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An Amphiphilic Resin-dispersion of Nanoparticles of Platinum (ARP-Pt): A Highly Active and Recyclable Catalyst for the Aerobic Oxidation of a Variety of Alcohols in Water

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Abstract: An amphiphilic polystyrene-poly(ethylene glycol) (PS-PEG) resin-dispersion of nanoparticles of platinum (ARP-Pt, **4**) was developed with a view towards use in catalysis in an aqueous environment under heterogeneous conditions. ARP-Pt **4** was prepared by the reduction of PS-PEG-NH_2-$PtCl_2(C_2H_4)$ **3**, which was generated by mixing PS-PEG-NH_2 **1** and Zeise's salt **2** ($K[PtCl_3(CH_2CH_2)]$), with benzyl alcohol in water (80 °C, 12 h). Benzyl alcohol was an essential reducing agent for the preparation of Pt nanoparticles with a narrow size distribution ($\phi = 5.9 \pm 0.75$ nm) throughout the PS-PEG resin, whereas the reduction of **3** with $NaBH_4$ gave Pt nanoparticles with broad size distribution ($\phi = 2$—150 nm). ARP-Pt **4** was found to catalyze the aerobic oxidation of a wide variety of alcohols, including non-activated aliphatic and alicyclic alcohols, in water with atmospheric oxygen or air under heterogeneous conditions, and was reused without loss of its catalytic activity, to achieve a highly environmentally-friendly reaction.

Keywords: aerobic oxidation · nanoparticles · platinum · sustainable chemistry · water

Introduction

The development of highly active immobilized catalysts for the aerobic oxidation of a variety of alcohols in aqueous media is a tremendously important topic in chemistry today.[1] Although aerobic oxidation of non-activated alcohols, such as aliphatic and alicyclic alcohols, using immobilized catalysts generally proceeds poorly, the catalytic system for the aerobic oxidation of activated alcohols, benzylic and allylic alcohols, is fairly developed (Figure 1).[2] There have been reports of heterogeneous metal catalysts being used for the aerobic oxidation of various alcohols, but the catalysts were regularly used in harmful organic solvents[3] and/or under vigorous conditions.[4] Recently, we,[5] Kaneda,[6] Sheldon,[7] Corma,[8] and Sakurai[9] reported the aerobic oxidation of some aliphatic and alicyclic alcohols in water using reusable catalysts.[10,11] While acknowledging the pioneering work in this area, we believe the development of a novel catalyst system exhibiting a wide range of substrate tolerance under mild and aqueous conditions still remains a major challenge. Consequently, we have devised an amphiphilic polystyrene-poly(ethylene glycol) (PS-PEG) resin-dispersion of nanoparticles of palladium (ARP-Pd) that catalyzes the aerobic oxidation of alcohols in water at 100 °C.[12] However, despite such progress, the reactivity and versatility

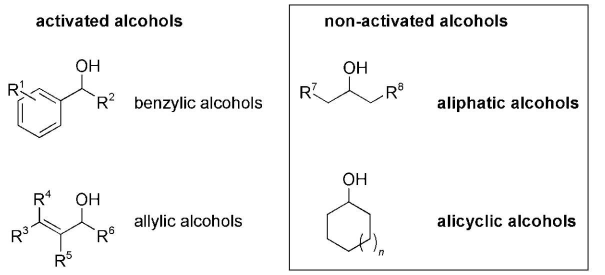

Figure 1. Activated and non-activated alcohols.

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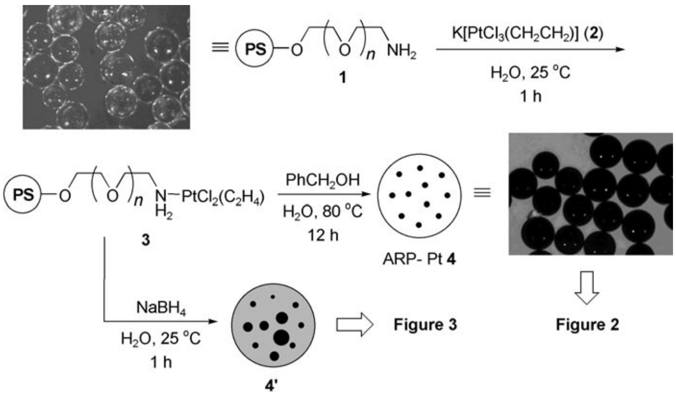
of ARP-Pd for the oxidation of alicyclic and aliphatic alcohols was inadequate (see below). We therefore considered platinum nanoparticles[13,14] since platinum has a stronger oxidizing ability ($Pt/Pt^{2+} = +1.12$ V vs $Pd/Pd^{2+} = +0.95$ V) than palladium. However, deactivation of platinum by oxygen renders it problematic to reuse efficiently,[15] and Pt particles possess a latent tendency to explode under the oxidative conditions in organic solvents.[16] Our concept for the preparation of ARP, where metal particles would be stabilized by amphiphilic resins in aqueous media, should overcome these drawbacks. Herein, we report a successful example for developing amphiphilic resin-dispersion of nanoparticles of platinum (ARP-Pt) and its application to the aerobic oxidation of a wide variety of alcohols, including not only benzylic and allylic but also alicyclic and aliphatic alcohols, in water.[17] It is noteworthy that ARP-Pt efficiently promoted the reaction at 60 °C with high recyclability.

