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Functionalized Poly(ethylene glycol)-Stabilized Water-Soluble Palladium Nanoparticles: Property/Activity Relationship for the Aerobic Alcohol Oxidation in Water

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Received July 28, 2009. Revised Manuscript Received November 9, 2009

The preparation, characterization, and catalytic properties of water-soluble palladium nanoparticles stabilized by the functionalized-poly(ethylene glycol) as a protective ligand were demonstrated for aerobic oxidation of alcohols in aqueous phase. UV/vis spectra and X-ray photoelectron spectroscopy (XPS) proved that there was an electronic interaction between the bidentate nitrogen ligand and palladium atoms. Transmission electron microscopy and XPS analysis showed that the particle size and surface properties of the generated palladium nanoparticles can be controlled by varying the amount of protective ligand and the kinds of reducing agents. It was found that both the size and surface properties of palladium nanoparticles played very important roles in affecting catalytic performance. The stabilized metallic palladium nanoparticles were proven to be the active centers for benzyl alcohol oxidation in the present system, and the water-soluble Pd nanocatalysts can also be extended to the selective oxidation of various alcohols.

1. Introduction

The selective oxidation of alcohols to the corresponding carbonyl compounds has been extensively studied, because of its ubiquitous importance in production of fine chemicals and intermediates.¹ As a consequence of the ever-growing concerns over green chemistry and chemical processes, numerous efforts have been made to develop new catalytic protocols for the oxidation of alcohols particularly with O2 as oxidant in place of the stoichiometric metal oxidants.² Among these studies, the progress for the alcohol oxidation in green solvents has received much attention in recent years.³ Especially, the aerobic oxidation of alcohols in water is considerably notable. A number of homogeneous or heterogeneous catalysts including palladium complexes or palladium nanoparticles have been investigated for the aerobic oxidation of alcohols in water.⁴ In contrast to the traditional supported metal nanoparticles that are restricted by support surfaces, soluble metal nanoparticles have many superiorities, such as controllable size, more active sites accessible to reactants, and unique nature which is freely rotational and three-dimensional.⁵ However, by referring to the previous studies on the alcohol oxidation by soluble-metal nanoparticle catalysts in water, only several examples have been demonstrated to date, that is, Pd, Pt, and Au nanoparticles stabilized by microgels or polymers (PVP, P123, or vinyl ether star polymer), respectively.⁶

The water-soluble polymer poly(ethylene glycol) (PEG) is known to be inexpensive, thermally stable, nontoxic, nonvolatile, and recoverable media for catalysis.⁷ In particular, it was reported that adding PEG in water as a cosolvent would lead to an apparent decrease in the polarity of the aqueous solution, then the consequent increase in the solubility of organic molecules.⁸ Moreover, the use of PEG as the support has attracted particular attention because of the easy recovery of the catalyst/ligand and attractive catalytic performance of the resultant catalysts. Recently, PEG-supported Pd catalysts have been successfully used in many reactions, including oxidation reactions,⁹ but Pd catalysts always suffer from deactivation due to the formation of palladium black. Therefore, the bidentate nitrogen ligands have been utilized to stabilize palladium(0) active species.¹⁰ However, there is no

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previous report of PEG anchoring bidentate dipyridyl ligand as a ligand to stabilize palladium nanoparticles employed for aerobic oxidation in water.

Although many papers have been contributed to the Pd nanoparticle-catalyzed oxidation of alcohols and moderate to excellent turnover numbers or selectivities can be obtained, studies on the relationships between nanoparticle properties and catalytic performance are unexpectedly scarce.¹¹ For better understanding the structure/activity relationship in the Pd nanoparticle-catalyzed aerobic oxidation of alcohols, further investigations are still highly required. Needless to say, an accurate control of the nanoparticle sizes is very crucial to the further application. It has been reported that the size control of the nanoparticles can be achieved by various methods.¹² But the preparation of Pd nanoparticles with controllable sizes is still a challenging task.

