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Hydrogenation and Dehalogenation under Aqueous Conditions with an Amphiphilic-Polymer-Supported Nanopalladium Catalyst

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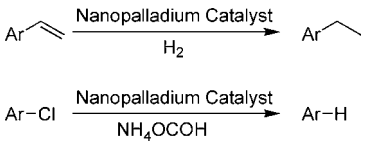
ABSTRACT



An amphiphilic polystyrene–poly(ethylene glycol) resin supported nanopalladium particle catalyzed hydrogenation of olefins and hydrodechlorination of chloroarenes under aqueous conditions is presented.

In recent years, much attention has been focused on aqueous[1] and heterogeneous switching[2] of organic transformations. We have developed a variety of amphiphilic polystyrene−poly(ethylene glycol) (PS−PEG) resin supported transition metal complexes, which catalyze various synthetic organic reactions smoothly in water under heterogeneous conditions.[3] However, with the advent of accessible methods for the preparation and/or handling of nanometal particles, catalytic organic transformations with nanometal particles have been gaining popularity.[4] One approach employs functional polymer-supported nanoparticles that can be used in an appropriate reaction medium and readily removed by filtration. We previously reported that alcohol oxidation to produce carbonyl compounds was catalyzed by an amphiphilic PS−PEG resin dispersion of nanoparticles of palladium (ARP-Pd, Figure 1) in water under aerobic conditions to realize clean, safe oxidation.[5,6] The ARP-Pd catalyst was designed to combine the amphiphilic polymer-based heterogeneous aquacatalytic properties and high catalytic activity because of the large surface area of the nanoparticles. Our continuing interest in the utility of ARP-Pd under aqueous conditions led us to examine its catalytic potential in reductive reactions. We wish to report the catalytic hydrogenation of olefins and hydrodechlorination of aryl chlorides catalyzed by ARP-Pd under mild, aqueous conditions.

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(1) For reviews on aqueous switching, see: (a) Li, C.-J.; Chan, T.-H. *Organic Reactions in Aqueous Media*; Wiley-VCH: New York, 1997. (b) Grieco, P. A., *Organic Synthesis in Water*; Kluwer Academic Publishers: Dordrecht, 1997. (c) Herrmann, W. A.; Kohlpaintner, C. W. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1524. (d) Lindström, U. M. *Chem. Rev.* **2002**, *102*, 2751.

(2) (a) For reviews on heterogeneous switching, see: Bailey, D. C.; Langer, S. H. *Chem. Rev.* **1981**, *81*, 109. (b) Shuttleworth, S. J.; Allin, S. M.; Sharma, P. K. *Synthesis* **1997**, 1217. (c) Shuttleworth, S. J.; Allin, S. M.; Wilson, R. D.; Nasturica, D. *Synthesis* **2000**, 1035. (d) Dörwald, F. Z. *Organic Synthesis on Solid Phase*; Wiley-VCH: Weinheim, 2000. (e) Leadbeater, N. E.; Marco, M. *Chem. Rev.* **2002**, *102*, 3217. (g) McNamara, C. A.; Dixon, M. J.; Bradley, M. *Chem. Rev.* **2002**, *102*, 3275. (h) De Vos, D. E., Vankelecom, I. F. J., Jacobs, P. A., Eds. *Chiral Catalyst Immobilization and Recycling*; Wiley-VCH: Weinheim, 2000. (i) Ley, S. V.; Baxendale, I. R.; Bream, R. N.; Jackson, P. S.; Leach, A. G.; Longbottom, D. A.; Nesi, M.; Scott, J. S.; Storer, R. I.; Taylor, S. J. *J. Chem. Soc., Perkin Trans. 1* **2000**, 3815. (j) Fan, Q.-H.; Li, Y.-M.; Chan, A. S. C. *Chem. Rev.* **2002**, *102*, 3385.

(3) For examples of aquacatalytic organic transformations with amphiphilic polymer-supported palladium catalysts reported by the author's group, see: (a) Uozumi, Y.; Shibatomi, K. *J. Am. Chem. Soc.* **2001**, *123*, 2919. (b) Uozumi, Y.; Nakai, Y. *Org. Lett.* **2002**, *4*, 2997. (c) Uozumi, Y.; Kimura, T. *Synlett* **2002**, 2045. (d) Hocke, H.; Uozumi, Y. *Synlett* **2002**, 2049. (e) Uozumi, Y. *J. Synth. Org. Chem. Jpn.* **2003**, *60*, 1063. (f) Uozumi, Y.; Tanaka, H.; Shibatomi, *Org. Lett.* **2004**, *6*, 281.