Results and Discussion

A novel ARP-Pt **4** was prepared from commercially available PS-PEG-NH_2 (**1**) (TentaGel S NH_2, $\phi = 90$ μm) and Zeise's salt ($K[PtCl_3(CH_2CH_2)]\cdot H_2O$) (**2**) (Scheme 1). Thus, the complexation of **1** (loading value of amino residue: 0.31 mmol g^{-1}) and **2** (1 mol equiv) was carried out in water at 25 °C for 1 h to give PS-PEG resin-supported Pt complex **3** that was reduced with benzyl alcohol in water at 80 °C for 12 h to afford ARP-Pt **4** as black beads. To elucidate the structure of **4**, several spectroscopic measurements were carried out. High resolution TEM analysis of ARP-Pt **4** revealed, as shown in Figure 2 (a)–(d), that the Pt nanoparticles in **4** had a mean diameter of 5.9 nm with a very narrow size distribution (±0.75 nm) throughout the resin, and that the density of the Pt particles was uniform in the resin (Figure 2 (a)). SEM analysis indicated the existence of no cracks or fragments in **4**. EDS/SEM analysis also confirmed a uniform dispersion of Pt throughout the resin. As far as we know, a uniform dispersion of nanoparticles over the entire region of insoluble resins with uniform density-distribution is realized for the first time.[18]



Scheme 1. Preparation of ARP-Pt **4** and **4′** (with microscopic images of **1** and **4**).

Abstract in Japanese:

白金ナノ粒子（平均粒径 5.9 nm）を両親媒性ポリスチレン-ポリエチレングリコール共重合レジン内で発生・固定化した ARP-Pt は，不活性な脂肪族アルコール類を含む広範なアルコール類の水中での常圧酸素酸化を良好に触媒し対応するカルボニル化合物を与えた。限定された粒径分布を得るナノ粒子調製の条件，触媒の回収再利用などについても詳述する。

In contrast, the Pt nanoparticles of ARP-Pt **4′** which were generated by the reduction of **3** with $NaBH_4$ (Scheme 1), had a very broad size distribution and localized density (Figure 3). Thus, platinum particles having a diameter of 2–12 nm were often observed at the shell area of the resin (Figure 3 (c), position (1) and (2)), and more aggregated platinum particles whose diameter was 50–150 nm were formed in the core of the resin (Figure 3 (c), position (5)).

With an amphiphilic resin catalyst ARP-Pt **4**, containing uniform size- and density-distribution of Pt nanoparticles, we conducted the oxidation of a variety of primary and secondary alcohols to the corresponding carbonyl compounds. Representative results are summarized in Table 1 where several palladium (ARP-Pd)-catalyzed results are included for comparison (Pt vs Pd).[5] The oxidation of **5a** (20 mmol; 2.2 g) with 1.0 mol %[19] of ARP-Pt was performed at 60 °C for 24 h to give **7a** in an isolated yield of 99 % (2.4 g) (Table 1, run 1). Activated alcohols such as benzylic alcohols **6a–c**, and allylic alcohols **5b**, **6d**, and **6e**, were transformed to the corresponding carbonyl compounds **7b** and **8a–e** in 72–93 % yield (runs 3–8).[20] It should be noted that the benzylic ethers as well as the carbon–carbon double bonds were tolerated under the conditions (entries 5–8), though a platinum hydride species should be generated during the alcohol oxidation process (Scheme 2). We were pleased to find that the aerobic oxidation of a variety of non-activated alicyclic alcohols, cyclopentanol (**6f**), cyclohexanol (**6g**), cycloheptanol (**6h**), and cyclooctanol (**6i**), also took place smoothly at 60 °C to provide the corresponding alicyclic ketones in 80–93 % yield (runs 9, 11, 13, and 14). Moreover, it was found that the non-activated aliphatic primary and secondary alcohols, 1-, 2-, 3-, and 4-octanol (**5c**, **6j–l**), were efficiently converted into the corresponding aliphatic carbonyl compounds in 81–95 % yield (runs 15, 16, 18, and 19) under similar conditions. ARP-Pd catalyst exhibited a lower activity even at higher reaction temperature (runs 10, 12, and 17).

