Oxidation Catalysts

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A Nanoplatinum Catalyst for Aerobic Oxidation of Alcohols in Water**

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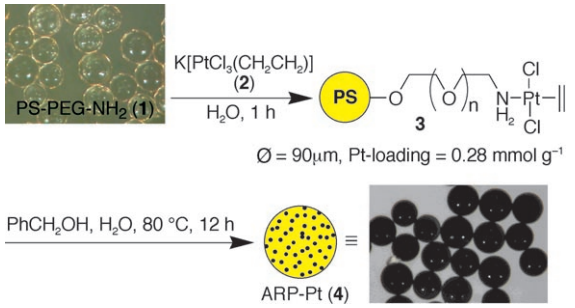
The development of highly active immobilized catalysts for the aerobic oxidation of a variety of alcohols in aqueous media is a tremendously important topic in chemistry today.[1] Yet aerobic oxidation of nonactivated alcohols, such as aliphatic and alicyclic alcohols, using immobilized catalysts generally proceeds poorly.[2] There have been reports of heterogeneous metal catalysts being applied to the aerobic oxidation of various alcohols, but the catalysts were regularly used in harmful organic solvents[3] and/or under vigorous conditions.[4] Over the last few years, our group,[5] Kaneda et al.,[6] Sheldon et al.,[7] and Corma et al.[8] reported the aerobic oxidation of some aliphatic and alicyclic alcohols in water with reusable catalysts.[9] While acknowledging the pioneering work in this area, we believe the development of a novel catalyst system that exhibits a wide range of substrate tolerance under mild and aqueous conditions still remains a major challenge. Consequently, we devised a dispersion of nanoparticles of palladium in an amphiphilic polystyrene–polyethylene glycol (PS-PEG) resin (ARP-Pd; ARP: amphiphilic resin particles) that catalyzes the aerobic oxidation of alcohols in water at 100 °C.[10]

However, despite such progress, the reactivity and versatility of ARP-Pd for the oxidation of alicyclic and aliphatic alcohols was inadequate (see below). We therefore considered platinum nanoparticles,[11,12] since platinum has a stronger oxidizing ability than palladium (Pt/Pt^{2+} $E_{ox} = +1.12$ V versus Pd/Pd^{2+} $E_{ox} = +0.95$ V). However, deactivation of platinum by oxygen is problematic for its efficient reuse,[13] and Pt particles possess a latent tendency to explode under oxidative conditions in organic solvents.[14] Our concept for the preparation of ARPs, where metal particles would be stabilized by amphiphilic resins in aqueous media, should overcome these drawbacks. Herein, we report the development of an ARP-Pt and its application to the aerobic oxidation in water of a wide variety of alcohols, including not only benzylic and allylic but also alicyclic and aliphatic alcohols. Notably, ARP-Pt promoted the reaction efficiently at 60 °C with high recyclability.

ARP-Pt (**4**) was prepared by complexation of commercially available PS-PEG-NH_2 (**1**; TentaGel S NH_2) with Zeise's salt (**2**·H_2O) in water followed by reduction (Scheme 1). High-resolution transmission electron microscopy (TEM) analysis of **4** revealed that the Pt nanoparticles in it had a mean diameter of 5.9 nm with a very narrow size distribution throughout the resin, and that the density of the Pt particles was uniform in the resin (Figure 1). Energy-dispersive spectroscopy/scanning electron microscopy (EDS/SEM) analysis also revealed a uniform dispersion of Pt throughout the resin.[15] To the best of our knowledge, a uniform dispersion of nanoparticles into the entire region of an insoluble resin with uniform density distribution was realized for the first time.[16]



Scheme 1. Preparation of ARP-Pt (**4**).