(4) For reviews, see: (a) Králik, M.; Biffis, A. *J. Mol. Catal. A* **2001**, *177*, 113. (b) Corain, B.; Králik, M. *J. Mol. Catal. A* **2001**, *173*, 99.

(5) Uozumi, Y.; Nakao, R. *Angew. Chem., Int. Ed.* **2003**, *42*, 194.

(6) ARP is the abbreviation for Amphiphilic Resin-dispersion of nano-Particles.

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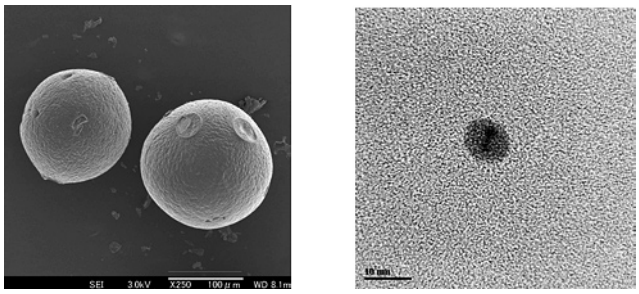


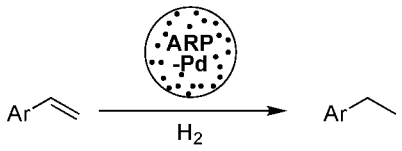
Figure 1. Microscopic images of ARP-Pd: (left) SEM image of ARP-Pd beads; (right) TEM image of palladium nanoparticles of ARP-Pd.

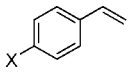
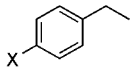
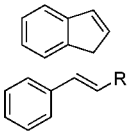
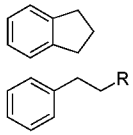
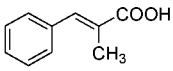
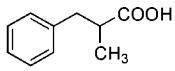
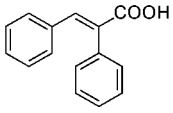
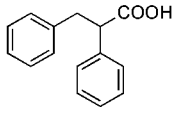
A preliminary study on the catalytic utility of ARP-Pd[7] in reductive reactions examined the hydrogenation of styrenes (Table 1).[8] A mixture of styrene and 4 mol % palladium of ARP-Pd in water was shaken under an atmospheric pressure of hydrogen gas at 25 °C for 24 h to give a quantitative yield of ethylbenzene (run 1). Styrene derivatives bearing electron-donating and -withdrawing substituents on their aromatic rings, indene, and β-methylstyrene underwent hydrogenation under similar conditions to give the corresponding olefin-reduced products in >99% yield (runs 2−6). Hydrogenation of styrenes having hydroxymethyl, formyl, acetyl, methyl ester, and carboxylic acid groups at their β-positions took place at their olefinic units with their β-functional groups intact to give hydrocinnamic products in yields of 87−100% (runs 7−11). Trisubstituted olefins, α-methylcinnamic acid and α-phenylcinnamic acid, were also subjected to ARP-Pd-catalyzed hydrogenation in water to give the hydrocinnamic acids in quantitative yields (runs 12 and 13).

Hydrodehalogenation of aryl halides, especially of chloroarenes, has been recognized as an important chemical transformation in organic synthesis as well as in industrial applications.[9] Furthermore, because of the harmful nature of aryl chlorides, dechlorination has attracted increasing attention. Consequently, a wide variety of hydrodehalogenation reaction systems have recently appeared in the literature, among them catalytic systems, which are usually performed with transition metal catalysts (e.g., Ni, Rh, Pd) and hydrogen sources (e.g., H_2, metal hydrides, formic acid, hydrazine).[10] If the hydrodechlorination of aryl chlorides proceeded in aqueous media with a recyclable catalyst and a mild hydrogen source, the reaction system would be an enormous plus since it would meet most environmental requirements.