Recently, Hou et al.¹³ have studied the structure/activity relationship in the aerobic alcohol oxidation using Pd nanoparticles supported on hybrid mesoporous silica under supercritical carbon dioxide (scCO₂) conditions, and found that the size and agglomeration of the nanoparticles have a prominent influence on the catalytic performance of the materials. In the previous work, we have demonstrated that the functionalized PEG-stabilized Pd nanoparticles can catalyze aerobic oxidation of alcohols efficiently in PEG or scCO₂/PEG biphasic media.¹⁴ These results indicated that the bidentate nitrogen ligand functionalized-PEG played an important role in stabilizing and immobilizing catalytically active palladium(0) species. Herein, we presented the synthesis and characterization of a water-soluble palladium nanocatalyst stabilized by the functionalized-PEG, and also employed the nanocatalyst for aerobic oxidation of alcohols in aqueous phase. We attempted to establish the methods to control the size of ligand-protected Pd nanoparticles by changing the synthetic conditions systematically, and then explored the relationships between nanoparticle properties and catalytic performance in detail. Although the size effect of water-soluble metal nanoparticles on the catalytic oxidation of alcohols has been observed in the previous publication,¹⁵ to the best of our knowledge, no more detailed research about the effect of the surface properties of water-soluble metal nanoparticles on the catalytic activity for alcohols oxidation is reported.

2. Experimental Section

2.1. Materials. PEG-2000 and potassium carbonate (K_2CO_3) were obtained from SCRC (Sinopharm Chemical Reagent Co, Ltd., Shanghai). 2,2'-Dipyridylamine and palladium acetate were purchased from Aldrich. All organic solvents used in this work were dried by standard procedures.

Scheme 1. The Chemical Structure of the Functionalized-PEG2000 (L)



2.2. Preparation of Various Pd Nanoparticle Catalysts. The bidentate nitrogen ligand functionalized PEG (L) (Scheme 1) was prepared as previously reported ¹⁴ First, Pd(OAc)₂ was added to a solution of L in water, and then the mixture was stirred at room temperature overnight to give a clear pale yellow solution (Pd(II)–L complex). The different reducing agents such as NaBH₄, benzyl alcohol, H₂, and ethanol were used to prepare various Pd nanoparticles, and then the corresponding nanoparticles were designated as Pd–NaBH₄, Pd–benzyl alcohol, Pd–H₂ and Pd–ethanol, respectively.

For the synthesis of Pd-NaBH₄ catalysts, four samples were prepared by varying the molar ratio of L to Pd. For example, 1.0 mL of a fresh 0.1 M NaBH₄ solution was rapidly added to the mixture of 9.6×10^{-3} mmol Pd(OAc)₂ and 9.6×10^{-3} mmol L in 5.0 mL water under vigorous stirring for 30 min. The color of the reaction mixture immediately turned to dark brown, indicating the formation of small Pd nanoparticles (Pd-NaBH₄-1, where 1 designated the molar ratio of L/Pd). Afterward, the solution was dialyzed overnight (through a cellulose ester dialysis membrane with a cutoff molecular-weigh of 1000) using deionized water to completely remove the inorganic impurities. Then the solution of the Pd nanoparticles after dialysis was concentrated to 6.0 mL under vacuum at room temperature. The pH value of the solution changed from 8.8 to 7 after dialysis. The other Pd-NaBH₄ catalysts (Pd-NaBH₄-0.5, Pd-NaBH₄-1.5, and Pd-NaBH₄-3) were obtained in the same way by only varying the amount of L $(4.8 \times 10^{-3}, 1.44 \times 10^{-2}, \text{ and } 2.88 \times 10^{-2} \text{ mmol})$ correspondingly.

For the synthesis of Pd-benzyl alcohol, the mixture of 9.6×10^{-3} mmol L and 9.6×10^{-3} mmol Pd(OAc)₂ in 6.0 mL of water was stirred with benzyl alcohol (0.52 g, 4.8 mmol) at 90 °C for 12 h. After reduction, the brown mixture was extracted with ethyl ether three times to remove excess of benzyl alcohol, and then evaporated ethyl ether under reduced pressure at room temperature to give a brown aqueous solution. The solution was subsequently used for catalysis without further purification.

For the preparation of Pd-H₂, the mixture of 9.6×10^{-3} mmol L and 9.6×10^{-3} mmol Pd(OAc)₂ in 6.0 mL water was placed into a 50 mL autoclave and reduced by H₂ (3.0 MPa) at 25 °C for 1 h. Afterward, the autoclave was cooled down. A black solution was obtained and then used directly for catalysis.

