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Linear polystyrene-stabilized Pt nanoparticles for aerobic alcohol oxidation and hydrogen-transfer reduction in aqueous media

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ABSTRACT

Linear polystyrene-stabilized Pt nanoparticles were prepared using phenylboronic acid and $NaBH_4$ as the reductant. The size of Pt nanoparticles was dependent on the reductant, while the immobilization degree of Pt was not. The resultant polystyrene-stabilized Pt nanoparticles showed high catalytic activity for aerobic alcohol oxidation in water and hydrogen-transfer reduction of olefin, ketone, and nitro group using 2-propanol as a hydrogen donor. The catalyst was recycled without significant loss of activity.

1. Introduction

Organic reactions in water have recently received much attention because water is a readily available, safe, and environmentally benign solvent [1,2]. On the other hand, there is strong interest in developing reactive and selective catalysts that can be easily separated from products after the reaction [3,4]. The oxidation of alcohols is one of the most important transformations in organic synthesis because the corresponding carbonyl compounds serve as important and versatile intermediates for the synthesis of fine chemicals [5,6]. Since the pioneering study on the aerobic oxidation of alcohol in water using a palladium(II) bathophenantoroline complex by Sheldon and co-workers [7], numerous efforts have been made to develop new catalytic protocols for the oxidation of alcohols particularly with molecular oxygen as the sole oxidant. Several examples have been reported for the aerobic oxidation of alcohol in water using recyclable metal nanoparticles (PdNPs [8–11], PtNPs [12–17], and AuNPs [18–20]). Among them, PtNPs were found to be superior catalysts compared with other metals. For example, Uozumi et al. developed amphiphilic polystyrene-poly(ethylene glycol) resin-stabilized PtNPs that have higher aerobic alcohol oxidation activity than PdNPs in water [13,17]. Kou and Liu found that PtNPs stabilized by poly(*N*-vinyl-2-pyrrolidone) (PVP) were capable of catalyzing the aerobic oxidation in the absence of base and were more active than PdNPs and AuNPs [14,16].

Recently, we found that linear polystyrene was capable of stabilizing PdONPs or PdNPs, and that the resultant polystyrene-stabilized PdONPs or PdNPs (PS-PdONPs or PS-PdNPs) have high catalytic activities for Suzuki, Heck, and copper-free Sonogashira coupling reactions in water [21–25]. Our continuing interest in the scope and applicability of this methodology led us to investigate the preparation of polystyrene-stabilized PtNPs (PS-PtNPs). Herein, we report the preparation and application of PS-PtNPs for aerobic alcohol oxidation in water of various alcohols and hydrogen-transfer reduction of olefin, ketone, and nitro group to prove its efficiency in promoting the reaction with high recyclability.

2. Experimental

2.1. General comments

^1H NMR spectra in $CDCl_3$ were recorded with a 300 MHz NMR spectrometer (UNITY 300, Varian, Palo Alto, CA) using tetramethylsilane ($\delta = 0$) as an internal standard. Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) was performed using ICPS-8100 (Shimadzu Co., Kyoto, Japan). Pt nanoparticles were investigated by transmission electron microscopy (TEM) on a JEM 2100F transmission electron microscope (JEOL Ltd., Tokyo, Japan). The samples were prepared by placing a drop of the solution on carbon coated copper grids and allowed to dry in air. X-ray

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photoelectron spectroscopy (XPS) analysis was carried out using a PHI 5700MC (ULVAC-PHI, Inc., Kanagawa, Japan). Polystyrene of narrow molecular weight distribution standards was purchased from Tosoh Co., Ltd. (Tokyo, Japan). K_2PtCl_4 was obtained from Sigma–Aldrich Co. (MO, USA).