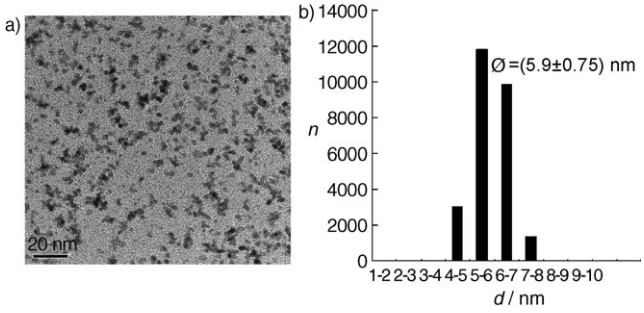


Figure 1. a) High-resolution TEM image of **4**. b) Histogram of the size distribution of the Pt particles (*n*: number of Pt particles per μm²; *d*: diameter of the particles).

With an amphiphilic resin catalyst containing Pt nanoparticles of uniform size and density distribution in hand, we conducted the oxidation of a variety of primary and secondary alcohols to the corresponding carbonyl compounds. Representative data are summarized in Table 1, where several results from Pd catalysis are included for comparison (Pt versus Pd). The oxidation of **5a** (20 mmol, 2.2 g) with 1.0 mol% ARP-Pt[17] was performed at 60 °C for 24 h to

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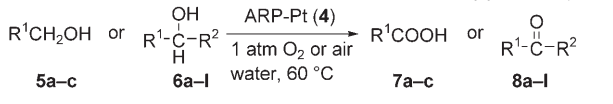
Table 1: The aerobic oxidation of alcohols **5** with ARP-Pt (**4**) as catalyst.[a]



5a–c **6a–l** **7a–c** **8a–l**

Run	Substrate/ Product	R^1	R^2	**4** [mol%]	*t* [h]	Yield [%]
1[b]	**5a/7a**	Ph		1.0	24	99
2[b]				5.0	8	97
3	**6a/8a**	Ph	CH_3	5.0	24	82
4				(2nd use)		81
5				(3rd use)		84
6				(4th use)		92
7				(5th use)		90
8	(under air)			10	36	79
9				5.0[c]	24	86
10	**6b/8b**	Ph	C_7H_{15}	10	36	80
11	**6c/8c**	Ph	$(CH_2)_3OBn$	10	36	82
12[b]	**5b/7b**	$PhCH{=}CH_2$		10	18	93
13	**6d/8d**	$PhCH{=}CH_2$	CH_3	5.0	15	87
14	**6e/8e**	$-CH{=}CH(CH_2)_3-$		5.0	36	72
15	**6f/8f**	$-(CH_2)_4-$		5.0	12	80
16				5.0[d]	20	<2
17	**6g/8g**	$-(CH_2)_5-$		5.0	12	81
18				5.0[d]	20	<2
19	**6h/8h**	$-(CH_2)_6-$		5.0	12	93
20	**6i/8i**	$-(CH_2)_7-$		5.0	12	87
21	(under air)			20	60	93
22[b]	**5c/7c**	*n*-C_7H_{15}		10	36	95
23	**6j/8j**	*n*-C_6H_{13}	CH_3	5.0	15	87
24	(under air)			20	60	82
25				5.0[d]	20	29
26	**6k/8k**	*n*-C_5H_{11}	C_2H_5	10	30	84
27	**6l/8l**	*n*-C_4H_9	*n*-C_3H_7	10	36	81

[a] All the reactions were carried out with **4** at 60°C in water under atmospheric oxygen unless otherwise noted (Bn = benzyl). [b] 1 mol equivalent of K_2CO_3 was added. [c] ARP-Pt made of 10-μm-diameter resin was used ($\mathbf{4}_{\varnothing 10}$). [d] With ARP-Pd under O_2 at 100°C.

give **7a** in 99% yield of isolated product (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 (Table 1, runs 3 and 10–14).[18]

We were pleased to find that the aerobic oxidation of a variety of nonactivated alicyclic alcohols, cyclopentanol (**6f**), cyclohexanol (**6g**), cycloheptanol (**6h**), and cyclooctanol (**6i**), also took place smoothly to provide the corresponding alicyclic ketones in 80–93% yield (Table 1, runs 15, 17, 19, and 20). Moreover, it was found that the nonactivated 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 (Table 1, runs 22, 23, 26, and 27) under similar conditions. Chemoselective oxidation was also accomplished, in that alkenes and a benzyl ether were tolerated (Table 1, runs 11–14).