It was found that hydrodechlorination of aryl chlorides took place smoothly in aqueous reaction media with ammonium formate in the presence of the amphiphilic resin

Table 1. Hydrogenation of Styrenes with ARP-Pd Catalyst[a]



run	substrate	product	yield (%)[b]
			
1	X = H		>99
2	X = CH_3		>99
3	X = OCH_3		>99
4	X = CF_3		>99
5			>99
6	R = CH_3		>99
7	R = CH_2OH		81
8	R = CHO		87
9	R = $COCH_3$		97
10	R = $COOCH_3$		99
11[c]	R = COOH		98
12[c]			99
13[c]			99

[a] All reactions were carried out in the presence of 5 mol % Pd of ARP−Pd in water under H_2 (1 atm) at 25 °C for 24 h. [b] GC yields for runs 1−6. Isolated yields for runs 7−13. All products showed >95% similarity with authentic data on GC−MS analysis. [c] One equivalent of KOH was added.

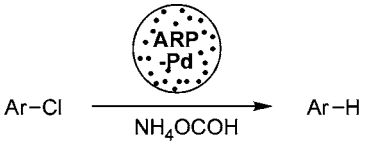
(7) 1% DVB cross-linked, average diameter of polymer beads = 170 μm, average diameter of palladium particle = 9.0 nm, palladium loading = 0.4 mmol/g.

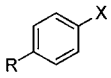
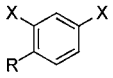
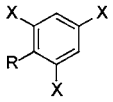
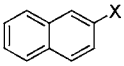
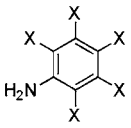
(8) For several examples of polymer-stabilized palladium nanoparticles, see: (a) Ley, S. V. Mitchell, C.; Pears, D.; Ramarao, C.; Yu, J.-Q.; Zhou, W. *Org. Lett.* **2003**, *5*, 4665. (b) Bremeyer, N.; Ley, S. V.; Ramarao, C.; Shirley, I. M.; Smith, S. C. *Synlett* **2002**, 1843. (c) Ley, S. V.; Ramarao, C.; Gordon, R. S.; Holmes, A. B.; Morrison, A. J.; McConvey, I. F.; Shirley, I. M.; Smith, S. C.; Smith, M. D. *Chem. Commun*. **2002**, 1134. (d) Yu, J.-Q.; Wu, H.-C.; Ramarao, C.; Spenver, J. B.; Ley, S. V. *Chem. Commun*. **2002**, 678. (e) Toshima, N.; Shiraishi, Y.; Teranishi, T.; Miyake, M.; Tominaga, T.; Watanabe, H.; Brijoux, W.; Bönemann, H.; Schmid, G. *Appl. Organomet. Chem.* **2001**, *15*, 178. (f) Teranishi, T.; Miyake, M. *Chem. Mater*. **1998**, *10*, 594. (g) Bergbreiter, D. E.; Chen, B.; Lynch, T. J. *J. Org. Chem.* **1983**, *48*, 4179.

(9) For a review, see: Alonso, F.; Beletskaya, I. P.: Yus, M. *Chem. Rev*. **2002**, *102*, 4009.

(10) For recent examples of palladium-mediated hydrodechlorination of chloroarenes, see: (a) Kang, R.; Ouyang, X.; Han, J.; Zhen, X. *J. Mol. Catal. A* **2001**, *175*, 153. (b) Desmarets, C.; Kuhl, S.; Schneider, R.; Fort, Y. *Organometallics* **2002**, *21*, 1554. (c) Maleczka, R. E., Jr.; Rahaim, R. J., Jr.; Teixeira, R. R. *Tetrahedron Lett*. **2002**, *43*, 7087. (d) Sajiki, H.; Kume, A.; Hattori, K.; Hirota, K. *Tetrahedron Lett*. **2002**, *43*, 7247. (e) Sajiki, H.; Kume, A.; Hattori, K.; Nagase, H.; Hirota, K. *Tetrahedron Lett.* **2002**, *43*, 7251. (f) Cellier, P. P.: Spindler, J.-F.; Taillefer, M.; Cristau, H.-J. *Tetrahedron Lett.* **2003**, *44*, 7191. (g) Navarro, O.; Kaur, H.; Mahjoor, P.; Nolan, S. P. *J. Org. Chem*. **2004**, *69*, 3173. (h) Selvam, P.; Sonavane, S. U.; Mohapatra, S. K.; Jayaram, R. V. *Tetrahedron Lett*. **2004**, *45*, 3071.