*2.2. Preparation of PS-PtNPs by reduction with phenylboronic acid (**1a**)*

To a screw-capped vial with a stirring bar were added 14 mg of polystyrene (22 μmol of styrene unit), K_2PtCl_4 16 mg (38 μmol), $PhB(OH)_2$ 91 mg (0.75 mmol), and 1.5 M aqueous KOH solution (2 mL). After stirring at 80 °C for 20 h, the reaction mixture was cooled to room temperature by immediately immersing the vial in water (~20 °C). Subsequently, the aqueous phases were removed, and the polystyrene-stabilized Pt nanoparticles were washed with water (5 × 1.5 mL) and diethyl ether (5 × 1.5 mL).

*2.3. Preparation of PS-PtNPs by reduction with $NaBH_4$ (**1b**)*

To a screw-capped vial with a stirring bar were added 14 mg of polystyrene (22 μmol of styrene unit), K_2PtCl_4 16 mg (38 μmol), and water (2 mL). After adding methanol solution of $NaBH_4$ (0.01 mol L^{-1}) dropwise, the mixture was stirring at 25 °C for 1 h, and then the aqueous solution was decanted. Subsequently, the polystyrene-stabilized Pt nanoparticles were washed with water (5 × 1.0 mL) and acetone (5 × 1.0 mL).

2.4. Determination of the amount of platinum

PS-PtNPs (1.0 mg) was placed in a screw-capped vial and then added 10 M hydrochloric acid (5 mL). The mixture was heated at 80 °C to dissolve completely. After cooled to room temperature, the solution was adjusted to 40 g by water and then measured the amount of Pt metal by ICP-AES analysis (13.0 ppm).

After the catalytic reaction, the aqueous phase was adjusted to 10 g by hydrochloric acid and then measured the amount of Pt metal by ICP-AES analysis.

2.5. Typical procedure for aerobic alcohol oxidation

To a screw-capped test tube with a stirring bar were added 0.5 mmol of 4-methylbenzyl alcohol, PS-PtNPs (2.0 mol% of Pt), and H_2O (1 mL). The mixture was stirred at 30 °C for 10 h under O_2. Oxygen gas was introduced into the test tube from an O_2 balloon under atmospheric pressure. After the reaction, the aqueous phases were removed, and recovered catalyst was washed with water (5 × 1.5 mL) and diethyl ether (5 × 1.5 mL), which were then added to the aqueous phase. After the aqueous phase was extracted five times with diethyl ether, the combined organic extracts were dried over $MgSO_4$, concentrated under reduced pressure. The product was analyzed by ^1H NMR. The recovered catalyst was dried *in vacuo* and reused. Furthermore, the amount of Pt metal in the aqueous phase determined by ICP-AES analysis was 0.75 ppm.

The structures of all products were confirmed by the comparison of ^1H NMR with those of authentic samples in the literature; *p*-tolualdehyde [26], *p*-toluic acid [27], *p*-methoxybenzaldehyde [26], *p*-chlorobenzaldehyde [28], *p*-chlorobenzoic acid [27], *o*-tolualdehyde [26], *o*-toluic acid [27], *trans*-cinnamaldehyde [26], citral [29], benzyl [30], benzophenone [31], acetophenone [31], 1-indanone [31], cyclohexanone [32], cyclooctanone [33], 2-octanone [34].

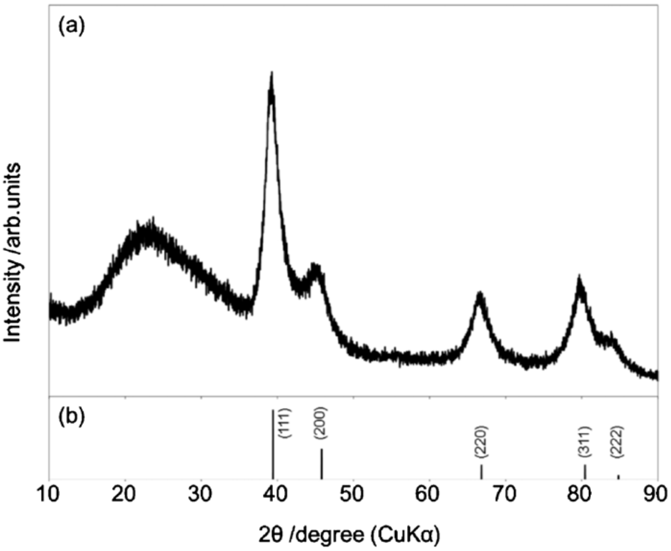


Fig. 1. (a) XRD patterns of **1a**; (b) JCPDS data (#04-0802) for Pt.

