pd/C. At a low H₂ gas pressure of 100 psi, TC₈ABr–Pd nanoparticles were found to be much more reactive than 10% Pd/C toward bulkier linear olefins. The gross-TON ratios of TC₈ABr–Pd versus 10% Pd/C were measured to be 34:1 for styrene (entry 1), 44:1 for trans-stilbene (entry 4), and 25:1 for 1-octene (entry 3). For the case of cyclic olefin such as cyclohexene, the relative reactivity of TC₈ABr–Pd is ~20-fold as high as that of 10% Pd/C (entry 5). Apparently, the catalytic activity in both systems decreases as the steric bulk increases on the olefin substituents. For the case of the trisubstituted olefin such as 2-methyl-2-butene, the hydrogenation has to be performed at an H₂ gas pressure as high as 800 psi to obtain a gross-TON value comparable to that of styrene (entries 1 and 2).

Table 2 summarizes the results of styrene hydrogenation promoted by three different catalyst systems, TC₈ABr–Pd nanoparticles, bare-Pd nanoparticles, and 10% Pd/C. The selectivity in converting styrene to ethylbenzene was demonstrated by the lack of detecting any ethylcyclohexane in all three systems using GC and/or ¹H NMR spectroscopic analyses. At an H₂ gas pressure of 100 psi, partial styrene conversions were observed in all three systems, affording the gross-TON values of 8167, 3511, and 238 (styrene mol/(Pd mol h), with an error percentage of ~5%) for TC₈ABr–Pd nanoparticles, bare-Pd nanoparticles, and 10% Pd/C, respectively. The catalytic activity increased with an increase of the H₂ gas pressure for all three systems. At an H₂ gas pressure of 600 psi, an approximate unity styrene conversion was attained for both TC₈ABr–Pd, and bare-Pd nanoparticle catalyst systems (entries 1 and 3), while ca. 97% styrene conversion with a gross-TON value of 537 was observed by using 10% Pd/C catalyst (entry 2). When the H₂ gas pressure was lowered from 100 to 50 psi, a drop of ~5% in relative catalytic activity was observed for the TC₈ABr–Pd system (entry 1, the gross-TON value changed from 8167 to 7769). Under similar reaction conditions, however, a noticeable drop of 32% in catalytic

### Table 1

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate (mmol)</th>
<th>H₂ (psi)</th>
<th>For TC₈ABr–Pd</th>
<th>For 10% Pd/C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>gross-TON&lt;sup&gt;a&lt;/sup&gt;</td>
<td>specific-TON&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>1</td>
<td>Styrene (2.6)</td>
<td>100</td>
<td>8167</td>
<td>4.4 x 10⁵</td>
</tr>
<tr>
<td>2</td>
<td>2-M ethyl-2-butene (2.8)</td>
<td>800</td>
<td>7803</td>
<td>4.2 x 10⁵</td>
</tr>
<tr>
<td>3</td>
<td>1-Octene (0.6)</td>
<td>100</td>
<td>3128</td>
<td>1.7 x 10⁵</td>
</tr>
<tr>
<td>4</td>
<td>trans-Stilbene (1.0)</td>
<td>100</td>
<td>2418</td>
<td>1.3 x 10⁵</td>
</tr>
<tr>
<td>5</td>
<td>Cyclohexene (0.5)</td>
<td>100</td>
<td>2048</td>
<td>1.1 x 10⁵</td>
</tr>
</tbody>
</table>

<sup>a</sup>R reaction conditions: mmol of substrate are given in the table; 3 ml of ethyl acetate solvent; ambient temperature; 1-h reaction time.

<sup>b</sup>0.01 M tetraoctylammonium bromide (TC₈ABr) surfactant; catalyst loading was quantified by AA spectroscopy to give 21 µg (entry 1), 21 µg (entry 2), 20 µg (entry 3), 22 µg (entry 4), and 20 µg (entry 5).

<sup>c</sup>Catalyst loading: 5 mg for entries 1-5.

<sup>d</sup>Gross-TON is defined as moles of product produced per mole of palladium per hour.

<sup>e</sup>Specific-TON is defined as the number of product molecules produced per square nanometer of Pd per hour.

<sup>f</sup>% conversion is determined by GC.

<sup>g</sup>Products were identified by both GC and NMR spectrosopies.
activity was measured for the 10% Pd/C system (entry 2, the gross-TON value changed from 238 to 163).