Atmospheric air was likewise applied as an oxidant in this catalytic system. Thus, the efficient conversion of benzylic, alicyclic, and aliphatic secondary alcohols **6a**, **6i**, and **6j** was achieved to afford **8a**, **8i**, and **8j** in 79, 93, and 82% yield, respectively (Table 1, runs 8, 21, and 24). The ARP-Pd catalyst exhibited lower activity even at a higher reaction temperature (Table 1, runs 16, 18, and 25). Notably, the aerobic oxidation of **6a** with ARP-Pt $\mathbf{4}_{\varnothing 10}$, which was prepared from 10-μm-diameter PS-PEG resin beads, gave a similar result to that obtained with **4** ($\varnothing = 90$ μm; Table 1, runs 3 and 9). These observations indicate that the 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.

The workup of the reactions was performed under organic-solvent-free conditions by extraction with supercritical carbon dioxide, and recovered **4** was readily reused without further purification and/or reactivation.[19,20] In general, the catalytic activity of Pt nanoparticle catalysts seriously declines, while catalytic deactivation of reused **4** was not observed at all (Table 1, run 3–7). In addition, no change of the particle structure was observed by TEM. 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 one year.

In conclusion, we have developed a highly active and reusable catalytic system 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.

Experimental Section

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 $\mathbf{2}\cdot H_2O$ (372 mg, 1.01 mmol) in water (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}; swollen-resin magic-angle spinning (SR-MAS) ^{13}C 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.

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 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: $\tilde{\nu} = 3557$, 3661 cm^{-1}; SR-MAS ^{13}C 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.

General procedure for the catalytic aerobic oxidation of primary alcohols in water: A mixture of **4** (0.002 mmol of effective platinum), primary alcohol (0.2 mmol), and potassium carbonate (0.2 mmol) in water (2 mL) was stirred at 60°C under oxygen gas at atmospheric pressure. After cooling, 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 the catalytic aerobic oxidation of secondary alcohols in water: A mixture of **4** (0.002 mmol of effective platinum) and the secondary alcohol (0.2 mmol) in water (2 mL) was stirred at 60°C under oxygen gas at atmospheric pressure. After cooling, the mixture was filtered to give the resin beads **4** that held the resulting ketone.

Post-treatment procedure A: extract with EtOAc: The resin beads were rinsed three times with ethyl acetate (3×1 mL) and 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 ketones **8**.

Post-treatment procedure B: extract with $scCO_2$: The resin beads were extracted with supercritical (sc) carbon dioxide (296 atm, 40 °C, 24 min) to afford the corresponding ketones **8**. The recovered catalyst beads were reused without any further purification or activation.

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[17] Total loading of Pt species (0.02 mmol) was 1212 Pt atoms; the number of surface atoms was estimated from the average diameter of the particles.

[18] Control experiments were carried out at 60 and 160 °C without Pt species: the aerobic oxidation of **6a** did not proceed at 60 °C at all, whereas at 160 °C under neat conditions **8a** was obtained in 64 % yield (24 h; not optimized); Y. Uozumi, Y. M. A. Yamada, unpublished results.

[19] The obtained 2-octanone (Table 1, entry 23) was not contaminated with platinum residue (checked by inductively coupled plasma (ICP) analysis). Over 99.9 % of Pt was retained in the resin: ICP analysis showed that leaching of Pt to the aqueous solution was less than 1 ppm, and the aqueous filtrate did not show any catalytic activity.

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