2.6. Typical procedure for hydrogen-transfer reduction

To a screw-capped vial with a stirring bar were added 0.5 mmol of cinnamic acid, PS-PtNPs (5.0 mol% of Pt), 2-propanol (0.19 mL, 2.5 mmol), and 1.5 M aqueous KOH solution (0.5 mL). The mixture was stirred at 70 °C for 20 h. After the reaction, the aqueous phases were removed, and recovered catalyst was washed with water (5 × 1.5 mL) and diethyl ether (5 × 1.5 mL), which were then added to the aqueous phase. After the aqueous phase was extracted five times with diethyl ether, the combined organic extracts were dried over $MgSO_4$, concentrated under reduced pressure. The product was analyzed by ^1H NMR.

The structures of all products were confirmed by the comparison of ^1H NMR with those of authentic samples in the literature: hydrocinnamic acid [32], bibenzyl [35], diphenylmethanol [36], aniline [37].

3. Results and discussion

3.1. Preparation of PS-PtNPs

PS-PtNPs were prepared using phenylboronic acid and $NaBH_4$ as the reductant [23]. An X-ray diffraction (XRD) pattern of PS-PtNPs is presented in Fig. 1. In addition to the broad diffraction with 2θ ranging from 12° to 30° ascribed to polystyrene, five other

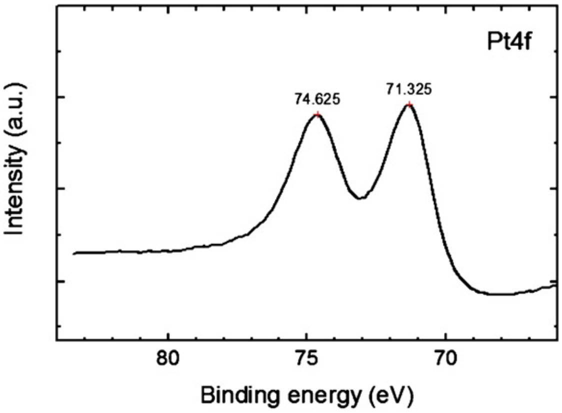


Fig. 2. XPS analysis for Pt 4f spectra of **1a**.