It is noteworthy that atmospheric air was likewise applied as an oxidant in this catalytic system (Table 2). Thus, the efficient conversion of benzylic, alicyclic, and aliphatic secondary alcohols **6a**, **6i**, and **6j** was achieved under atmospheric pressure of air (21 % (v/v) oxygen) in water at 60 °C to afford the corresponding ketones **8a**, **8i**, and **8j** in 79 %, 93 %, and 82 % yields, respectively.

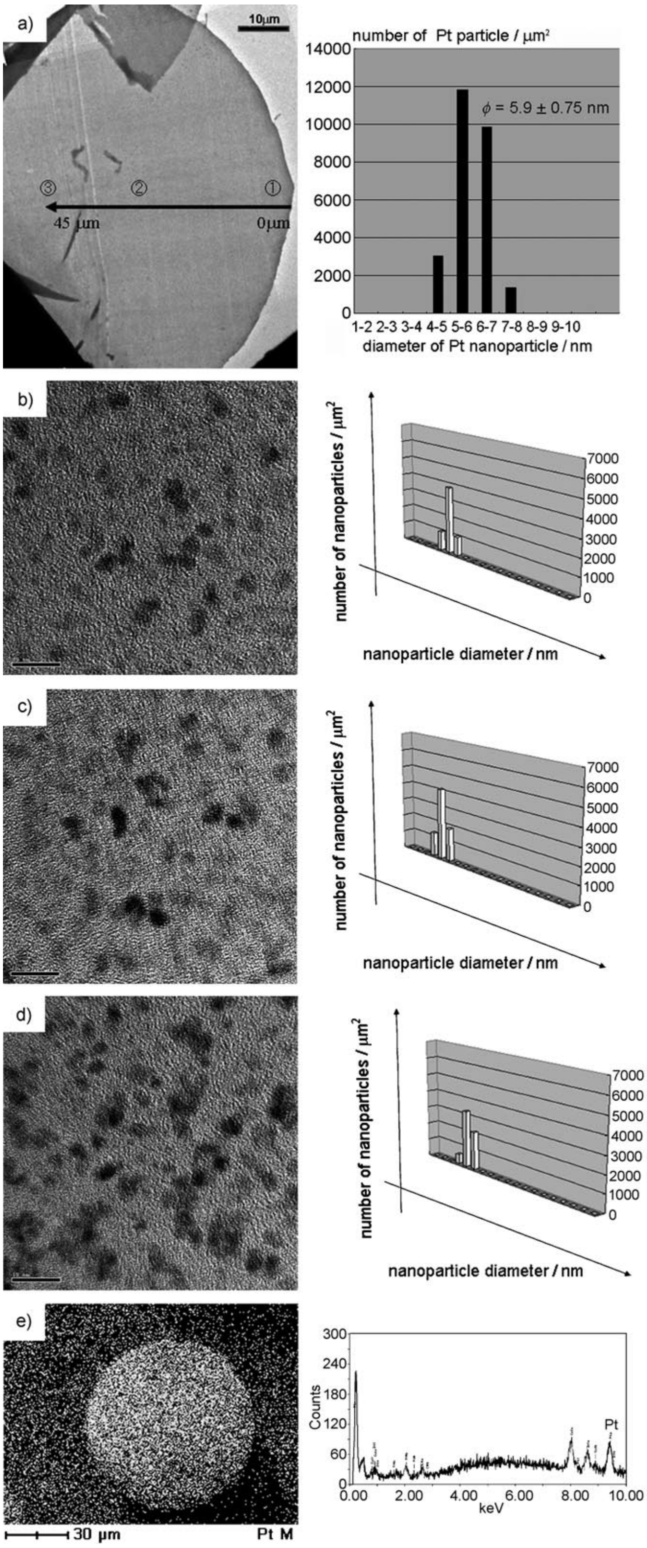
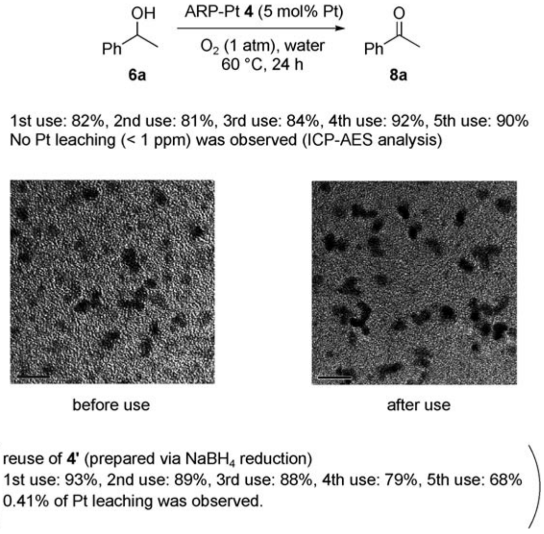


