DOI: 10.1002/adsc.200700350

Size-Dependent Catalytic Activity of Supported Palladium Nanoparticles for Aerobic Oxidation of Alcohols

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Received: July 17, 2007; Revised: December 29, 2007; Published online: February 11, 2008

Abstract: Silica-alumina (SiO_2-Al_2O_3)-supported palladium catalysts prepared by adsorption of the tetrachloropalladate anion ($PdCl_4^{2-}$) followed by calcination and reduction with either hexanol or hydrogen were studied for the aerobic oxidation of alcohols. The mean size of the Pd particles over the SiO_2-Al_2O_3 support was found to depend on the Si/Al ratio, and a decrease in the Si/Al ratio resulted in a decrease in the mean size of the Pd nanoparticles. By changing the Si/Al ratio, we obtained supported Pd nanoparticles with mean sizes ranging from 2.2 to 10 nm. The interaction between the Pd precursor and the support was proposed to play a key role in tuning the mean size of the Pd nanoparticles. The Pd/SiO_2-Al_2O_3 catalyst with an appropriate mean size of Pd particles could catalyze the aerobic oxidation of various alcohols to the corresponding carbonyl compounds, and this catalyst was particularly efficient for the solvent-free conversion of benzyl alcohol. The intrinsic turnover frequency per surface Pd atom depended significantly on the mean size of Pd particles and showed a maximum at a medium mean size (3.6–4.3 nm), revealing that the aerobic oxidation of benzyl alcohol catalyzed by the supported Pd nanoparticles was structure-sensitive.

Keywords: aerobic oxidation; alcohols; heterogeneous catalysis; palladium; solvent-free reactions; structure-activity relationships

Introduction

The selective oxidation of alcohols to the corresponding carbonyl compounds is one of the most essential transformations in the synthesis of fine chemicals and intermediates.[1] Currently, many such transformations are still being carried out using stoichiometric oxidants such as dichromate and permanganate. However, these stoichiometric oxidants are expensive and/or toxic, and have the problem of producing a large amount of wastes. From the viewpoints of green chemistry, there is an urgent need to develop a catalytic oxidation process using oxygen or air as the oxidant in place of the stoichiometric metal oxidants. A number of homogeneous catalysts including palladium(II) salts or complexes has been investigated for the aerobic oxidation of alcohols.[2] As compared with the homogeneous catalysts, heterogeneous catalysts generally possess advantages in product isolation and catalyst recycling operations, and have received much attention for the aerobic oxidation of alcohols in recent years.[3]

Among various heterogeneous catalysts reported, palladium-based catalysts showed particularly promising performances for the aerobic oxidation of alcohols. Some of these catalysts were heterogenized analogues of homogeneous Pd complexes. For example, the Pd(II) acetate-pyridine complex supported on hydrotalcite was found to be effective for the aerobic oxidation of various alcohols in the presence of pyridine in toluene as solvent, and the catalyst could be reused several times.[4] A 1,10-phenanthroline ligand-preserved Pd cluster (*ca.* 3 nm in size) immobilized on TiO_2 catalyzed the oxidation of primary alcohols by oxygen in acetic acid.[5] A bipyridylamide-bound ionic Pd species located inside the mesoporous channels of SBA-15 could catalyze the aerobic oxidation of alcohols in the presence of K_2CO_3 in toluene,[6] but it was also pointed out that the derived Pd nanoparticles may also account for the actual activity.

Simple heterogeneous Pd catalysts without any additives and organic ligands have attracted particular interest for the aerobic oxidation of alcohols in recent years. Mori et al.[7] reported an efficient alcohol oxidation catalyst based on a hydroxyapatite-immobilized Pd(II) catalyst. Benzylic alcohols could even be oxidized with this catalyst under solvent-free conditions, and the turnover frequency (TOF) for the oxidation of 1-phenylethanol reached 9800 h^{-1}, markedly higher than both the heterogeneous and the homogeneous catalysts reported previously. An induction period was observed during the oxidation of 1-phenylethanol over this catalyst, and it was demonstrated that the monomeric Pd(II) species were transformed to Pd nanoparticles (3–4 nm) during the reaction, which were proposed to be the genuine active species.[7b] Grunwaldt et al.[8] recently clarified that metallic Pd is more active for the aerobic oxidation of benzyl alcohol than the oxidic Pd species using *in situ* X-ray absorption spectroscopy. Although a few papers report that palladium oxide can act as the active phase for alcohol oxidation,[9,10] most of recent studies have shown that the supported Pd nanoparticles are excellent catalysts for the selective oxidation of alcohols by oxygen or air.[11–15] For example, Pd/MgO containing Pd particles with a mean size of 6.9 nm was reported to be efficient for the aerobic oxidation of various alcohols in trifluorotoluene solvent.[11] Pd nanoparticles with a mean diameter of *ca.* 9 nm supported on an amphiphilic resin catalyzed the aerobic oxidation of benzylic and allylic alcohols in water medium.[12] Palladium nanoparticles entrapped in aluminum hydroxide with sizes of *ca.* 2–3 nm or supported on aluminum oxide with diameters of *ca.* 5 nm were efficient catalysts for the aerobic oxidation of alcohols.[13,14] Pd nanoparticles located in zeolite NaX or mesoporous silica SBA-15 could catalyze the solvent-free aerobic oxidation of several kinds of alcohols.[15,16] A Pd-Au/TiO_2 catalyst could give excellent TOFs for the aerobic oxidation of various alcohols, and it was suggested that the Au-Pd nanocrystals made of an Au-rich core with a Pd-rich shell accounted for the superior catalytic performances of this catalyst.[17]

It is well known that catalytic performances can be very sensitive to the size of the active phase.[18] Many Pd nanoparticles-catalyzed organic reactions such as hydrogenation, Heck and Suzuki couplings, and vinyl acetate synthesis are structure sensitive.[19–22] In other words, the conversion rate per surface Pd atom in these reactions changes with the size of Pd particles. Although many papers have been contributed to the Pd nanoparticles-catalyzed oxidation of alcohols,[11–17] studies on the effect of Pd particle size are unexpectedly scarce.[7b,15] Mori et al.[7b] compared the catalytic activities of two Pd/hydroxyapatite catalysts containing Pd nanoclusters with mean diameters of 3.8 and 7.8 nm for the aerobic oxidation of 1-phenylethanol and benzhydrol, and found that the smaller Pd nanoclusters (3.8 nm) gave a higher TOF than the larger Pd nanoclusters.

Further studies using catalysts containing Pd nanoparticles prepared on other general supports and with mean sizes variable over a larger range are undoubtedly helpful in better understanding the size-dependence in the Pd nanoparticles-catalyzed aerobic oxidation of alcohols. The preparation of Pd nanoparticles with controllable mean sizes is still a challenging task. Generally, Pd nanoparticles can be prepared by reduction of ionic or oxidic Pd species with a proper reductant such as hydrogen or alcohol. The presence of a stabilizer such as linear polymers, surfactants or heterogeneous supports may prevent the nanoparticles from aggregation.[23] For the reduction with alcohols, previous studies showed that the kind of alcohols used for reduction could control the mean size of Pd nanoparticles finally obtained.[7b,23] Very recently, we succeeded in preparing silica-alumina (SiO_2-Al_2O_3)-supported Pd nanoparticles with tunable mean sizes. We found that, by varying the ratio of Si/Al in the oxide support, catalysts containing Pd nanoparticles with mean sizes of 2.2 to 10 nm could be prepared after reduction. In this paper, we report the characterizations of the Pd nanoparticles supported on the SiO_2-Al_2O_3 mixed oxides and the size-dependent catalytic activity of the prepared Pd nanoparticles in the aerobic oxidation of benzyl alcohol.