Pd-ethanol was prepared according to the method reported by Miyake et al.¹⁶ with slight modifications. To the mixture of 9.6×10^{-3} mmol L and 9.6×10^{-3} mmol Pd(OAc)₂ in 6.0 mL of water was added 12.0 mL of ethanol, and the mixture was further refluxed for 3 h. After reaction, the color of the solution was brown. Then the aqueous solution was evaporated under reduced pressure to remove ethanol and water. Afterward, the brown residue was redispersed in 6.0 mL of water. The brown aqueous solution was subsequently used for catalysis without further purification.

2.3. Characterization of Pd Nanoparticle Catalysts. The Pd nanoparticle catalysts were characterized by UV/vis spectra, powder X-ray diffraction (XRD), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS). UV/vis spectra were obtained in aqueous solution using a Varian Cary 500 spectrophotometer. The XRD analysis was performed in D/MAX 2550 VB/PC using a graphite crystal as monochromator. The palladium nanoparticles were isolated by centrifuging and washing before XRD measurements. The TEM micrographs were

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Figure 1. UV/vis spectrum of (a) the functionalized PEG (L), (b) Pd(II)-L complex, (c) $Pd-NaBH_{4}-1$, (d) Pd(II)-L complex in aqueous solution after oxidation of benzyl alcohol at 80 °C for 8 h.

recorded on a JEOL JEM 2010 transmission electron microscope at 200 kV. Samples were prepared by directly dropping the Pd nanoparticles aqueous solutions onto carbon-coated Cu grids. More than 200 particles for each sample were randomly counted to determine the particle size distributions. XPS measurements were performed on a Thermo ESCALAB 250 spectrometer. Nonmonochro Al K α radiation was used as a primary excitation. The binding energies were calibrated with the C1s level of adventitious carbon (284.8 eV) as the internal standard reference. The samples for XPS analysis were prepared by evaporating the catalyst aqueous solution to dryness at 50 °C for 24 h under high vacuum. The molar ratio of Pd(0)/Pd(II) was approximately obtained as the ratio of peak area of the Pd(0) species of Pd 3d_{5/2} to that of the Pd(II) species of Pd 3d_{5/2}. Generally, the errors for the molar ratios of Pd(0)/Pd(II) are in the range of 10–20%.¹⁷

2.4. Typical Procedures for Oxidation of Alcohols. The typical procedure for the alcohol oxidation was described briefly. Into a reaction vessel equipped with a reflux condenser and balloon were placed the catalyst solution (0.0096 mmol Pd in 6.0 mL water), K_2CO_3 (0.2 g, 1.45 mmol), benzyl alcohol (0.10 g, 0.96 mmol). Then the mixture was heated at 80 °C for 8 h under an atmospheric pressure of O_2 with vigorous stirring. After reaction, the solution was reused after removal of diethyl ether from the aqueous phase at room temperature under vacuum. For each reaction, a parallel experiment was carried out to analyze the aqueous mixture was acidified with 7.5 mL of 2 M HCl and then extracted with diethyl ether three times.

The products in diethyl ether phase were analyzed by GC and GC–MS equipped with a HP-5MS column (30 m long, 0.25 mm i.d., $0.25 \,\mu$ m film thickness). The conversion and selectivity were determined using *n*-heptane as an internal standard in all reactions. The selectivity was defined as the moles of the designated product divided by the total moles of all the products. In the oxidation of secondary alcohols, no other byproducts were detected. But for the oxidation of primary alcohols, the very small amounts of the corresponding acids were produced as byproducts. Turnover frequency (TOF) was based on substrate turnover per mole of Pd per hour.

3. Results and Discussion

3.1. Synthesis and Characterization of Various Pd Nanoparticle Catalysts. The catalyst solution was prepared by stirring $Pd(OAc)_2$ and L overnight in water to give a clear yellow



Figure 2. X-ray diffraction pattern of Pd $-NaBH_{4}$ -1 nanoparticles. The peaks are labeled with the *hkl* of the planes for the corresponding Bragg angles.



Figure 3. XPS analysis for (a) N 1s spectra of L and Pd–NaBH₄-1, (b) Pd 3d spectra of the surface Pd centers in Pd–NaBH₄-1.

solution. Consecutively, various Pd nanoparticle catalysts were obtained by reducing the Pd(II)–L complex with different reducing agents.