Figure 2. a) A TEM image of a section of **4**; and a histogram of the size distribution of Pt particles in **4** (x-axis: diameter of Pt nanoparticles (nm); y-axis: numbers of Pt nanoparticles (/μm²)); b) a TEM image of **4** at the (1) position, and a histogram of the size distribution of Pt particles (bar: 10 nm); c) a TEM image of **4** at the (2) position, and a histogram of the size distribution of Pt particles (bar: 10 nm); d) a TEM image of **4** at the (3) position, and a histogram of the size distribution of Pt particles (bar: 10 nm); e) EDS/SEM images of Pt in **4**.

It is noteworthy that the aerobic oxidation of **6a** with ARP-Pt $\mathbf{4}_{\phi=10}$, which was prepared from 10 μm diameter of PS-PEG resin beads ($\phi=10$ μm), gave a similar result to that obtained with **4** ($\phi=90$ μm) (Table 3). Thus, ARP-Pt $\mathbf{4}_{\phi=90}$ and ARP-Pt $\mathbf{4}_{\phi=10}$ were prepared from the corresponding PS-PEG-NH$_2$ resin beads ($\phi=90$ μm and $\phi=10$ μm), whose calculated spherical surface areas were 3.05×10^{-2} m^2 g^{-1} and 2.47 m^2 g^{-1}, respectively. Pt loading values of ARP-Pt $\mathbf{4}_{\phi=90}$ and ARP-Pt $\mathbf{4}_{\phi=10}$ were controlled at the platinum complexation step (from **1** to **3**) and were determined by ICP analysis to both be 0.21 mmol g^{-1}. TEM images of ARP-Pt $\mathbf{4}_{\phi=90}$ and ARP-Pt $\mathbf{4}_{\phi=10}$ ($\phi=90$ μm and $\phi=10$ μm) revealed that Pt nanoparticles were obtained with similar uniform size- and density-distribution inside each resin (Figure 4). The catalytic activity of ARP-Pt $\mathbf{4}_{\phi=90}$ and ARP-Pt $\mathbf{4}_{\phi=10}$ was examined for the aerobic oxidation of 1-phenethyl alcohol (**6a**). Thus, the oxidation reactions of **6a** were carried out in water at 60 °C with 5 mol% Pt of ARP-Pt $\mathbf{4}_{\phi=90}$ and ARP-Pt $\mathbf{4}_{\phi=10}$. Acetophenone (**8a**) was obtained both in 46% yield after 10 h, and in 81% (ARP-Pt $\mathbf{4}_{\phi=90}$) and 86% (ARP-Pt $\mathbf{4}_{\phi=10}$) yield, respectively. These observations indicate that this oxidation took place not only on the surface of the polymer beads but also throughout the polymer matrix where the Pt nanoparticles were dispersed with uniform size- and density-distribution. Thus, the importance of preparing well-organized and distributed Pt nanoparticles in the resins was demonstrated.

The work-up of the reactions was performed under organic solvent-free conditions by extraction with supercritical carbon dioxide, and the recovered ARP-Pt **4** was readily reused without further purification and/or reactivation.[21] While, in general, a serious decline of catalytic activity of Pt nanoparticle catalysts was problematic, catalytic deactivation of the reused **4** was not observed at all. Thus, after the oxidation of **6a** producing acetophenone (**8a**) in 82% yield (Scheme 2), the uniform-sized particle catalyst ARP-Pt **4** was reused 4 times to afford **8a** with stable chemical yield (1st use: 82%, 2nd use: 81%, 3rd use: 84%, 4th use: 92%, and 5th use: 90%) during which no significant change of the particle structure was observed by TEM.[22] In contrast, the random-sized particle **4′** suffered from significant deactivation during the reusing experiments (yield of **8a**; 1st use: 93%, 2nd use: 89%, 3rd use: 88%, 4th use: 79%, and 5th use: 68%). Notably, ARP-Pt **4** was stable, reusable, and not flammable under aerobic and aqueous conditions, and was stored in an open vessel for at least 1 year. Moreover, uniform-sized formation of Pt nanoparticles prevented leaching of Pt from the resin although random formation of Pt particles caused leaching. In Table 1, entry 16, the obtained 2-octanone (**8j**) was not contaminated with platinum residue (checked by ICP analysis). Over 99.9% of Pt was retained in the resin of ARP-Pt **4**: ICP analysis showed leaching of Pt to the aqueous solution was <1 ppm, and the aqueous filtrate did not show any catalytic activity. These observations indicate that the aerobic oxidation should take place inside the polymer matrix, presumably at the surface of the nanoparticles, though the catalysis with homogeneous platinum