Table 2. Hydrodechlorination of ArCl using ARP-Pd and Ammonium Formate[a]

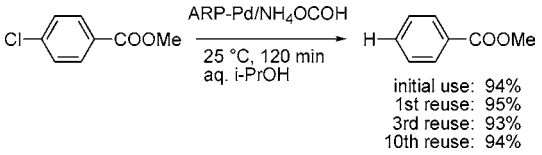


run	Ar-Cl/Ar-H (X = Cl/H)	yield (%)[b]	run	Ar-Cl/Ar-H (X = Cl/H)	yield (%)[b]
					
1	R = H	>99[c]	13	R = H	99[c]
2	R = CH_3	>99[c]	14	R = OH	97
3	R = CH_2OH	99	15	R = NH_2	92
4	R = OCH_3	89	16	R = COOH	99
5	R = OH	93			
6	R = NH_2	91			
7	R = $COCH_3$	97			
8	R = $CONH_2$	99	17	R = H	>99[c]
9	R = COOH	>99	18	R = OH	96
10	R = $COOCH_3$	94	19	R = NH_2	92
11		95[c]	20	R = COOH	99
12		>99[c]	21		85

[a] All reactions were carried out in 10% aqueous 2-propanol in the presence of 5 mol % palladium (with respect to substrate) of ARP−Pd and 3 equiv of ammonium formate with respect to the chloroarene at 25 °C for 120 min. [b] Isolated yield unless otherwise noted. [c] GC yield.

dispersion of palladium nanoparticles, ARP-Pd. Representative results are shown in Table 2. When chlorobenzene was treated with ammonium formate in 10% aqueous 2-propanol in the presence of 5 mol % palladium of the ARP-Pd catalyst at 25 °C for 120 min, hydrodechlorination proceeded smoothly to give benzene in quantitative yield (>99% GC yield) (Table 1, run 1). Electron-rich (runs 2−6) as well as electron-deficient (runs 7−10) aromatics were readily dechlorinated under similar conditions to give the corresponding reduced products in high yields ranging from 89% to >99%, where wide functional group tolerance for benzylic hydroxyl, phenolic hydroxyl, amine, ketone, amide, carboxylic acid, and carboxylic ester was noted. Naphthyl chloride and pyridyl chloride underwent hydrodechlorination to afford naphthalene and pyridine in 95% and 99% yield, respectively (runs 11 and 12). Complete dechlorination of perchlorinated aromatics to nonchlorinated aromatics is of great value because of the high toxicity of the perchloroarenes. Hydrodechlorination of dichloroarenes (runs 13−16) and trichloroarenes (runs 17−20) took place smoothly with the ARP-Pd catalyst and ammonium formate to give benzene, phenol, aniline, and benzoic acid in excellent yields. Neither partially dechlorinated monochloroarenes or dichloroarenes were detected by GC−MS analysis. Dechlorination of pentachloroaniline was carried out using 3 equiv of ammonium formate, with respect to the chloroarene, under otherwise similar conditions to give aniline in 85% isolated yield, using 1 mol % of palladium to the chloroarene (run 21). Recycling experiments were examined for dechlorination of methyl 4-chlorobenzoate (Scheme 1). After the first use

Scheme 1



of the polymeric nanopalladium catalyst (Table 2, run 10) to give 94% of methyl benzoate, the recovered catalyst ARP-Pd was taken on to 10 subsequent reuses and exhibited stable catalytic activity. Thus, all 10 recycling runs gave >99% GC yields of methyl benzoate, the first, third, and tenth runs of which were chosen to confirm the isolated chemical yields of the dechlorinated product to give 95%, 93%, and 94% yield of methyl benzoate, respectively.

In summary, a novel amphiphilic PS−PEG resin dispersion of nanoparticles of palladium exhibited high catalytic performance in the hydrogenation of olefins and the hydrodechlorination of chloroarenes under aqueous conditions. Dechlorination was found to take place smoothly using aqueous ammonium formate with high recyclability, which would provide a safe and clean detoxification protocol for aqueous chloroarene pollutants. Development of a flow system for the dechlorination catalysis is currently underway.

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Supporting Information Available: Experimental procedure for hydrogenation (Table 1) and hydrodechlorination (Table 2). This material is available free of charge via the Internet at http://pubs.acs.org.

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