The preparation processes were monitored and confirmed with UV/vis spectrum, XRD, XPS, and TEM. As shown in Figure 1, the UV/vis absorption spectrum of L appeared in the range of 200–350 nm. The peaks at 231.6 and 271.4 nm were ascribed to the intraligand $\pi - \pi^*$ transition of pyridyl rings, and the band at 312.3 nm may be due to the $n-\pi^*$ transition.^{18,19} After L was coordinated with Pd(OAc)₂ in aqueous phase, the blue shifts of the absorption bands of L were observed (Figure 1a,b), which implied the charge transfer between Pd(II) species and L, in other words, the formation of the Pd(II)-L complex. After reduction, the absorption spectrum of the solution was totally different from that of the Pd(II)-L complex, which indicated the formation of the Pd nanoparticles (Figure 1b,c). And some changes were also

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Figure 4. TEM micrographs and size distributions of Pd nanoparticles with different reducing agents (scale bar = 50 nm): (a) Pd-benzyl alcohol; (b) Pd-H₂; (c) Pd-ethanol.

observed between the absorption spectra of $Pd-NaBH_4$ -1 and L (Figure 1a,c), but the changes were rather small probably because of a decrease in both an electron-withdrawing force and the number of Pd atoms coordinated to N atoms for the reduced Pd(0) species compared with Pd(II)-L complex.

XRD was also used to examine the crystal structure of the Pd nanoparticles (Figure 2). XRD pattern of the Pd–NaBH₄-1 nanoparticles clearly showed the diffraction peaks corresponding to (111), (200), (220), and (311) lattice planes, indicating a face-centered-cube (fcc) phase.

To gain insight into the surface characteristic of the modified Pd nanoparticles, the XPS spectra of L and Pd–NaBH₄-1 were measured. Figure 3 showed the spectra of Pd 3d and N 1s regions. As shown in Figure 3a, compared to the N 1s binding energy of L (397.6 eV), that of Pd–NaBH₄-1 was shifted toward higher

binding energy (+1.1 eV), indicating that the N atoms of L was in an electron-poor state due to the coordination of these atoms to Pd atoms.²⁰ Furthermore, the Pd 3d spectrum of Pd–NaBH₄-1 showed two distinct signals, which indicated the presence of two surfacebound species (Figure 3b). As presented in Figure 3a, because the N atoms of L was in an electron-poor state, the surface Pd atoms coordinating to N atoms should be in an electron-rich state, so the binding energy of the surface palladium atoms would shift to a lower value. Nevertheless, the main peak, Pd $3d_{5/2}$, was virtually the same as the specimens of the giant clusters of Pd(0) or the bulk metal Pd (334.8 eV), corresponding to palladium in a zero oxidation state.²¹ This may be ascribed to the size effect that the values of binding energy have a tendency to become larger for the smaller nanoparticles.^{20a,22} The competition of the opposite factors resulted in a little

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Figure 5. TEM micrographs and size distributions of different Pd nanoparticle catalysts at various molar ratio of L/Pd (scale bar = 50 nm): (a) Pd-NaBH₄-0.5; (b) Pd-NaBH₄-1; (c) Pd-NaBH₄-1.5; (d) Pd-NaBH₄-3.

change of the binding energy. Besides, a very small shoulder with the binding energy $E_{\rm b} = 336.8$ eV in the spectra might be assigned to the interaction between Pd(II) species and 2,2'-dipyridylamine ligand,¹³ which indicated that the Pd(II) species were in

an electron-rich state, compared with $Pd(OAc)_2 (E_b = 338.6 \text{ eV}).^{21}$ As a result, the XPS results indicated that the Pd centers were reduced to a great extent by NaBH₄ treatment, resulting in the 9.9 ± 1.98 molar ratio of Pd(0)/Pd(II) at the surface of Pd nanoparticles.

 Table 1. Comparison of the Catalytic Performance of Different Pd

 Species^a

entry	catalyst	<i>t</i> (h)	conversion $(\%)^b$
1^c	Pd(II)-L	1	0.2
2		8	1.9
3 ^c	Pd-NaBH ₄ -1	1	28.0
4		8	38.9

^{*a*} Reaction conditions: 0.96 mmol benzyl alcohol, 6 mL of catalyst solution, without K_2CO_3 , 80 °C, 1 atm O_2 . ^{*b*} Based on GC, benzaldehyde was detected as the only product. ^{*c*} A total of 1.92 mmol benzyl alcohol.