Scheme 2. Recyclability of ARP-Pt **4** and **4a** for the aerobic oxidation of **6a** to **8a**. Scale bar = 10 nm.

species leached inside the matrix is still plausible where the metal species may redeposit back on the nanometal surface.[23] In contrast, the oxidation of **6j** mediated by ARP-Pt **4′** was performed in aqueous solution where 4.1 ppm of Pt was detected with ICP analysis. This means that 0.41 % of Pt leached out from ARP-Pt **4′** through the oxidation reaction.

Conclusions

In conclusion, we have developed a highly active and reusable amphiphilic resin-dispersion of nanoparticles of platinum (ARP-Pt). ARP-Pt was a useful catalyst for the aerobic oxidation of a wide variety of alcohols, including benzylic, allylic, alicyclic, and aliphatic alcohols, in aqueous media with high recyclability and stability. The reduction of **3** with benzyl alcohol afforded ARP-Pt **4** with uniform size and distribution of Pt nanoparticles although that with $NaBH_4$ gave **4′** with disordered size and distribution. Moreover, ARP **4** was readily reused without loss of catalytic activity as opposed to **4′**.

Experimental Section

General Methods

The aerobic oxidation of alcohols was performed in a glass tube under an atmospheric pressure of oxygen gas or air in a balloon. Water was deionized with a Millipore system. NMR spectra were recorded on a JEOL JNM-AL400 spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13}C) or a

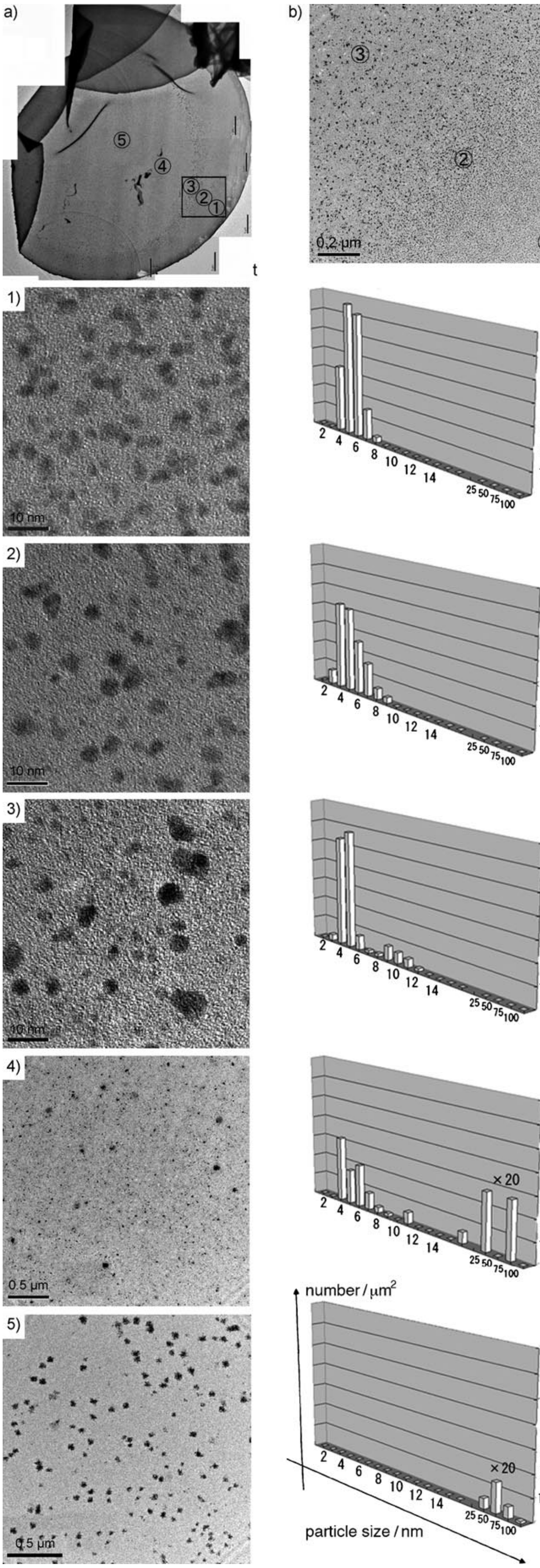
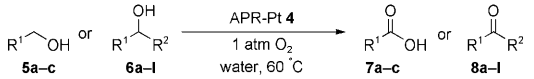
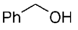
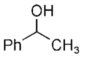
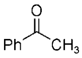
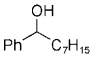
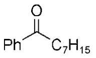
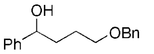
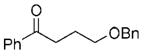
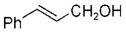
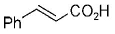
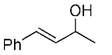
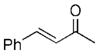
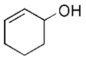
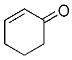
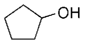
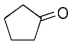
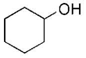
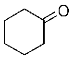
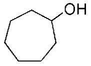
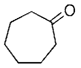
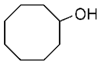
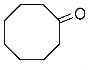
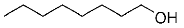
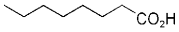
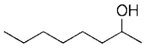
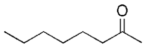
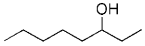
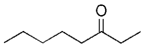
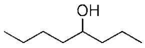
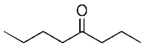