Results and Discussion

Characterization of SiO_2-Al_2O_3-Supported Pd Nanoparticles

Figure 1 shows the XRD patterns of the SiO_2-Al_2O_3 mixed oxides. Al_2O_3 without SiO_2 exhibited three peaks at 2θ of *ca.* 37.5, 46.0 and 66.7°, which could be assigned to γ-Al_2O_3, while SiO_2 alone showed a broad diffraction peak at 2θ of 22–23°, assignable to the amorphous silica. The diffraction peaks belonging to γ-Al_2O_3 were observable for the SiO_2-Al_2O_3 mixed

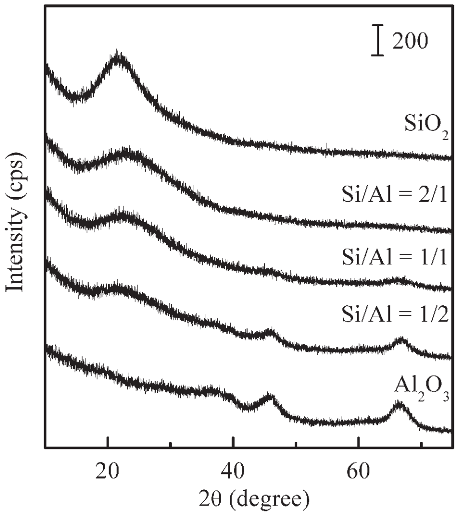


Figure 1. XRD patterns of SiO_2-Al_2O_3 samples with different Si/Al ratios along with SiO_2 and Al_2O_3.

oxides with Si/Al ratios of 1/1 and 1/2, suggesting that these samples were comprised of γ-Al_2O_3 together with amorphous silica. On the other hand, the SiO_2-Al_2O_3 mixed oxide with an Si/Al ratio of 2/1 was only comprised of an amorphous silica phase, and Al_2O_3 might be dispersed on SiO_2 or also exist in amorphous phase. After loading of palladium, the XRD patterns did not change, and no additional diffraction peaks assignable to any palladium compounds such as PdO or metallic Pd could be observed before or after reduction because the content of Pd in the samples we prepared using the adsorption method was low (Table 1).

Because the change in Si/Al ratio may affect the acidity of the catalyst and may thus change the catalytic behavior, we have investigated the acidic properties of some typical Pd/SiO_2-Al_2O_3 catalysts after H_2 reduction by NH_3-TPD measurements. As shown in Figure 2, the samples using SiO_2 and SiO_2-Al_2O_3 with lower Al contents (Si/Al = 2/1 and 1/1) as the supports only exhibited a single NH_3 desorption peak at 455–476 K, which could be attributed to the desorption from weak Lewis acid sites. On the other hand, in addition to this lower temperature peak, a broad desorption peak at ~660 K was also observed for the samples with higher Al contents, i.e., Pd/Al_2O_3 and Pd/SiO_2-Al_2O_3 (Si/Al = 1/2). Thus, acid sites with medium strength appeared on these samples. As compared with the pure Al_2O_3, the doping of SiO_2 into Al_2O_3 with an Si/Al ratio of 1/2 increased the concentrations of both weak- and medium-strength acid sites. It is known that the formation of composite metal oxides may enhance the acidity.[24,25]

The oxidation state of palladium before and after reduction was determined by XPS. Figure 3 shows the spectra of Pd 3*d* for some typical samples before and after the reduction with hexanol. The binding energies of Pd $3d_{5/2}$ for the samples before reduction (but after calcination) were observed at *ca.* 336.3 eV, which can be assigned to Pd(II) in palladium oxide or halide.[26] After the reduction with hexanol under refluxing conditions for 6 h, the binding energy of Pd $3d_{5/2}$ in each sample decreased to *ca.* 335.1 eV, corresponding to metallic palladium species.[26] The reduction with H_2 at 573 K for 30 min also shifted the binding energy of Pd $3d_{5/2}$ in each sample to *ca.* 335.1 eV, confirming that Pd(II) was also reduced to Pd(0) in this case. We also recorded the XPS spectra of the

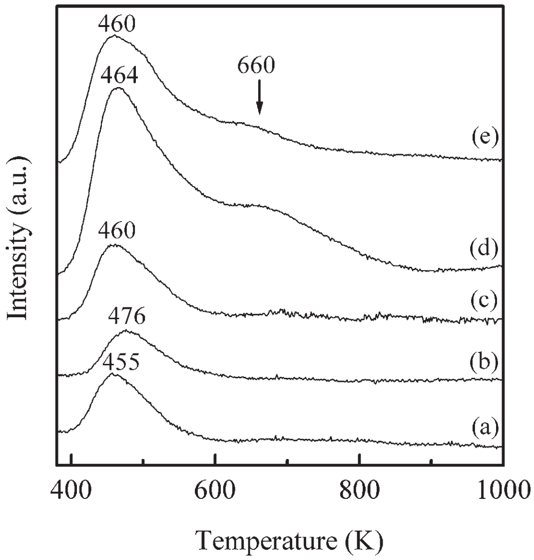


Figure 2. NH_3-TPD profiles of samples after H_2 reduction. (a) 0.55 wt% Pd/SiO_2, (b) 0.52 wt% Pd/SiO_2-Al_2O_3 (Si/Al = 2/1), (c) 0.30 wt% Pd/SiO_2-Al_2O_3 (Si/Al = 1/1), (d) 0.52 wt% Pd/SiO_2-Al_2O_3 (Si/Al = 1/2), (e) 0.53 wt% Pd/Al_2O_3.

Table 1. Content, particles size and dispersion of palladium in SiO_2-Al_2O_3-supported Pd catalysts.

Sample[a]	Pd content [wt%]	Mean size of Pd [nm]	Pd dispersion[b]	Pd dispersion[c]
Pd/SiO_2-*hexanol*	0.55	5.7	0.20	n.d.[d]
Pd/SiO_2-Al_2O_3-*hexanol* (2/1)	0.52	5.1	0.22	n.d.
Pd/SiO_2-Al_2O_3-*hexanol* (1/1)	0.30	4.2	0.27	n.d.
Pd/SiO_2-Al_2O_3-*hexanol* (1/2)	0.52	3.2	0.35	n.d.
Pd/Al_2O_3-*hexanol*	0.53	2.6	0.43	n.d.
Pd/SiO_2-H_2	0.55	10	0.11	0.04
Pd/SiO_2-Al_2O_3-H_2 (2/1)	0.52	4.3	0.26	0.27
Pd/SiO_2-Al_2O_3-H_2 (1/1)	0.30	3.6	0. 31	0.34
Pd/SiO_2-Al_2O_3-H_2 (1/2)	0.30	3.1	0.36	0.39
Pd/SiO_2-Al_2O_3-H_2 (1/2)	0.52	3.1	0.36	0.37
Pd/SiO_2-Al_2O_3-H_2 (1/4)	0.39	2.9	0.39	0.43
Pd/SiO_2-Al_2O_3-H_2 (1/4)	0.56	2.7	0.42	0.48
Pd/Al_2O_3-H_2	0.53	2.2	0.51	0.69

[a] The ratio in the parenthesis is the Si/Al ratio; *hexanol* and H_2 denote the reductant used for the preparation.
[b] Estimated from the mean size of Pd particles by 1.12/(mean size of Pd) (nm).
[c] Evaluated from CO chemisorption measurements.
[d] Not detectable.