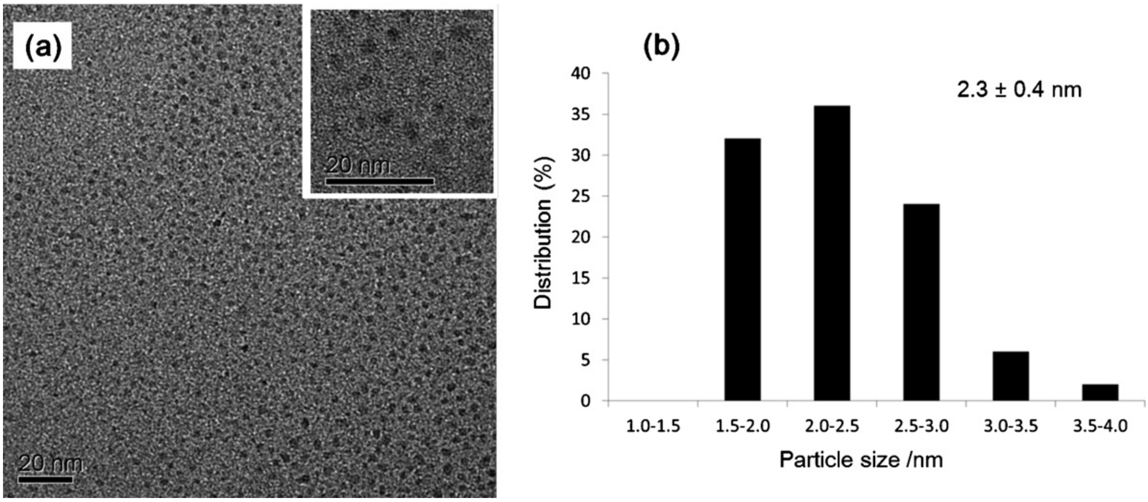


Fig. 3. (a) TEM image of **1a**. (b) Size distribution of PtNPs in **1a**.

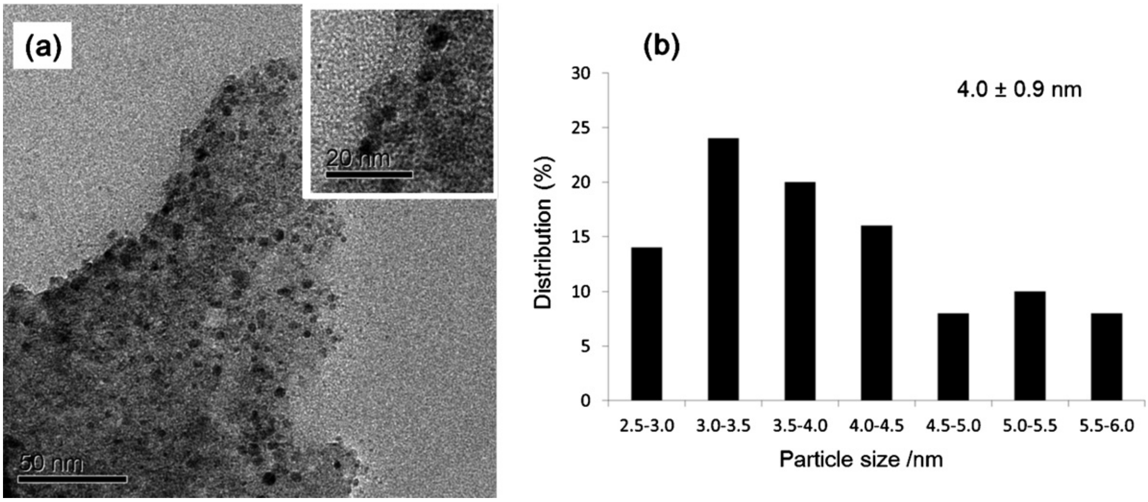


Fig. 4. (a) TEM image of **1b**. (b) Size distribution of PtNPs in **1b**.

diffraction peaks at Bragg angles of 39.8°, 46.2°, 67.5°, 81.3°, and 85.7° can be indexed to the (1 1 1), (2 0 0), (2 2 0), (3 1 1), and (2 2 2) lattice planes of face centered cubic (fcc) platinum [38]. An X-ray photoelectron spectroscopy (XPS) analysis showed binding energy at 71.3 eV, which assigned to Pt $4f_{7/2}$ for metallic Pt (Fig. 2). A transmission electron microscopy (TEM) image of PS-PtNPs (**1a**) reduced by phenylboronic acid revealed a fairly uniform particle size of 2.3 ± 0.4 nm (Fig. 3), probably due to the stabilization