Figure 3. a) A TEM image of a section of **4′**; b) a TEM image of **4′** at (1)–(3) positions; (C) TEM images and histograms of **4′** at (1)–(5) positions; (x-axis: diameter of Pt nanoparticles (nm); y-axis: numbers of Pt nanoparticles (/µm^2)).

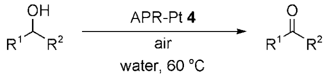
Table 1. The aerobic oxidation of alcohols **5** or **6** with ARP-Pt **4**.[a]



entry	substrate		**4** [mol %]	time [h]	product		conversion [%]	yield [%]
1[b]		**5a**	1	24	PhCO$_2$H	**7a**	99	99
2[b]			5	8			99	97
3		**6a**	5	24		**8a**	87	82
4		**6b**	10	36		**8b**	83	80
5		**6c**	20	36		**8c**	85	82
6[b]		**5b**	10	18		**7b**	99	93
7		**6d**	5	15		**8d**	88	87
8		**6e**	5	36		**8e**	99	72
9		**6f**	5	12		**8f**	91	80
10	ARP-Pd, 100 °C	**6f**	5	20		**8f**	<2	
11		**6g**	5	12		**8g**	85	81
12	ARP-Pd, 100 °C	**6g**	5	20		**8g**	<2	
13		**6h**	5	12		**8h**	99	93
14		**6i**	5	12		**8i**	99	87
15[b]		**5c**	10	10		**7c**	99	95
16		**6j**	5	15		**8j**	94	85
17	ARP-Pd, 100 °C	**6j**	5	20		**8j**	–	29
18		**6k**	10	30		**8k**	99	84
19		**6l**	10	36		**8l**	99	81

[a] All the reactions were carried out with **4** at 60 °C in water under atmospheric oxygen unless otherwise noted. [b] One mol equiv of K_2CO_3 was added.

Table 2. The air oxidation of alcohols **6** with ARP-Pt **4**.[a]



entry	substrate	**4** [mol %]	time [h]	product	conversion [%]	yield [%]
1	**6a**	10	24	**8a**	96	79
2	**6i**	20	60	**8i**	99	93
3	**6j**	20	60	**8j**	99	82

[a] All the reactions were carried out with **4** at 60 °C in water under air.