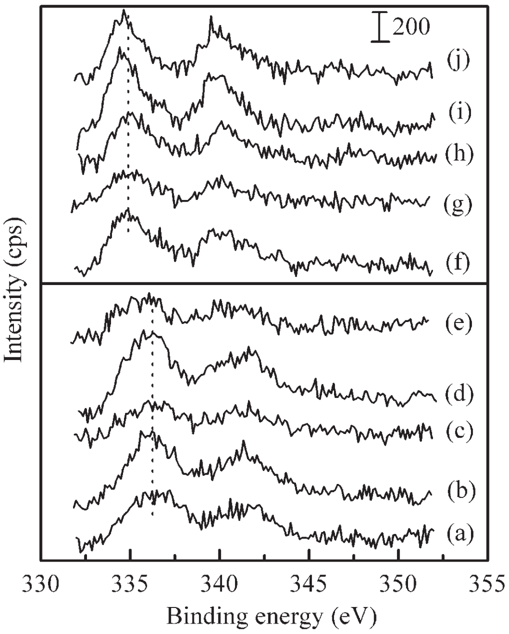


Figure 3. Pd 3*d* XPS spectra of Pd/SiO_2-Al_2O_3 before and after reductions with hexanol. Before reductions: (a) 0.53 wt% Pd/Al_2O_3, (b) 0.52 wt% Pd/SiO_2-Al_2O_3 (Si/Al = 1/2), (c) 0.30 wt% Pd/SiO_2-Al_2O_3 (Si/Al = 1/1), (d) 0.52 wt% Pd/ SiO_2-Al_2O_3 (Si/Al = 2/1), (e) 0.55 wt% Pd/SiO_2; after reduction: (f) 0.53 wt% Pd/Al_2O_3, (g) 0.52 wt% Pd/SiO_2-Al_2O_3 (Si/Al = 1/2), (h) 0.30 wt% Pd/SiO_2-Al_2O_3 (Si/Al = /1), (i) 0.52 wt% Pd/SiO_2-Al_2O_3 (Si/Al = 2/1), (j) 0.55 wt% Pd/SiO_2.

samples reduced with H_2 at 573 K for 10 min. We found that the binding energies of Pd $3d_{5/2}$ for the Pd/ SiO_2 and Pd/SiO_2-Al_2O_3 (Si/Al = 2/1) samples were shifted to *ca.* 335.1 eV while those for the Pd/SiO_2-Al_2O_3 (Si/Al = 1 and 1/2) and Pd/Al_2O_3 samples still remained at *ca.* 336.3 eV. This observation suggests that the palladium species on the first two samples have already been reduced to Pd(0) after 10 min of reduction, whereas those on the latter three samples remained mostly in the Pd(II) state. Thus, it is likely that the nature of Pd species or the interaction between the Pd species and the support before reduction may be different for the samples with different Si/Al ratios.

To gain insight into the nature of the palladium species before reduction, we have performed diffuse reflectance UV-vis spectroscopic studies for some typical samples after calcination. From the UV-vis spectra shown in Figure 4, we could see that the Pd/SiO_2 (curve a) showed very broad absorption in the visible region without a defined structure. This was quite similar to that for the reference compound PdO, suggesting that PdO particles were formed on the Pd/ SiO_2 sample. On the other hand, the Pd/Al_2O_3 showed an intense absorption band at *ca.* 220 nm along with a weak band at *ca.* 420 nm (curve d). These bands could be assigned to the highly dispersed Pd(II) species attached to Al_2O_3 *via* oxygen.[27–29] For the Pd/SiO_2-Al_2O_3 with an Si/Al ratio of 1, a shoulder at *ca.* 280 nm assignable to small PdO nanoclusters could be observed in addition to the bands at *ca.* 220 and 420 nm (curve c). The band at *ca.* 280 nm became more intense for the sample with a higher Si/Al ratio (2/1) (curve b), and moreover, with increasing the Si/Al ratio, the broad absorption at 340–600 nm became intense, suggesting the gradual aggregation of dispersed Pd(II) species to PdO nanoclusters and further to larger PdO particles with increasing the Si/Al ratio in the SiO_2-Al_2O_3 support.[27] These observations allow us to speculate that the interaction between the precursor Pd(II) species and the support before calcination is weaker in the sample with a higher Si/Al ratio. In other words, the interaction between the adsorbed Pd(II) species and Al_2O_3 was the strongest, leading to highly dispersed Pd(II) species after calcination, whereas aggregated PdO particles were mainly obtained on SiO_2 because of the weakest interaction between the adsorbed Pd(II) and SiO_2.

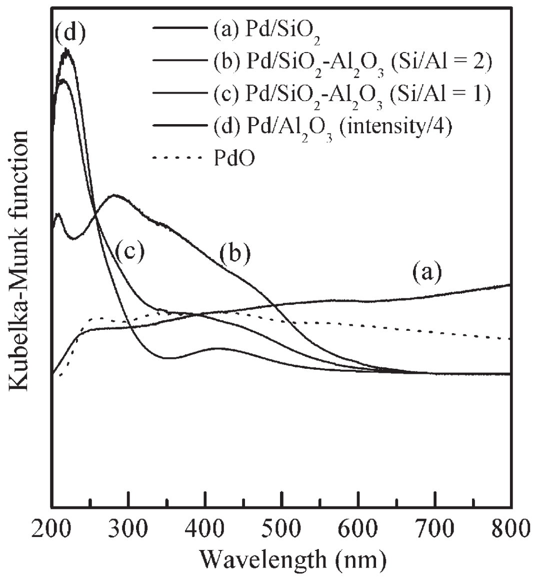


Figure 4. Diffuse reflectance UV-vis spectra for samples before reduction together with PdO. (a) 0.55 wt% Pd/SiO_2, (b) 0.52 wt% Pd/SiO_2-Al_2O_3 (Si/Al = 2/1), (c) 0.30 wt% Pd/ SiO_2-Al_2O_3 (Si/Al = 1/1), (d) 0.53 wt% Pd/Al_2O_3.