As stated above, TC8ABr–Pd nanoparticles were demonstrated to be a relatively more reactive catalyst system in terms of gross-TON values when compared with bare-Pd nanoparticles. Theoretically, the overall surface areas of nonsupported metal catalysts are limited by the size of the catalyst particles. The fractions of surface atoms were estimated to be 40 and 7.5% for TC8ABr–Pd (2.4 nm in diameter) and bare-Pd nanoparticles (12.7 nm in diameter), respectively. Aiso, the total surface areas for both systems, TC8ABr–Pd and bare-Pd, used for catalytic studies can be estimated based on (i) TEM to determine the averaged particle diameters, (ii) AA to extract the concentrations of Pd atoms, and (iii) the roughly calculated number of atoms in each Pd particle. Accordingly, the total surface areas exposed to the reactants in the typical 3-ml sample suspensions for the TC8ABr–Pd nanoparticles are estimated to be ca. 4.5 times larger than that of the bare-Pd nanoparticles. Therefore, the TC8ABr–Pd nanoparticles are capable of providing greater catalyst surface area and facile H2/styrene adsorption to afford higher TON values. However, the accessibility of the reactant to the Pd surface is also known to be limited by the presence of surfactant aggregates. Furthermore, the aggregation of bare-Pd nanoparticles might lead to the deactivation of their catalytic property. At this stage, each individual parameter unfortunately cannot be singled out; however, it is believed that the overall catalytic activity of the TC8ABr–Pd system should result from the combination of the aforementioned factors.

In general, the relative catalytic activity (i.e., gross-TON) of nano-sized Pd particles with or without surfactant protection was found to be higher than that of 10% Pd/C by a factor of 40 and 20, respectively. However, differences in the relative catalytic activities between Pd nanoparticles and 10% Pd/C might have to be further rationalized by the results of surface area, size effect, structures sensitivity, and/or support dependency (14, 18). Therefore, an attempt has been made to take into account of the contributions of the surface areas of Pd alone in three catalyst systems from the reported gross-TONs, namely, the specific-TON (see the Experimental section for the definition). We realized that the associated catalytic mechanisms may well be different and the correction is simply to the first-order approximation. The total surface area can be calculated by knowing the estimated number and size of particles participating in the reaction. It is directly related to the number of Pd atoms per particle, n, which is roughly estimated by n = (r/r0)3, where r0 is the atomic radius of Pd and r is the radius of the Pd nanoparticles. The average radius of the particles has been determined directly by TEM images and/or XRD analyses. As a result, values of specific-TON for the hydrogenation of styrene were estimated to be ca. $4.4 \times 10^5$ for the case of the TC8ABr–Pd catalyst (see entry 1, Table 1). For the 10% Pd/C system, which is a product with Pd nanoparticles supported on the activated carbon carrier, both TEM and XRD analyses were conducted to give an average size of Pd particle of 5 nm in diameter. By using 10% Pd/C as catalysts, the values of specific-TON corresponding to the same reaction were estimated to be $2.7 \times 10^4$ (19), which is a factor of 16 less than that of the TC8ABr–Pd catalyst. Similarly, the normalized catalytic activities after surface area correction (i.e., specific-TON) for TC8ABr–Pd stabilized Pd nanoparticles are still higher than that of 10% Pd/C by a factor of 6, 9, 15, and 9 for the other four types of hydrogenation reactions listed in Table 1 (entries 2 to 5). The results indicate that excluding the surface area effect, other parameters such as particle size (quantum effect), surface structure, shape, etc., of the nanoparticles also play key roles in determining the catalytic property of the Pd nanoparticles. Further support can be given by the comparative catalytic property between two types of laser-ablated Pd nanoparticles. The specific-TON of the bare-Pd system is found to be ca. 2-fold higher (calculated from the data in Table 2) than that for the TC8ABr–Pd system on styrene hydrogenation, which simply manifests the influence of