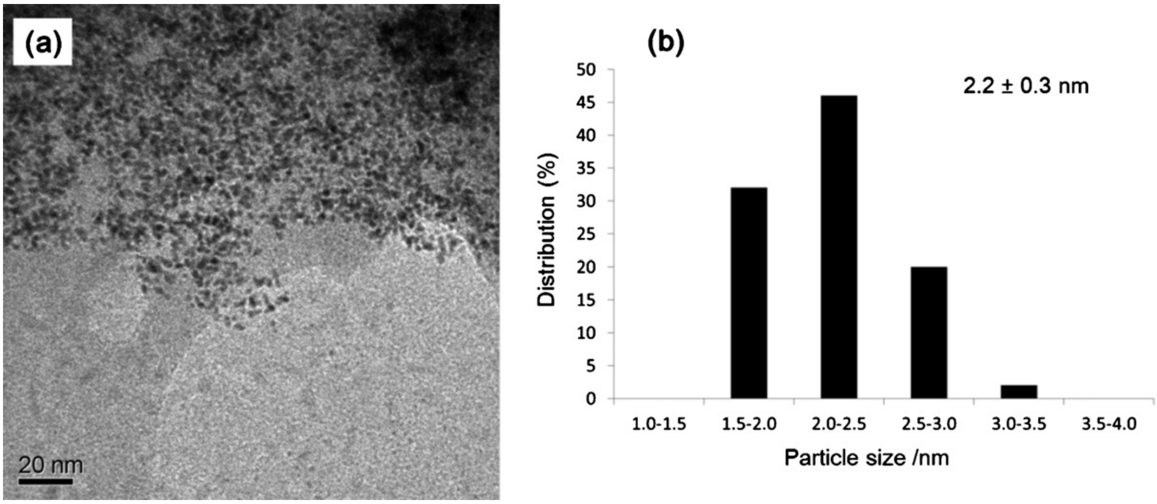
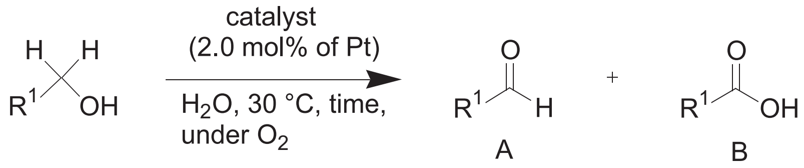
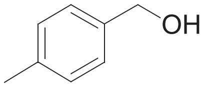
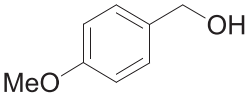
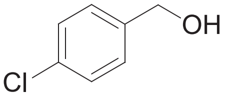
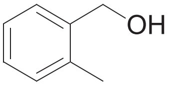
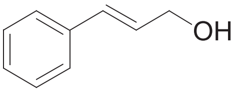
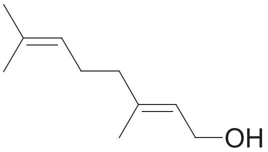


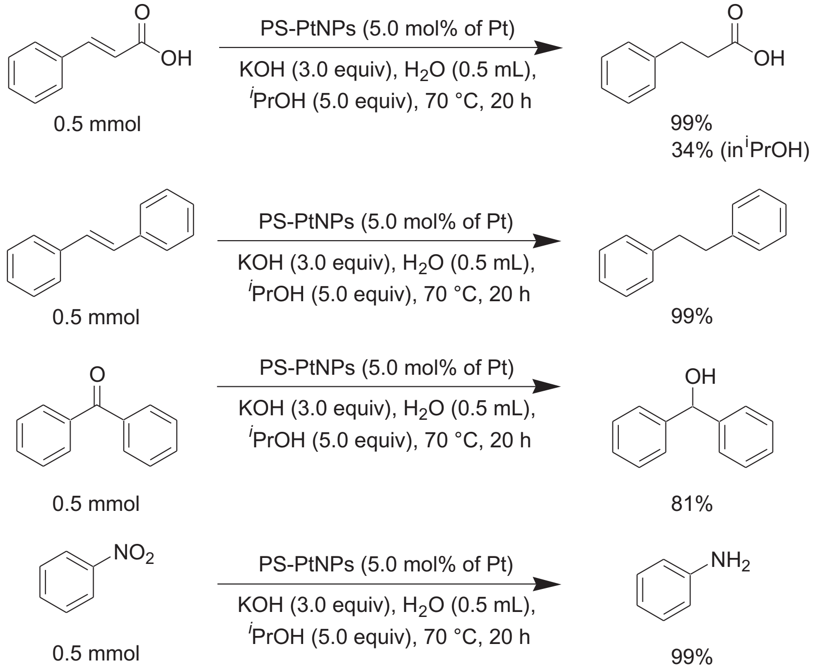
Fig. 5. (a) TEM image of recovered catalyst. (b) Size distribution of PtNPs in recovered catalyst.