The size of metallic Pd particles formed after reduction with either hexanol or H_2 was determined by TEM observations. Typical TEM micrographs for some representative samples reduced with hexanol and H_2 are shown in Figure 5 and Figure 6, respectively. Particle size distributions derived from the TEM micrographs by counting *ca.* 150–200 particles in each case are also plotted in Figure 5 and Figure 6. It is of interest that, for both series of samples, the centers of particle size distributions shift to smaller sizes with decreasing Si/Al ratio. In other words, smaller Pd particles were obtained over the samples with lower Si/

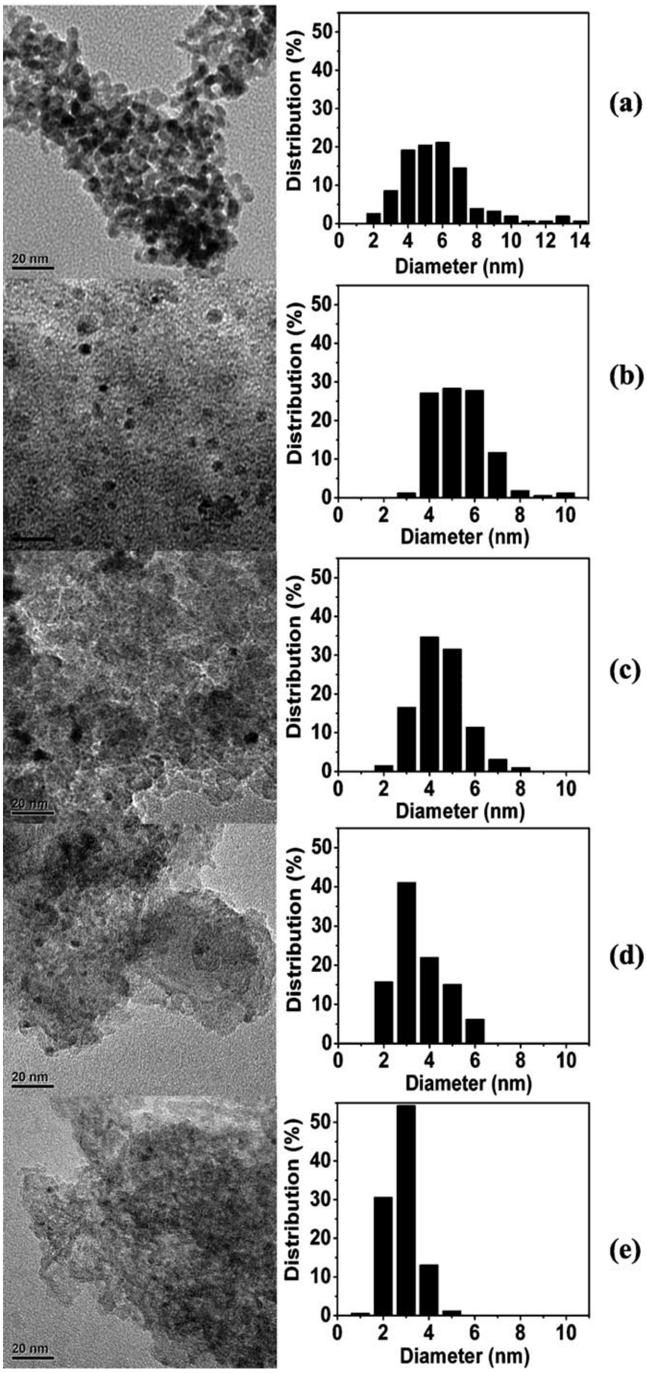


Figure 5. TEM micrographs and Pd particle size distributions for the samples reduced with hexanol. (a) 0.55 wt% Pd/SiO_2, (b) 0.52 wt%Pd/SiO_2-Al_2O_3 (Si/Al=2/1), (c) 0.30 wt% Pd/SiO_2-Al_2O_3 (Si/Al=1/1), (d) 0.52 wt% Pd/SiO_2-Al_2O_3 (Si/Al=1/2), (e) 0.53 wt% Pd/Al_2O_3.

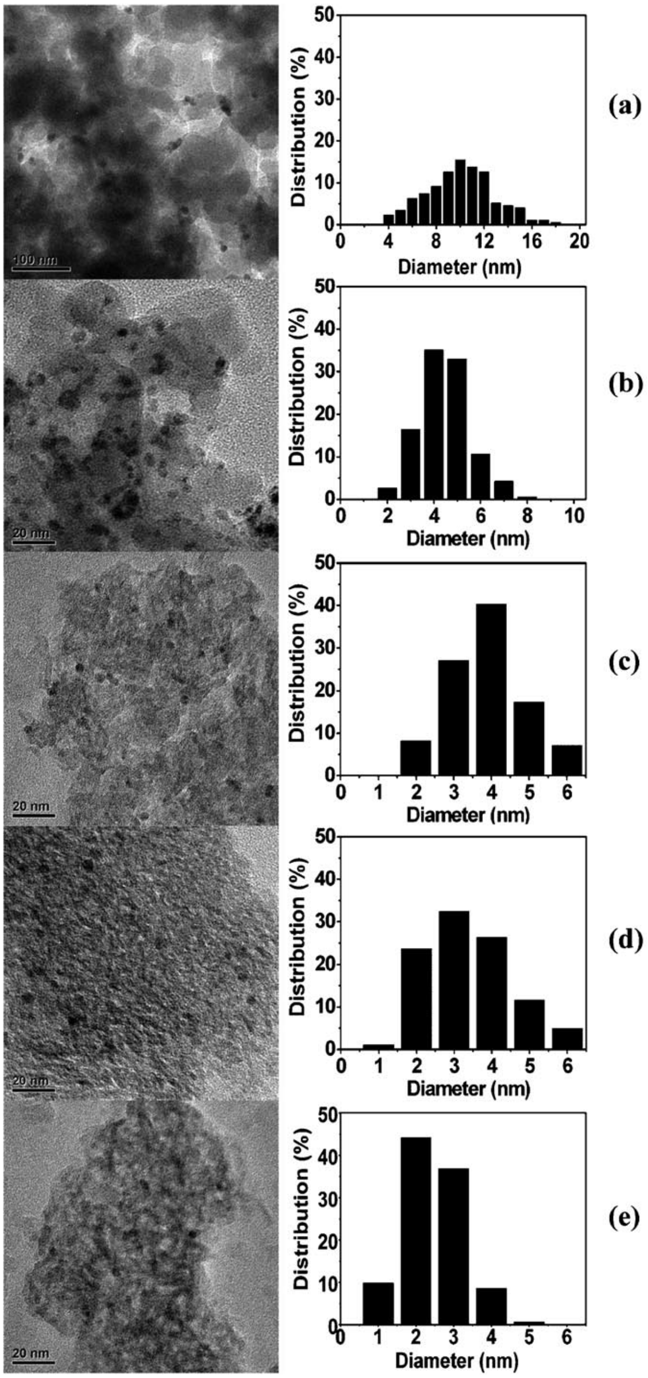


Figure 6. TEM micrographs and Pd particle size distributions for the samples reduced with H_2. (a) 0.55 wt% Pd/SiO_2, (b) 0.52 wt% Pd/SiO_2-Al_2O_3 (Si/Al=2/1), (c) 0.30 wt% Pd/SiO_2-Al_2O_3 (Si/Al=1/1), (d) 0.52 wt%Pd/SiO_2-Al_2O_3 (Si/Al=1/2), (e) 0.53 wt% Pd/Al_2O_3.

Al ratios. The mean sizes of Pd particles in the two series of samples were calculated and are summarized in Table 1. We have also prepared the Pd/SiO_2-Al_2O_3-H_2 (reduced with H_2) samples with the same Si/Al ratio (1/2 or 1/4) but different Pd contents (*ca.* 0.3–0.6 wt%) by changing the concentration of $PdCl_4^{2-}$ used for adsorption. As can be seen from Table 1, the variation in the content of Pd in such a range did not alter the mean size of Pd particles significantly. Thus, the Si/Al ratio was a key factor in determining the size of Pd nanoparticles. By changing the Si/Al ratio of the support, we could obtain supported Pd nanoparticles with mean sizes ranging from 5.7 to 2.6 nm and from 10 to 2.2 nm for the series of samples reduced with hexanol and H_2, respectively.