### TABLE 2

**Styrene Hydrogenation over Three Different Palladium Catalyst Systems**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Pd loading (µg)</th>
<th>600 psi H₂</th>
<th>100 psi H₂</th>
<th>50 psi H₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Gross-TON</td>
<td>Specific-TON</td>
<td>Gross-TON</td>
<td>Specific-TON</td>
</tr>
<tr>
<td>1</td>
<td>TC8ABr–Pd</td>
<td>21</td>
<td>NA</td>
<td>8167</td>
<td>4.4 × 10⁵</td>
</tr>
<tr>
<td>2</td>
<td>10% Pd/C</td>
<td>500</td>
<td>537</td>
<td>238</td>
<td>2.7 × 10⁴</td>
</tr>
<tr>
<td>3</td>
<td>bare-Pd</td>
<td>26</td>
<td>NA</td>
<td>3511</td>
<td>7.7 × 10⁵</td>
</tr>
</tbody>
</table>

*Product: Ethylbenzene

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Pd loading (µg)</th>
<th>600 psi H₂</th>
<th>100 psi H₂</th>
<th>50 psi H₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Gross-TON</td>
<td>Specific-TON</td>
<td>Gross-TON</td>
<td>Specific-TON</td>
</tr>
<tr>
<td>1</td>
<td>TC8ABr–Pd</td>
<td>21</td>
<td>NA</td>
<td>8167</td>
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<td>2</td>
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<td>bare-Pd</td>
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<td>NA</td>
<td>3511</td>
<td>7.7 × 10⁵</td>
</tr>
</tbody>
</table>

*a Reaction conditions: 3 ml of ethyl acetate solvent; ambient temperature; 1-h reaction time.

*b 0.01 M tetraoctylammonium bromide (TC8ABr) surfactant.

*c Catalytic loading was quantified by AA spectroscopy.

*d ND = not available, 100% conversion of styrene to ethylbenzene was observed.

*e Na = not determined, the experiment was not performed.

f Ethylbenzene was the only detectable product and was identified by both GC and NMR spectrosopies.
the surfactant molecules on the H₂/olefin adsorption and possible size and structural effects. The size- and structure-dependent catalytic activities for both supported and non-supported metal nanoparticles have been reported in the literature. For example, a significant increase in pyrene hydrogenation activity with a decrease in size of palladium nanoparticles have been reported in the literature. For example, a significant increase in pyrene hydrogenation activity with a decrease in size of palladium nanoparticles has been demonstrated (14). Also, a pronounced hydrogenation activity with a decrease in size of palladium nanoparticles has also been discussed (3b).

A series of cyclic styrene hydrogenation reactions were performed to study the relative degree of deactivation upon catalysis. Figure 2 shows the results of catalyst deactivation in terms of the decrease in styrene conversion during 10 continuous hydrogenation cycles among three systems. A high H₂ gas pressure of 600 psi, TC₈ABr–Pd nanoparticles exhibit the greatest catalyst stability with ~100% styrene conversion throughout 10 continuous cycles. Also, the TEM images of TC₈ABr–Pd nanoparticles after 10 hydrogenation cycles showed negligible difference from those freshly prepared by the laser ablation, suggesting that neither significant particle aggregation nor decomposition occurred during the course of hydrogenation. Conversely, the bare-Pd system underwent 17% deactivation (styrene conversion dropped from 100 to 83%) presumably due to a certain degree of particle aggregation. The 10% Pd/C, however, deactivated the most under the same conditions, in which the styrene conversion dropped from 98 to 48%.

CONCLUSION

In summary, various types of nano-sized Pd catalysts can be easily prepared by the laser ablation method. Smaller Pd particle sizes were obtained with the use of TC₈ABr surfactant to prevent aggregation as compared to that of the bare-Pd system. Both TC₈ABr–Pd and bare-Pd nanoparticles are proven to be powerful olefin hydrogenation catalysts over commercially available 10% Pd/C. Although surface areas should be considered to be one factor, other factors such as particle size, surface structure, etc., of the nanoparticles also play key roles to account for the indisputable differences in their relative catalytic properties toward various olefin hydrogenation. Three catalyst systems investigated in the present study exhibit different catalyst stability, which is on the order of TC₈ABr–Pd > bare-Pd > 10% Pd/C. More insights into the study of size- and structure-dependant catalytic properties are currently in progress.

ACKNOWLEDGMENTS

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REFERENCES


SUSPENDED PALLADIUM NANOPARTICLES

19. Specific-TON was obtained by assuming that the entire surface areas calculated for each Pd particle are available for the hydrogenation reaction. Note that the calculated specific-TON for the Pd/C system should be considered as a lower-limit number since a certain percentage of the surface atoms is occupied by the activated carbon carrier and only part of the surface atoms is exposed to the reactant molecules.