 Table 2. Comparison of the Catalytic Performance of Various Pd

 Nanoparticles Using Different Reducing Agents^a

entry	catalyst	particle size (nm)	oxidation state of surface Pd (XPS) (Pd(0)/Pd(II))	TOF (h^{-1})
1	Pd−NaBH₄-1	2.6 ± 0.4	9.9 ± 1.98	56.0
2	Pd-ethanol	2.4 ± 0.3	0.3 ± 0.06	28.4
3	Pd-H ₂	3.5 ± 0.5	3.7 ± 0.74	49.8
4	Pd-benzyl	3.8 ± 0.5	0.7 ± 0.14	32.0
	alcohol			

 a Reaction conditions: 1.92 mmol benzyl alcohol, 6 mL of catalyst solution, without K₂CO₃, 80 °C, 1 atm O₂, 1 h. Benzaldehyde was detected as the only product.

It has been reported that the reduction method used in the preparation of nanoparticles has a decisive influence on the particle size and surface properties, which in turn defines the catalytic performance of the materials.²³ For comparison, three other water-soluble Pd nanoparticle catalysts were prepared using different reducing agents instead of NaBH₄, including benzyl alcohol (Pd-benzyl alcohol), H₂ (Pd-H₂), and ethanol (Pd-ethanol). As shown in Figure 4, these Pd nanoparticles were well dispersed in aqueous phase and the TEM images showed mean diameters of 3.8, 3.5, and 2.4 nm, respectively. XPS analysis was also performed to assess the surface characteristic of these Pd nanoparticles, and the results were summarized in Table 2. Compared with Pd-NaBH₄-1, the other three Pd nanocatalysts contained significant amounts of unreduced Pd sites, corresponding to 0.7 ± 0.14 , 3.7 ± 0.74 , and 0.3 ± 0.06 molar ratio of Pd(0)/ Pd(II) at the surface, respectively.

UV/vis spectrum showed that the functionalized-PEG would coordinate with the surface Pd atoms of the nanoparticles. Besides, the analysis of XPS confirmed the ligands (L) were strongly adsorbed on the surface Pd atoms. These results explained perfectly the reasons why the Pd nanoparticles can be stabilized effectively by the functionalized-PEG (L). As a result, the amount of L added to the solution was expected to affect the growth process of the Pd nanoparticles. Therefore, the influence of the molar ratio of L to Pd on the size of the Pd nanoparticles was investigated. Figure 5 showed the TEM micrographs and size distributions of different Pd nanoparticle catalysts at various molar ratios of L/Pd. As shown in Figure 5, the particles were roughly spherical and possessed mean diameters of 2.8, 2.6, 2.4, and 2.2 nm, respectively, with narrow size distributions. Notwithstanding limited dependence of Pd nanoparticle size on the amount of L under the present conditions, a small decrease in size with increasing L was still observed. As a consequence, the size control of the Pd nanoparticles could be achieved by varying the kind of reducing agents or the amount of L. Moreover, the surface composition of the nanoparticles can also be tuned by

 Table 3. Comparison of the Catalytic Performance of Various Pd

 Nanoparticles with Different L/Pd (Molar Ratio)^a

entry	catalyst	particle size (nm)	$TOF(h^{-1})$
1	Pd-NaBH ₄ -0.5	2.8 ± 0.4	41.2
2	Pd-NaBH ₄ -1	2.6 ± 0.4	56.0
3	Pd-NaBH ₄ -1.5	2.4 ± 0.2	32.4
4	Pd-NaBH ₄ -3	2.2 ± 0.2	30.0

 $^{\it a}$ Reaction conditions: 1.92 mmol benzyl alcohol, 6 mL of catalyst solution, without $K_2CO_3,$ 80 °C, 1 atm $O_2,$ 1 h. Benzaldehyde was detected as the only product.

Table 4. Aerobic Oxidation of Benzyl Alcohol in Water Using $Pd-NaBH_4-1^a$

entry	$T(^{\circ}\mathrm{C})$	<i>t</i> (h)	run	conversion $(\%)^b$	selectivity $(\%)^b$
1 ^c	80	8	1	53.6(38.9) ^e	$99.8(100)^{e}$
2^d	80	8	1	83.0	99.5
3	50	8	1	60.2	99.8
4	80	4	1	83.5	99.0
5	80	8	1	$96.4(98.1)^{e}$	$98.8(99.0)^{e}$
6			2	$96.1(96.5)^{e}$	$98.2(98.0)^{e}$
7			3	$95.2(94.0)^{e}$	$98.5(98.8)^{e}$
8			4	93.0	97.1

^{*a*} Reaction conditions: 0.96 mmol benzyl alcohol, 0.2 g of K₂CO₃, 6 mL of Pd–NaBH₄-1 catalyst solution without dialysis/purification, 1 atm O₂. ^{*b*} Based on GC, benzoic acid was detected as a byproduct. ^{*c*} Without K₂CO₃. ^{*d*} A total of 0.1 g of K₂CO₃. ^{*e*} The conversion and selectivity in parentheses were obtained with the Pd–NaBH₄-1 catalyst purified by dialysis.

adopting appropriate reducing agents in the preparation of nanoparticles.