It is expected that the size of a metal particle is determined mainly by the rate of nucleation and the rate of nuclei growth during the reduction.[30] The interaction between the Pd species and the support would affect the mobility of the species and the rate of nuclei growth. Therefore, it is understandable that the weaker interaction between the PdO particles and SiO_2 leads to the formation of larger Pd particles for Pd/SiO_2, while smaller Pd particles have been formed over Al_2O_3 because of the stronger interaction between the highly dispersed Pd(II) species and Al_2O_3. Medium mean sizes of Pd particles have been obtained over the Pd/SiO_2-Al_2O_3 samples, probably because the use of SiO_2-Al_2O_3 mixed oxide as the support could create a medium interaction between the Pd species and the support.

The dispersion of Pd, i.e., the fraction of surface Pd atoms in all of the Pd atoms in each sample can be estimated from the size of Pd particles. By assuming spherical particles, we could calculate the dispersion of Pd using the diameter of Pd particles by the following equation: dispersion = 1.12/diameter (nm).[31] Values of the dispersion of Pd thus calculated are summarized in Table 1. We also performed CO chemisorption measurements for the evaluation of the dispersion of Pd. However, for the samples reduced with hexanol, CO chemisorption was hard to detect probably because the surface Pd sites were occupied by hexanol molecules, which were difficult to remove during the pre-treatment used for CO chemisorption (evacuation at 373 K). On the other hand, CO chemisorption could be obtained for the samples reduced by H_2. By assuming a chemisorption stoichiometry of CO to surface Pd atom of 1, the dispersion of Pd could be evaluated using the ratio of CO chemisorbed to all of the Pd atoms in the catalyst. The dispersion of Pd evaluated from CO chemisorption (Table 1) also increased with decreasing Si/Al ratio, and the value was in good agreement with that estimated from the mean size of Pd particles, except for the Pd/SiO_2 sample.

Aerobic Oxidation of Alcohols Catalyzed by SiO_2-Al_2O_3-Supported Pd Nanoparticles

Catalytic performances of the two series of Pd/SiO_2-Al_2O_3 samples for the solvent-free aerobic oxidation of benzyl alcohol are shown in Table 2. We confirmed that no conversion of benzyl alcohol occurred over the support alone, i.e., SiO_2, Al_2O_3 or SiO_2-Al_2O_3 under the reaction conditions shown in Table 2. Moreover, the SiO_2-Al_2O_3-supported Pd(II) or PdO samples without reduction were also inactive under the same reaction conditions (343 K) although benzyl alcohol could be converted by the unreduced catalysts at temperatures $>$*ca.* 358 K, where Pd(II) or PdO became reducible to Pd(0) by benzyl alcohol during the reaction. Therefore, the catalytic activities shown in Table 2 should arise mainly from the supported Pd nanoparticles.

Table 2 shows that, for both series of catalysts, the Pd/SiO_2-Al_2O_3 catalysts with appropriate Si/Al ratios give remarkably better catalytic performances than either Pd/SiO_2 or Pd/Al_2O_3. A further inspection of catalytic results for the two series of catalysts informed us that the mean diameter of Pd rather than the Si/Al ratio likely determined the catalytic activity because the catalysts with similar mean sizes of Pd particles but not similar Si/Al ratios exhibited comparable benzyl alcohol conversions. Moreover, the com-

Table 2. Catalytic activities of Pd/SiO_2-Al_2O_3 for solvent-free aerobic oxidation of benzyl alcohol.[a]

Entry	Catalyst[b]	Pd content [wt%]	Mean size of Pd [nm]	Conversion [%]	Aldehyde selectivity [%]
1	Pd/SiO_2-*hexanol*	0.55	5.7	7.8	83[c]
2	Pd/SiO_2-Al_2O_3-*hexanol* (2/1)	0.52	5.1	37	99
3	Pd/SiO_2-Al_2O_3-*hexanol* (1/1)	0.30	4.2	75	97
4	Pd/SiO_2-Al_2O_3-*hexanol* (1/2)	0.52	3.2	81	98
5	Pd/Al_2O_3-*hexanol*	0.53	2.6	64	99
6	Pd/SiO_2-H_2	0.55	10	2.8	98
7	Pd/SiO_2-Al_2O_3-H_2 (2/1)	0.52	4.3	73	98
8	Pd/SiO_2-Al_2O_3-H_2 (1/1)	0.30	3.6	97	98
9	Pd/SiO_2-Al_2O_3-H_2 (1/2)	0.30	3.1	87	$>$99
10	Pd/SiO_2-Al_2O_3-H_2 (1/2)	0.52	3.1	89	99
11	Pd/SiO_2-Al_2O_3-H_2 (1/4)	0.39	2.9	63	98
12	Pd/SiO_2-Al_2O_3-H_2 (1/4)	0.56	2.7	81	97
13	Pd/Al_2O_3-H_2	0.53	2.2	42	98

[a] *Reaction conditions:* catalyst, 0.1 g; benzyl alcohol, 48.5 mmol; O_2, 3 mL min^{-1}; temperature, 343 K; time, 10 h.

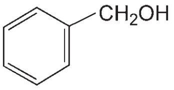
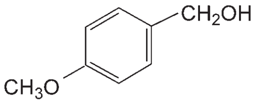
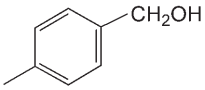
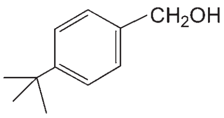
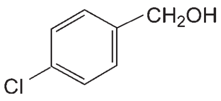
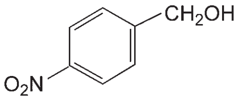
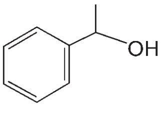
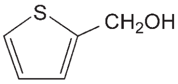
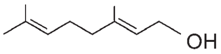
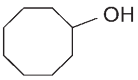
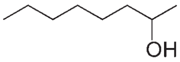
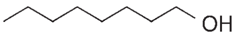
[b] The ratio in the parenthesis is the Si/Al ratio; *hexanol* and H_2 denote the reductant used for the preparation.

[c] The remaining product was toluene.

parison of the trend in Table 2 (catalytic activity) with that in Figure 2 (NH_3-TPD result) for the samples with different Si/Al ratios strongly suggests that there is no correlation between the catalytic activity and the acidity of catalyst. Therefore, we speculate that the support in our case mainly exerts effects on the mean size of the supported Pd nanoparticles, and it is reasonable to consider that the variation in catalytic behaviors with changing Si/Al ratio mainly arises from the change in the mean size of Pd nanoparticles. The two series of catalysts exhibited a similar tendency in the change of catalytic performance with the mean size of Pd particles; both the larger and smaller Pd nanoparticles show lower performances in the solvent-free aerobic oxidation of benzyl alcohol. The results in Table 2 reveal that the catalysts containing Pd nanoparticles with mean sizes of 2.7–4.3 nm exhibit higher catalytic performances for the solvent-free aerobic oxidation of benzyl alcohol.