Table 1
Oxidation of various primary alcohols in water.



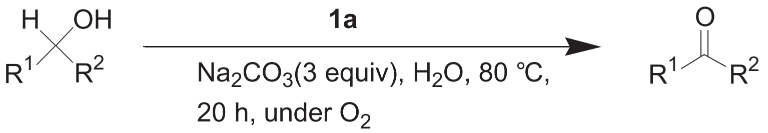
Entry	Substrate	Catalyst	Time (h)	Yield (%)[a]	
				A	B
1		PS-PtNPs (**1a**)	10	80	16
2		PS-PtNPs (**1b**)	10	56	4
3		Pt/C	10	60	10
4		K_2PtCl_4	10	0	0
5		PS-PdONPs	10	46	0
6		PS-PtNPs (**1a**)	10	96	0
7		PS-PtNPs (**1a**)	20	86	8
8		PS-PtNPs (**1a**)	20	43	41
9		PS-PtNPs (**1a**)	20	79	0
10		PS-PtNPs (**1a**)	20	99	0

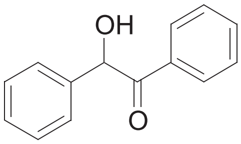
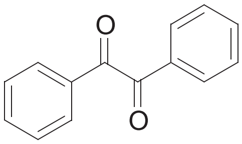
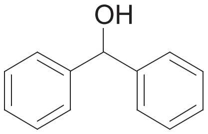
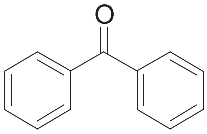
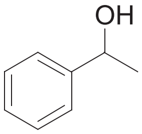
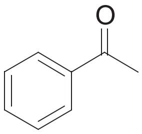
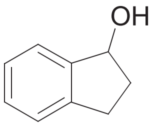
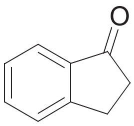
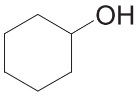
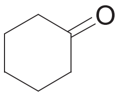
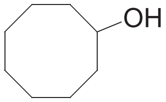
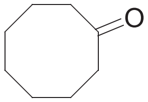
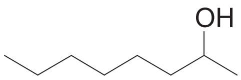
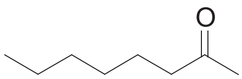
[a] NMR yield.



Scheme 1. Transfer hydrogenation of olefin, ketone, and nitro group.

Table 2
Oxidation of various secondary alcohols in water.



Entry	Substrate	Product	Pt (mol%)	Yield (%)[a]	TON
1			2.0	95	47.5
2				(2nd run) 96	48
3				(3rd run) 92	46
4				(4th run) 97	48.5
5				(5th run) 94	47
6			2.0	82	41
7			5.0	75	15
8			5.0	87	17.4
9			5.0	72	14.4
10			5.0	85	17
11			5.0	63	12.6

[a] NMR yield.

by phenylboronic acid [39]. However, the 1 s peak of B was not observed by XPS analysis, indicating no boronic acid was present in **1a**. PS-PtNPs (**1b**) prepared with $NaBH_4$ was examined by TEM, showing nanoparticles of about 4.0 ± 1.0 nm (Fig. 4). Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) revealed that **1a** and **1b** contained an average of 2.7 and 2.3 mmol g^{-1} of Pt, respectively. The PtNPs are immobilized on the polymer through interactions between π electrons of the benzene rings of the polystyrene and the vacant orbitals of the metal [40]. Unfortunately, however, we could not confirm any obvious differences between polystyrene and polystyrene-stabilized PtNPs in the FT-IR spectra [41]. These results indicated that linear polystyrene was useful as a stabilizer for PtNPs.