3.2. Active Pd Species for Aerobic Oxidation of Alco**hols.** First, in an effort to investigate the potential application of different Pd species, oxidation of benzyl alcohol was carried out under atmospheric O2 pressure using Pd catalysts in its oxidized and reduced state. The results were summarized in Table 1. It was important to note that Pd(II)-L complex exhibited hardly any catalytic activity for benzyl alcohol oxidation under the present conditions (entries 1 and 2, Table 1), where metallic Pd nanoparticles were much more active (entries 3 and 4, Table 1). Experimentally, no concomitant color change was observed and then no noticeable O_2 uptake was detected by using water-soluble Pd(II)-L complex as a catalyst. Furthermore, the UV/vis spectra of recovered Pd(II) catalyst was identical to that of fresh Pd(II) species, revealing that electronic configuration of the Pd species did not change (Figure 1b,d). TEM examination also proved that there was no formation of Pd particles after the alcohol oxidation. From the above results, it could be concluded that the catalytically active species were not the Pd(II) species but the Pd nanoparticles in the present catalytic system. Baiker et al.²⁴ investigated the oxidation of benzyl alcohol over Pd/Al₂O₃ catalysts by using FT-IR spectroscopy and in situ X-ray absorption spectroscopy combined with online catalytic measurements, and they found that the catalysts after in situ reduction by hydrogen-saturated cyclohexane were much more active (over 50 times) than before reduction. The studies on active species in Pd-catalyzed aerobic alcohol oxidation by the other groups also came to the similar conclusion.²⁵

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Figure 6. TEM micrographs and size distributions of $Pd-NaBH_4$ -1 after four successive runs in the oxidation of benzyl alcohol (scale bar = 50 nm).



Figure 7. (a) Pd nanoparticles in Pd–NaBH₄-1 were dispersed homogeneously in aqueous phase; (b) the bulk Pd particles were completely precipitated from aqueous solution when L was replaced by PEG2000.

3.3. The Relationships between Pd Nanoparticle Properties and Catalytic Performance in the Oxidation of Benzyl Alcohol. Catalytic activities of metal nanoparticles have been shown to depend strongly on the size of nanoparticles, the metal oxidation states, etc.²⁶ Generally, the alcohol oxidation is considered "structure-sensitive", and smaller metal particles containing more coordinately unsaturated metal sites are believed to be more active.²⁷ To further understand the nature of the Pd nanocatalysts, we examined the effects of the size of Pd nanoparticles and their surface properties on the catalytic activity. The catalytic activities of various Pd nanoparticle catalysts were evaluated for aerobic oxidation of benzyl alcohol at the initial reaction stage in water (conversion < 30%). We first examined the catalytic activities of various Pd nanoparticles with different reducing agents, and the results were summarized in Table 2. The TOF for oxidation of benzyl alcohol decreased as follows: $Pd-NaBH_{4}-1$ (56.0 h^{-1}) > $Pd-H_{2}$ (49.8 h^{-1}) > Pd-benzylalcohol $(32.0 \text{ h}^{-1}) > \text{Pd-ethanol} (28.4 \text{ h}^{-1})$. It was worth noting that the catalytic performance was not consistent with the size effect that the smaller the size, the higher the activity. Especially, two representative Pd nanoparticles (Pd-NaBH₄-1 and Pd-ethanol) with the similar size (2.6 and 2.4 nm) showed remarkable different catalytic activities. Similar phenomenon was also observed for Pd-H₂ (3.5 nm) and Pd-benzyl alcohol (3.8 nm) catalysts. The differences in the activities of four Pd nanoparticle catalysts indicated that some other factors may also contribute to the catalytic performance of the Pd nanoparticles. These factors can be ascribed to the different metal oxidation states of the surface of Pd nanoparticles. From the XPS analysis, the oxidation states of the various Pd nanoparticles were greatly different, and the oxidation state of Pd in the nanocatalyst had a significant influence on catalytic activity for benzyl alcohol oxidation under the present conditions. Upon consideration of the palladium(0) species as catalytically active species, the catalytic performance of the four Pd nanoparticle catalysts could correlate well with their states (entry 1 vs 2, 3 vs 4, Table 2). As a result, Pd-NaBH₄-1 with smaller particle size and more active metallic palladium showed the highest catalytic activity (entry 1, Table 2).