The 0.30 wt% Pd/SiO_2-Al_2O_3-*H_2* (Si/Al = 1/1, reduced with H_2) catalyst, which possesses a mean size of Pd particles of 3.6 nm, has been examined for the aerobic oxidation of various alcohols. Table 3 shows that the catalyst could catalyze the solvent-free aerobic oxidation of various substituted benzyl alcohols and 1-phenylethanol selectively to the corresponding carbonyl compounds (entries 2–7). The present catalyst was also effective for the oxidation of allylic alco-

Table 3. Aerobic oxidation of various alcohols over the Pd/SiO_2-Al_2O_3-*H_2* (Si/Al = 1).[a]

Entry	Alcohol	Temperature [K]	Time [h]	Conversion [%]	Carbonyl compound selectivity [%]
1		353	24	99	99
2		353	24	91	100
3		423	24	54	100
4		423	24	26	100
5		423	24	60	100
6		423	24	52	100
7		423	24	82	90[b]
8		373	24	93	100
9		353	24	96	100
10		373	24	80	100
11		373	24	83	100
12		373	24	75	100

[a] *Reaction conditions:* catalyst, 0.1 g (Pd, 2.82 μmol); O_2, 3 mL min^{-1}; entries 1–7: solvent-free, substrate 50 mmol; entries 8–12: solvent trifluorotoluene, substrate 2 mmol.

[b] The remaining product was benzaldehyde.

hol (entry 9) and non-activated alcohols such as cyclooctanol, 2-octanol and 1-octanol (entries 10–12) selectively to the corresponding aldehydes and ketones. Furthermore, the oxidation of heterocyclic alcohols, i.e., 2-thiophenemethanol proceeded efficiently over the present catalyst (entry 8), whereas such heterocyclic alcohols are generally difficult to convert by homogeneous metal complex catalysts due to the strong coordination of the substrate to the metal center. Another specific point of the present Pd/SiO_2-Al_2O_3 catalyst is that all the substituted benzyl alcohols investigated here exhibit lower reactivities than benzyl alcohol. However, for many homogeneous Pd complex catalysts,[32,33] it has been reported that the reactivities of substituted benzyl alcohols with electron-donating substituents are higher than that of benzyl alcohol, while the presence of electron-withdrawing substituents decreases the reactivity. The same phenomenon has also been reported for some heterogeneous catalysts such as $Ru(OH)_x/Al_2O_3$.[34] The unique observation in our system may indicate that the reaction mechanism or the rate-determining step for our system is different from that for the homogeneous catalytic systems or the $Ru(OH)_x/Al_2O_3$.

We have carried out recycling uses of the 0.30 wt% Pd/SiO_2-Al_2O_3-H_2 (Si/Al = 1/1) catalyst for the solvent-free aerobic oxidation of benzyl alcohol at 353 K. As shown in Figure 7, the conversion and selectivity did not undergo significant changes during the repeated use for 5 cycles. Thus, the present catalyst could be used recyclably.

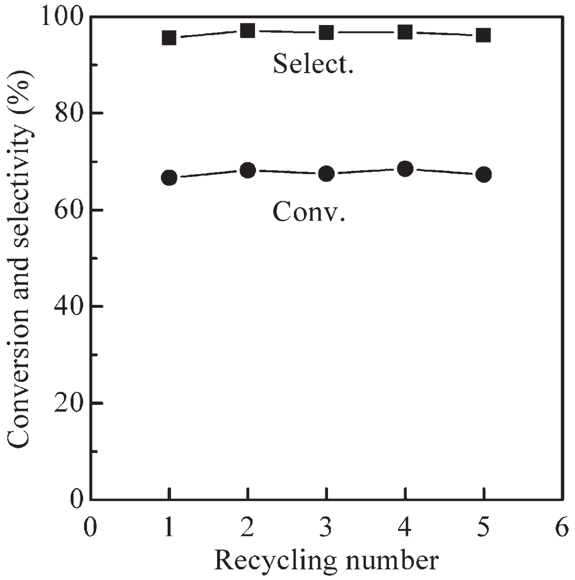


Figure 7. Recycling uses of 0.30 wt% Pd/SiO_2-Al_2O_3-H_2 (Si/Al = 1/1) for the aerobic oxidation of benzyl alcohol. *Reaction conditions:* catalyst, 0.1 g (Pd, 2.82 μmol); benzyl alcohol, 48.5 mmol; O_2, 3 mL min^{-1}; temperature, 353 K; reaction time, 4 h.

Structure-Sensitivity of Pd Nanoparticles-Catalyzed Oxidation of Benzyl Alcohol

To elucidate the effect of Pd particle size on intrinsic catalytic reactivities of Pd sites for the solvent-free aerobic oxidation of benzyl alcohol, we measured the conversion of benzyl alcohol at the initial reaction stage (conversion $<20\%$) at 353 K and evaluated the initial conversion rate (Table 4). From the initial conversion rate and the dispersion of Pd shown in Table 1, we calculated the intrinsic TOF, i.e., moles of benzyl alcohol converted per mole of surface Pd per second. For the catalysts reduced with H_2, because Pd dispersion had been evaluated by both the size of Pd particles and CO chemisorption, we obtained two intrinsic TOFs for this series of samples. To make a better comparison, we plotted the TOFs against the mean size of Pd nanoparticles in Figure 8. It becomes clear that the intrinsic TOFs depend significantly on the mean size of Pd particles. Moreover, because all the data points in Figure 8 can be fitted in one curve, it is reasonable to consider that the mean size of Pd particles is the essential factor to determine the intrinsic TOF, whereas the Si/Al ratio and the reagent (H_2 or hexanol) used for reduction influence the activity *via* changing the mean size of Pd particles. Furthermore, the results in Table 4 and Figure 8 also indicate that the content of Pd should not be a critical factor in determining the intrinsic TOF. Figure 8 reveals that the catalysts with both larger and smaller mean sizes of Pd particles exhibit lower intrinsic TOFs and there is an optimum mean size (3.6–4.3 nm) of Pd particles for the oxidation of benzyl alcohol. Although the requirement of an appropriate size of metal particles is known for several metal nanoparticles-catalyzed reactions,[18,35] our present observation is quite significant for Pd nanoparticles-catalyzed organic reactions because smaller Pd particles containing more coordinately unsaturated Pd sites are generally believed to be more active.[7b,19–22]

The unique observation in Figure 8 may be understood by thinking about the possible reaction mechanism. The reaction mechanism for the homogeneous Pd complex-catalyzed alcohol oxidation has been investigated extensively.[36,37] The ligand-coordinated Pd(II) species are proposed for the conversion of alcohol *via* Pd-alcoholate intermediate, which undergoes β-hydride elimination to give carbonyl compounds, and the generated Pd(0) should be oxidized to Pd(II) quickly to avoid decomposition of the homogeneous catalysts.[36,37] The β-hydride elimination, oxidation of Pd(0) to Pd(II), and the dissolution of O_2 have all been suggested to limit the rate of oxidation of alcohols depending on the systems and the reaction conditions. The mechanism for the aerobic oxidation of alcohols catalyzed by Pd- or Ru-based heterogeneous catalysts has also been discussed in several stud-

Table 4. Intrinsic turnover frequencies of Pd/SiO_2-Al_2O_3-catalyzed solvent-free aerobic oxidation of benzyl alcohol.[a]