3.2. *Catalytic performance*

For evaluation of the catalytic activity of PS-PtNPs, the aerobic oxidation of 4-methylbenzyl alcohol was carried out in water under atmospheric pressure of O_2 as a model reaction. The reaction with **1a** took place at 30 °C for 10 h in the absence of base to give a mixture of 4-methylbenzaldehyde and 4-methylbenzoic acid in 80% and 16% yields, respectively (Table 1, entry 1). In contrast, **1b** exhibited slightly lower catalytic activity, probably due to their large particle size (entry 2). Neither Pt/C nor K_2PtCl_4 were effective catalyst under these reaction conditions (entries 3 and 4). Recently, Lee and co-workers reported that highly dispersed PdONPs, instead of zerovalent Pd, are the catalytically active species for the aerobic oxidation of alcohol [42]. Therefore, the same reaction was also performed with PS-PdONPs for comparison. As shown in entry 5, PS-PdONPs have lower catalytic activity than **1a**. When the aerobic oxidation was performed with para-substituted benzyl alcohols, the electron-donating group facilitated the reaction (entries 1, 6, and 7) [43]. For 2-methylbenzyl alcohol, it needed 20 h to achieve a good conversion (entry 8). Cinnamyl alcohol and geraniol underwent selective oxidation reaction to give the corresponding aldehydes in 79% and 99% yields, respectively (entries 9 and 10).

Secondary alcohols, exhibited much lower catalytic productivity than primary alcohols, could be converted to the corresponding ketones with moderate to high conversion in the presence of Na_2CO_3. Thus, benzoin underwent catalytic oxidation to give benzil in 95% yield (Table 2, entry 1). The recovered **1a** showed a similar TEM image (Fig. 5) and was reused with negligible loss of catalytic activity (entries 2–5). The average yield in consecutive runs was 95%, and the total TON of PS-PtNPs in the 1st to the

5th cycled reactions reached 237. After the workup, the aqueous filtrate exhibited no catalytic activity for the oxidation. However, when the reaction solution was analyzed by ICP-AES after every run to determine the amount of Pt leaching during the reaction, the total amount of Pt leaching after the fifth run was <1.0%. For 1-phenylethanol, 1-indanol, and aliphatic alcohols, it needed 5.0 mol% Pt of **1a** to achieve good conversions (entries 7–11). In addition, a similar catalytic activity was observed on using a soluble PtNPs [14,16], suggesting that heterogeneous-switching does not inhibit the catalytic activity.

Since PS-PtNPs were proved to function efficiently for the aerobic alcohol oxidation in water, the hydrogen-transfer reduction of organic compounds [44–46] was also investigated. Transfer hydrogenation, which uses H donors instead of hazardous H_2, is an attractive methodology. 2-Propanol is most widely used as a hydrogen donor since it is cheap, nontoxic, volatile, and is converted to acetone, which is environmentally friendly and easy to remove from the reaction system. The hydrogenation of cinnamic acid was carried out at 70 °C in the presence of **1a** (5.0 mol% of Pt), 1.5 equiv of KOH, and 5.0 equiv of 2-propanol in water (Scheme 1). The reduction of cinnamic acid was accomplished in 20 h to afford 3-phenyl propionic acid in 99% yield. In contrast, the conversion of cinnamic acid was low (34%) when using 2-propanol as a sole solvent. The transfer hydrogenation of *trans*-stilbene gave bibenzyl in 99% yield. When acetophenone and nitrobenzene were used as substrate, diphenylmethanol and aniline were obtained in 81% and 99% yields, respectively.

4. Conclusions

Linear polystyrene was proven to be a useful stabilizer for PtNPs. XRD analysis and TEM observation indicated the formation of PtNPs on polystyrene. PS-PtNPs have high catalytic activity for the aerobic oxidation of alcohol and the transfer hydrogenation of olefin, ketone, and nitro group.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molcata.2012.04.007.

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