Then, Pd-NaBH₄ catalysts at different molar ratios of L/Pd were examined in the oxidation of benzyl alcohol under the same reaction conditions and the results were listed in Table 3. The TOF exhibited a notable dependence on the mole ratio of L/Pd that maximized at a L/Pd ratio of 1:1 (entry 2, Table 3). At the ratio of L/Pd below 1:1, the nanocatalyst was accompanied by Pd aggregation and then the activity was lower (entry 1, Table 3). Though the Pd nanoparticles were more stable in aqueous phase and also their sizes became smaller at increased ratio of L/Pd, the reaction rate was strongly inhibited possibly because of the poison of the excess ligands (entries 3 and 4, Table 3). The catalytic composition of L/Pd = 1:1 appeared to reflect a balance between optimal turnover rate and catalyst stability. Accordingly, we anticipated that these properties of the metal particles can be controlled by finely tuning the interactions between the ligand with the metal nanocluster surfaces, thus leading to improvement in the activities and stability of soluble Pd nanoparticles. These results indicated that the chosen reduction method of the Pd(II) precursor exerted a controlling effect on the particle size and oxidation state distribution of the obtained palladium species, resulting in very significant differences in the catalytic activity.

3.4. Catalytic Performance of Pd-NaBH₄-1 in the Aerobic Oxidation of Benzyl Alcohol. In detail, then we examined

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Table 5. Aerobic Oxidation of Various Alcohols Using Pd-NaBH₄-1^a

Entry	Substrate	Product	T (°C)	t (h)	Conv. (%) ^b	Sel. (%) ^b
1°	ОМ		80	6	99.3(97.0) ^f	98.9(99.0) ^f
2 ^{c, d}	С		90	16	95.4	95.6
3 ^{c, d}	ОН		80	12	41.4(40.5) ^f	99.0(99.2) ^f
4	OH		100	20	5.7	100
5°	OH		100	20	45.7	100
6	ОН	O	80	24	8.0(8.7) ^f	100(100) ^f
7 ^e	ОН	o	80	24	31.8(33.6) ^f	100(100) ^f

^{*a*} Reaction conditions: 0.96 mmol alcohol, 6 mL of Pd–NaBH₄-1 catalyst solution without dialysis/purification, 1 atm O₂, 0.2 g K₂CO₃. ^{*b*} Based on GC. ^{*c*} The corresponding acid was detected as a byproduct. ^{*d*} A total of 0.48 mmol alcohol. ^{*e*} There was 3.0 g of PEG-2000 in 3.0 mL of H₂O as cosolvent. ^{*f*} The conversion and selectivity in parentheses were obtained with the Pd–NaBH₄-1 catalyst purified by dialysis.

the catalytic activity of Pd-NaBH₄-1 toward aerobic oxidation of benzyl alcohol in water, and the results were summarized in Table 4. It was found that the activity and the selectivity to benzyladehyde were little affected by dialysis for purification of Pd nanoparticles in the presence of a base (entries 5, 6 and 7, Table 4). As shown in Table 4, the presence of K_2CO_3 can significantly promote selective oxidation of benzyl alcohol, and the amount of K₂CO₃ had an influence on the activity (entries 1, 2, and 5, Table 4). This may be explained by the previously reported mechanism of alcohol oxidation over Pd nanoparticles,25a,28 which involved β -H elimination of a dissociated alcohol on the Pd surface, followed by reaction of oxygen with Pd-H species, while the base can promote the deprotonation of the alcohol toward dehydrogenation. With the optimized conditions (entries 3, 4, and 5, Table 4), benzyl alcohol could be oxidized to form benzaldehyde with high conversion and selectivity. Compared with other recently reported Pd nanoparticle catalyst for alcohols oxidation with oxygen in water, the productivity of present catalysts appeared to be higher than that of palladium nanoparticles supported on hydroxyapatite (95% yield after 7 h at 100 °C).²⁹ Moreover, the present catalyst can be used under more mild conditions (80 °C).