Catalyst[b]	Pd content [wt%]	Mean size of Pd [nm]	Initial conversion rate[c] [mol $g^{-1}s^{-1}$]	TOF[d] [s^{-1}]	TOF[e] [s^{-1}]
Pd/SiO_2-*hexanol*	0.55	5.7	0.26	0.26	-
Pd/SiO_2-Al_2O_3-*hexanol* (2/1)	0.52	5.1	0.68	0.64	-
Pd/SiO_2-Al_2O_3-*hexanol* (1/1)	0.30	4.2	1.82	2.42	-
Pd/SiO_2-Al_2O_3-*hexanol* (1/2)	0.52	3.2	2.12	1.24	-
Pd/Al_2O_3-*hexanol*	0.53	2.6	1.78	0.83	-
Pd/SiO_2-H_2	0.55	10	0.094	0.16	0.46
Pd/SiO_2-Al_2O_3-H_2 (2/1)	0.52	4.3	3.22	2.53	2.45
Pd/SiO_2-Al_2O_3-H_2 (1/1)	0.30	3.6	2.15	2.45	2.25
Pd/SiO_2-Al_2O_3-H_2 (1/2)	0.30	3.1	1.14	1.12	1.03
Pd/SiO_2-Al_2O_3-H_2 (1/2)	0.52	3.1	2.30	1.30	1.28
Pd/SiO_2-Al_2O_3-H_2 (1/4)	0.39	2.9	0.62	0.44	0.40
Pd/SiO_2-Al_2O_3-H_2 (1/4)	0.56	2.7	1.39	0.64	0.55
Pd/Al_2O_3-H_2	0.53	2.2	1.45	0.57	0.42

[a] *Reaction conditions:* catalyst, 0.1 g; benzyl alcohol, 48.5 mmol; O_2, 3 mL min^{-1}; temperature, 353 K.

[b] The ratio in the parenthesis is the Si/Al ratio; *hexanol* and H_2 denote the reductant used for preparation.

[c] Evaluated from the benzyl alcohol conversion at the initial reaction stage (conversion <20%).

[d] Calculated from the initial conversion rate and the Pd dispersion evaluated from the mean size of Pd particles.

[e] Calculated from the initial conversion rate and the Pd dispersion evaluated from CO chemisorption.

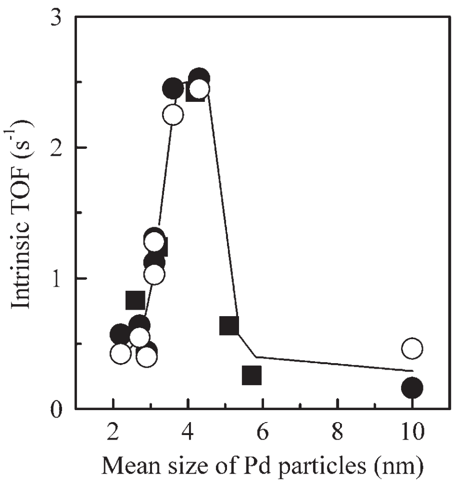


Figure 8. Dependence of the intrinsic turnover frequency on the mean size of Pd particles. Symbols: (■) catalysts reduced with hexanol, (●) catalysts reduced with H_2, and TOF based on Pd dispersion estimated by mean size of Pd, (○) catalysts reduced with H_2, and TOF based on Pd dispersion evaluated by CO chemisorption. See Table 4 for reaction conditions.

ies.[7b,11,34] It is generally accepted that the Pd- or Ru-alcoholate also acts as the intermediate in these heterogeneous catalytic systems. Nevertheless, for the heterogeneous Pd-catalyzed oxidation of alcohols, Pd(0) has been proposed as the active phase in many systems.[7,8,11–16] Solid evidence has been obtained to support this in some research papers. For examples, Mori et al.[7b] have confirmed that Pd species over hydroxyapatite are transformed to Pd(0) nanoparticles after the oxidation of 1-phenylethanol *via* EXAFS measurements; Grunwaldt et al.[8] have clarified that the metallic Pd over Al_2O_3 support is much more active (over 50 times) for the aerobic oxidation of benzyl alcohol than the oxidic Pd species. Our present study also suggests that Pd(0) nanoparticles are the active species because the Pd/SiO_2-Al_2O_3 catalysts without reduction are inactive under our reaction conditions. To further confirm that the reaction proceeds steadily over the Pd(0) nanoparticles, we have measured the O_2 consumption in the oxidation of benzyl alcohol at 343 K under the reaction conditions shown in Table 2. After 10 h of reaction, the amounts of O_2 consumed were 25 and 19 mmol over the 0.30 wt% Pd/SiO_2-Al_2O_3-H_2 (Si/Al=1/1) and the 0.52 wt% Pd/SiO_2-Al_2O_3-H_2 (Si/Al=1/2) catalysts, respectively. The molar ratio of O_2 consumption to benzaldehyde yield was calculated to be ~0.5 over either catalyst, suggesting that the oxidation of benzyl alcohol by O_2 to benzaldehyde and water proceeded stoichiometrically over the present Pd(0)-based catalysts. Furthermore, we have carried out XPS measurements for the recovered 0.30 wt% Pd/SiO_2-Al_2O_3-H_2 (Si/Al=1/1) catalyst after reaction. The result showed that the binding energy of Pd $3d_{5/2}$ remained at 335.1 eV, confirming that palladium species were kept in the Pd(0) state after the reaction.

It is reasonable to speculate that the aerobic oxidation of benzyl alcohol over our catalyst also proceeds through a Pd-alcoholate intermediate. By consulting the reaction mechanism proposed by Mori et al.,[7b] we speculate that, in the first step, benzyl alcohol may be chemisorbed *via* the interaction of the delocalized π-bond of benzene ring with the terrace Pd atoms of a Pd nanoparticle. Subsequently, the Pd-alcoholate intermediate may be formed through the interaction of the O−H bond of the alcohol with another type of Pd site, followed by the β-hydride elimination and the formation of benzaldehyde. The coordinately unsaturated edge and corner Pd atoms on the same Pd nanoparticle probably work for the formation of Pd-alcoholate and the β-hydride elimination. Mori et al.[7b] argued that the β-hydride elimination over the edge or corner Pd atoms was the rate-limiting step, and thus, these Pd sites played key roles in the oxidation of alcohols. On the other hand, through *in situ* ATR-IR spectroscopic studies combined with selective site blocking by co-adsorbed CO and isotope labeling, Ferri et al.[38] proposed that the dehydrogenation of alcohol to carbonyl product could occur virtually on all atoms on the Pd/Al_2O_3 catalyst. It is known that the ratio of coordinately unsaturated Pd atoms (edge and corner Pd atoms) to terrace Pd atoms increases as the size of Pd particles decreases.[39] Our observation that a medium size of Pd particles is beneficial to benzyl alcohol oxidation implies that there may exist an appropriate ratio of these two types of sites for the catalytic aerobic oxidation of benzyl alcohol. This allows us to further consider that not only the β-hydride elimination of Pd-alcoholate but the chemisorption of alcohol also play a crucial role in the aerobic oxidation of benzyl alcohol over our catalyst. It should be remembered that the substituted benzyl alcohols with either electron-donating or electron-withdrawing substituents in the benzene ring were all less reactive than benzyl alcohol over our catalyst (Table 3). This is also a quite unique observation because the benzyl alcohols with an electron-donating substituent, which can facilitate the β-hydride elimination, show higher reactivities in many homogeneous systems.[32,33] We speculate that the lower reactivity of the substrates with electron-donating substituents in our case may stem from the lower ability of chemisorption of these substrates on the Pd sites because of the steric hindrance. This further supports the speculation that both the coordinately unsaturated sites and the terrace sites are required for obtaining a high intrinsic TOF for benzyl alcohol conversion.