JEOL JNM-AL500 spectrometer (500 MHz for ^{1}H, 125 MHz for ^{13}C). SR-MAS ^{13}C NMR spectra were recorded on a JEOL JNM-AL400 spectrometer (100 MHz for ^{13}C). ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ at 25 °C. Chemical shifts were reported in δ ppm referenced to an internal tetramethylsilane standard for ^{1}H NMR. Chemical shifts of ^{13}C NMR were given relative to $CDCl_3$ as an internal standard (δ = 77.0 ppm). The GC-MS was measured by an Agilent 6890 GC/5973N MS detector that was used with biphenyl as an internal standard for the determination of the GC-yield. ATR-FT-IR spectra were measured with a FTIR-460 Plus spectrometer (JASCO). TEM images were obtained by using a transmission electron microscope (JEOL JEM-2100F) operated at 200 kV. TEM samples were prepared using a cryomicrotoming procedure for which sections of about 60 nm thick were cut by a cryomicrotome Ultracut UCT (Leica Ltd.) at −140 °C from beads, and were picked up on carbon-coated grids. Supercritical CO_2 extraction was performed with a JASCO SCF-Get. The alcohols, 1-phenylethanol (**6b**), benzyl alcohol (**5a**), cinnamyl alcohol (**5b**), 1-octanol (**5c**), cyclopentanol (**6f**), cyclohexanol (**6g**), cycloheptanol (**6h**), cyclooctanol (**6i**), 2-octanol (**6j**), 3-octanol (**6k**), 4-octanol (**6l**), 4-phenyl-3-buten-2-ol (**6d**), and 2-cyclohexenol (**6e**) were purchased from Aldrich or TCI. PS-PEG amino-resin **1** (TentaGel S NH_2, average diameter 0.90 μm, 1 % divinylbenzene cross-linked, loading value of amino residue 0.31 mmol g^{-1}) and PS-PEG amino-resin $\mathbf{1}_{\phi=10}$ (TentaGel N NH_2, average diameter 10 μm, 1 % divinylbenzene cross-linked, loading value of amino residue 0.23 mmol g^{-1}) were purchased from RAPP POLYMERE™.

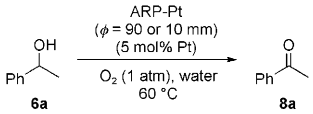
All oxidation products are known compounds whose CA registry numbers are provided as below:

5a: 100-51-6; **5b**: 108-93-0; **5c**: 104-54-1; **6a**: 98-85-1; **6b**: 19396-73-7; **6c**: 96-41-3; **6d**: 502-41-0; **6e**: 696-71-9; **6f**: 111-87-5; **6g**: 123-96-6; **6h**: 589-98-0; **6i**: 589-62-8; **6j**: 36004-04-3; **6k**: 822-67-3; **6l**: 139518-33-5; **7a**: 65-85-0; **7b**: 557-09-5; **7c**: 140-10-3; **8a**: 98-86-2; **8b**: 1674-37-9; **8c**: 120-92-3; **8d**: 108-94-1; **8e**: 502-42-1; **8f**: 502-49-8; **8g**: 111-13-7; **8h**: 106-68-3; **8i**: 589-63-9; **8j**: 1896-62-4; **8k**: 930-68-7; **8l**: 139518-43-7.

PS-PEG Resin-supported Dichloro(ethylene)platinum Complex 3

A mixture of PS-PEG amino-resin **1** (3.2 g, loading value of amino residue: 0.31 mmol g^{-1}) and Zeise's salt **2** (372 mg, 1.01 mmol) in water

Table 3. The effect of the diameter of the resins for the catalytic activity.[a]



ϕ(resin)	90 µm	10 µm
surface area [m^{2}g^{-1}]	3.05×10^{-2}	2.47
Pt loading [mmol g^{-1}]	0.21	0.21
yield [10 h]	46 %	46 %
yield [24 h]	81 %	86 %

[a] All the reactions were carried out with **4** at 60 °C in water under atmospheric oxygen.

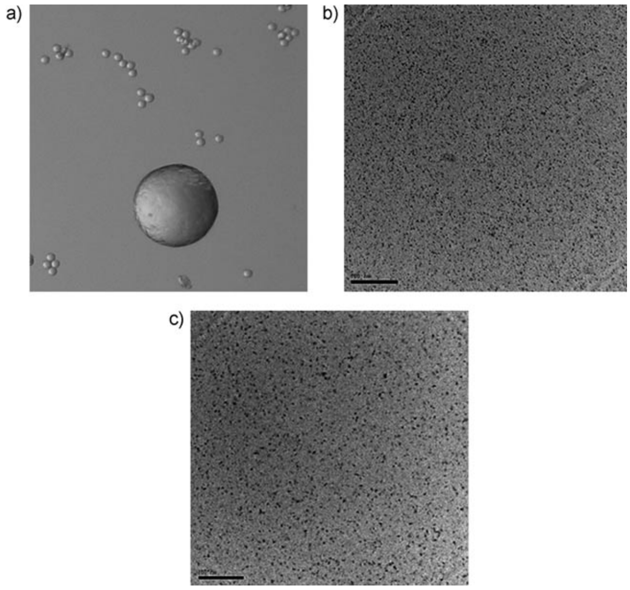


Figure 4. a) A microscopic image of the resins of ϕ 90 µm and ϕ 10 µm. b) and c) TEM images of **4** (B: ϕ 90 µm and C: ϕ 10 µm, bar 100 nm).