The recyclability of the Pd nanoparticle catalyst was also examined in the oxidation of benzyl alcohol. This catalyst can be readily recycled after simple extraction by ethyl ether. As shown in Table 4, the conversion and selectivity to benzaldehyde remained essentially constant for the four successive cycles (entries 5-8, Table 4); no Pd deposits were observed, reflecting high stability and reusability of the catalyst. Indeed, after four catalytic runs, the Pd nanoparticles were still well dispersed in water with a slight increase in the particle size (3.0 nm) (Figure 5b vs Figure 6). Such a stability was superior to that of the above-mentioned soluble metal nanoparticle catalysts in the alcohols oxidation in water.^{6a,15a}

It should be worth noting that when **L** was replaced by PEG2000 as the stabilizer to prepare a new catalyst under the same conditions, the bulk Pd particles were formed rapidly and deposited completely from the solution after reduction with NaBH₄ (Figure 7b), and the aqueous phase became colorless and clear, which was totally different from the case of Pd–NaBH₄-1 (Figure 7a). Therefore, we believed that almost all the Pd nanoparticles in Pd–NaBH₄-1 should be coordinated with the functionalized-PEG (L) that was effective for preventing the aggregation of Pd–NaBH₄-1.

3.5. The Scope of Pd-NaBH₄-1 Catalyst. Then, Pd-NaBH₄-1 was examined for the aerobic oxidation of various alcohols (Table 5). Allyl alcohols such as 3-methyl-2-buten-1-ol, geraniol, and cinnamyl alcohol were oxidized selectively into the corresponding aldehydes in moderate to high conversions, that is, 41.4, 95.4, and 99.3%, respectively (entries 1-3, Table 5). The high reactivity toward the oxidation of allyl alcohols could be ascribed to the high coordination ability of the C=C double bond of the alcohols to the Pd species as an anchor, which could also enhance the interaction of the hydroxyl group with Pd species. Unfortunately, some other nonactivated and poorly water-soluble aliphatic secondary alcohols exhibited much lower catalytic productivity than the benzylic ones; 2-octanol and cyclohexanol reached conversions of only 5.7% and 8.0%, respectively (entries 4 and 6, Table 5). This was not entirely surprising, however, because aliphatic alcohols were known to be much more demanding substrates for this kind of reaction whenever Pd metal catalysts were used, as can be inferred from the literatures.^{15a,25a} However, these nonactivated alcohols could be converted to corresponding ketones with moderate conversions (45.7% and 31.8%) in the presence of PEG (entries 5 and 7, Table 5). The improvement of the conversion may attribute to the increase in solubility of the substrates in water, due to an apparent

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decrease of the aqueous solution polarity after adding PEG as a cosolvent. 8

4. Conclusions

In the present work, we have synthesized stable, size-controlled, water-soluble Pd nanoparticle catalysts using bidentate nitrogen ligand functionalized PEG as a stabilizing reagent, and then investigated their properties as well as their catalytic performance for the aerobic oxidation of alcohols in water. UV/vis spectra and XPS analysis showed that there was an electronic interaction between the bidentate nitrogen ligand and palladium atoms. It was found that the particle size decreased with increasing the amount of the functionalized PEG. Also, the reduction methods used in the preparation of nanoparticles had a decisive influence on the particle size and surface properties. By relating activity data to the properties of Pd nanoparticles, we found that the metallic palladium was the active species for benzyl alcohol oxidation in the present system, moreover, the catalytic performance depended strongly on the properties (size and oxidation state) of Pd nanoparticles. The oxidation of various alcohols was carried out smoothly by using the water-soluble Pd nanoparticles. We have also illustrated that the nanocatalyst can be recycled at least four times without any loss of catalytic activity. Further efforts to extend the application of this system in other reactions are in progress in our laboratory.

Acknowledgment. We are grateful for the support from the National Natural Science Foundation of China (No. 20773037), ECUST (No. YJ0142136), the Commission of Science and Technology of Shanghai Municipality (No.07PJ14023), China, and Key Laboratory of Catalysis and Materials Science of the State Ethnic Affairs Commission and Ministry of Education, Hubei Province, South-Central University for Nationalities (No. CHCL08001), China. The authors would also like to express their thanks to Prof. Walter Leitner's helpful suggestions and Dr. Nils Theyssen's assistance.