Conclusions

We have succeeded in preparing SiO_2-Al_2O_3-supported Pd nanoparticles by adsorption of $PdCl_4^{2-}$ ions onto the support followed by calcination and reduction with either hexanol or H_2. The mean size of the Pd nanoparticles was tunable from 2.2 to 10 nm by changing the Si/Al ratio and the reductant. The supported Pd nanoparticles could catalyze the aerobic oxidation of various alcohols, and were particularly efficient for benzyl alcohol oxidation under solvent-free conditions. The Pd/SiO_2-Al_2O_3 catalysts with appropriate Si/Al ratios showed significantly higher benzyl alcohol conversions than both the Pd/SiO_2 and the Pd/Al_2O_3. The mean size of Pd particles played a key role in the aerobic oxidation of benzyl alcohol. With changing the mean size of Pd particles from 2.2 to 10 nm, the intrinsic turnover frequency per surface Pd atom for benzyl alcohol conversion showed a maximum at a medium size of 3.6–4.3 nm, revealing that the reaction was structure-sensitive. The existence of optimum particle size implies that an appropriate ratio of the edge and corner Pd atoms to the terrace Pd atoms is required for the conversion of benzyl alcohol. It is likely that not only the β-hydride elimination of the Pd-alcoholate intermediate but the chemisorption of alcohol on Pd nanoparticles also determines the rate of benzyl alcohol oxidation over our catalyst.

Experimental Section

Catalyst Preparation

SiO_2-Al_2O_3 mixed oxides with different Si/Al molar ratios were synthesized by a co-precipitation method. In this method, the aqueous solution of Na_2SiO_3 was added to that of $Al(NO_3)_3$, and the Si/Al ratio in the final sample was varied by changing the relative amounts of the two aqueous solutions. The pH value of the mixed solution was adjusted to 9.0 by aqueous NH_3 solution or diluted aqueous HNO_3 solution. The obtained suspension was further stirred for 1 h, and then the precipitate was filtered, washed thoroughly with deionized water, and dried at 393 K overnight. The dried powder was calcined at 773 K for 6 h to obtain the SiO_2-Al_2O_3 mixed oxide.

The Pd/SiO_2-Al_2O_3 catalysts were prepared by an adsorption method described in our previous paper for the preparation of Pd/Al_2O_3-*ads*.[14] The SiO_2-Al_2O_3 mixed oxide prepared above was added into an aqueous solution of $PdCl_4^{2-}$ with the pH value adjusted. To allow the adsorption of $PdCl_4^{2-}$ species onto the support, we adjusted the pH of the $PdCl_4^{2-}$ solution to 1.2–1.7 by dilute HCl aqueous solution. The surface would be transformed to $=Al-OH_2^+$ or $\equiv Si-OH_2^+$ because the points of zero charge for Al_2O_3 and SiO_2 were *ca.* 8–9 and 2–3, respectively.[40–42] The adsorption of $PdCl_4^{2-}$ could occur on the surfaces *via* coulombic interactions. The content of Pd in the final catalyst could be regulated to some extent by changing the concentration of $PdCl_4^{2-}$. After the adsorption, the powdery solid was recovered by filtration followed by thorough washing with a large amount of deionized water until no Cl^- could be detected in the filtrate by $AgNO_3$ aqueous solution. The sample was subsequently dried at 393 K overnight and calcined at 773 K in air for 3 h. The reduction of thus obtained Pd(II)/SiO_2-Al_2O_3 or PdO/SiO_2-Al_2O_3 was carried out by two methods, i.e., (i) hexanol reduction under refluxing conditions (at ~428 K) for 6 h and (ii) H_2 reduction at 573 K for 0.5 h. These two series of catalysts were denoted as Pd/SiO_2-Al_2O_3-*hexanol* and Pd/SiO_2-Al_2O_3-H_2, respectively.

Catalytic Reaction

The catalytic oxidation of alcohols by O_2 was carried out using a batch-type reaction vessel with a reflux condenser. Typically, the powdery catalyst (typically 0.1 g containing Pd of *ca.* 2.8–5.2 μmol) was added into the alcohol (benzyl alcohol, 48.5 mmol) placed in the reaction vessel, and the mixture was then heated to the reaction temperature with stirring. Then, an O_2 flow was bubbled into the mixture to start the reaction. After the reaction, the catalyst was separated by centrifugation, and the liquid products were analyzed by a gas chromatograph (Shimazu GC-14 B) after the addition of an internal standard.

Catalyst Characterization

The Pd content in each catalyst was determined by inductively coupled plasma (ICP) optical emission spectrometry using an Agilent ICP-MS 4500–300. Powder X-ray diffraction (XRD) patterns were recorded on a Panalytical X′Pert Pro Super X-ray diffractometer with Cu Kα radiation (40 kV, 30 mA). NH_3 temperature-programmed desorption (NH_3-TPD) was performed on a Micromeritics AutoChem II 2920 instrument. The adsorption of NH_3 was performed at 393 K in an NH_3-He (10 vol% NH_3) mixture for 1 h, and the remaining or weakly adsorbed NH_3 was purged by high purity He. TPD was performed in an He flow by raising the temperature to 973 K at a rate of 10 K min^{-1}. The desorbed NH_3 was detected with a mass spectrometer (ThermoStar GSD 301 T2) by monitoring the signal of $m/e = 16$.

Diffuse reflectance UV-Vis spectra were recorded on a Varian Cary-5000 spectrometer equipped with a diffuse-reflectance accessory. The spectra were collected at 200–800 nm with BaSO4 as a reference. X-ray photoelectron spectroscopic (XPS) measurements were performed with a Multilab 2000 system (Thermo Electron Co.) using Al-Kα radiation (1846.6 eV) as X-ray source to investigate the oxidation state of Pd before and after hexanol or H_2 reduction. Transmission electron microscopy (TEM) was taken on a Phillips Analytical FEI Tecnai 30 electron microscope operated at an acceleration voltage of 300 kV. Samples for TEM measurements were suspended in ethanol and ultrasonically dispersed. Drops of suspensions were applied on a copper grid coated with carbon. Chemisorption of CO was performed using a Micromeritics ASAP2010C. The sample after reduction with hexanol or H_2 was purged with high purity He (99.999%) at 373 K for 30 min and then was evacuated for 20 min. After the temperature had decreased to 308 K under vacuum, CO was introduced, and the first isotherm (total CO uptake) was measured. After the first isotherm, the sample was evacuated for ~10 min, and then the second isotherm (reversible CO uptake) was measured. Using the difference between the total and the reversible adsorbed CO, we obtained the amount of the chemisorbed CO.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (grants 20625310, 20773099 and 20433030), the National Basic Research Program of China (grants 2003CB615803 and 2005CB221408), the Key Scientific Project of Fujian Province of China (No. 2005HZ01–3) and the Program for New Century Excellent Talents in Fujian Province (grant to Q.Z.).

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