(20 mL) was shaken at room temperature for 1 h. The mixture was filtered and the resulting resin beads were rinsed three times with water and dried in vacuo to give **3** (3.5 g, loading value of platinum residue: 0.28 mmol g^{-1}): IR: $\tilde{\nu}=1602$, 3595, 3728 cm^{-1}; ^{13}C SR-MAS NMR (100 MHz, CDCl$_3$, 25 °C): $\delta=39.9$, 44.4, 70.1, 74.0, 104.2, 125.2, 127.5, 144.8 ppm.

PS-PEG Resin-dispersion of Platinum Nanoparticles (ARP-Pt) ***4***

A mixture of **3** (3.5 g; loading value of platinum residue: 0.28 mmol g^{-1}) and benzyl alcohol (5 mL) in water (24 mL) was shaken at 80 °C for 12 h. The mixture was filtered, and the resulting resin beads were rinsed three times with water (at 60 °C for 20 min) and three times with acetone (at 25 °C for 5 min), then dried in vacuo to give ARP-Pt **4** (3.4 g; loading value of platinum residue: 0.29 mmol g^{-1}): IR: $\tilde{\nu}=3557$, 3661 cm^{-1}; ^{13}C SR-MAS NMR (100 MHz, CDCl$_3$, 25 °C): $\delta=40.1$, 61.3, 66.6, 70.2, 104.0, 125.4, 127.8, 145.1 ppm.

PS-PEG Resin-dispersion of Platinum Nanoparticles ***4′***

A mixture of **3** (3.5 g; loading value of platinum residue: 0.28 mmol g^{-1}) and NaBH$_4$ (531 mg, 14 mmol) in water (25 mL) was shaken at 24 °C for 1 h. The mixture was filtered and the resulting resin beads were rinsed five times with water and three times with acetone, then dried in vacuo to give **4′** (3.4 g; loading value of platinum residue; 0.29 mmol g^{-1}): IR: $\tilde{\nu}=3573$, 3728 cm^{-1}; ^{13}C SR-MAS NMR (100 MHz, CDCl$_3$, 25 °C): $\delta=38.9$, 39.5, 39.9, 56.0, 60.9, 66.3, 69.9, 72.0, 101.4, 108.6, 123.1, 127.3, 144.7 ppm.

General Procedure for Catalytic Aerobic Oxidation of Primary Alcohols in Water

A mixture of ARP-Pt **4** (0.01 mmol of platinum), primary alcohol (0.2 mmol), and potassium carbonate (0.2 mmol) in water (2 mL) was stirred at 60 °C under an atmospheric pressure of oxygen gas. After being cooled, the mixture was washed with *tert*-butyl methyl ether, and acidified with 5 % hydrochloric acid. The mixture was extracted with ethyl acetate (5×1 mL). The extract was dried over magnesium sulfate and concentrated in vacuo to give the corresponding carboxylic acid.

General Procedure for Catalytic Aerobic Oxidation of Secondary Alcohols in Water

A mixture of ARP-Pt **4** (0.01 mmol of platinum) and the secondary alcohol (0.2 mmol) in water (2 mL) was stirred at 60 °C under an atmospheric pressure of oxygen gas. After it was cooled, the mixture was filtered to give the resin beads **4** holding the resulting ketone.

Post-treatment Procedure A: Extract with EtOAc

The resin beads were rinsed three times with ethyl acetate (3×1 mL). The aqueous layer was extracted with ethyl acetate (3×1 mL). The combined extracts were dried over magnesium sulfate and concentrated in vacuo to give the corresponding ketone **8**.

Post-treatment Procedure B: Extract with scCO$_2$

The resin beads were extracted with supercritical carbon dioxide (296 atm, 40 °C, 24 min), and the remaining product in aqueous media was isolated by evaporation of the water to afford the corresponding ketone **8**. The recovered catalyst beads were reused without any further purification or activation.

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[19] Total loading value of Pt species (0.02 mmol) whose surface atom number estimated from the average diameter of the particles was 1212 Pt atoms.

[20] When the reaction of **6a** was carried out at 80 °C, 15–20 % yield of ethylbenzene was obtained as a major side product.

[21] It was argued that the oxidation with leached homogeneous platinum species could be plausible where the metal species may redeposit back on the heterogeneous surface. For a recent review, see: N. T. S. Phan, M. V. D. Sluys, C. W. Jones, *Adv. Synth. Catal.* **2006**, *348*, 609, and references therein.

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