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# Resin-supported palladium nanoparticles as recyclable catalyst for the hydrodechlorination of chloroarenes and polychlorinated biphenyls

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This study focuses on the hydrodechlorination of chlorinated arenes as well as polychlorinated biphenyls (PCBs) utilizing a resinsupported Pd(0) catalyst. Bearing in mind the dangers associated with toxic PCBs, treatment of the remnants of industrial wastes containing PCB congeners is indispensable. One such method is reductive hydrodechlorination. Instead of utilizing traditional sources of hydrogen, ammonium formate is used for *in situ* hydrogen generation. Moreover, palladium nanoparticles are supported on an anionic exchange resin which makes the process recyclable with a negligible change of yield after recycling experiments. The catalyst is demonstrated in the hydrodechlorination of a wide range of chlorinated compounds and PCB congeners including aroclors 1242, 1248 and 1254. Copyright © 2016 John Wiley & Sons, Ltd.

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Keywords: Chlorine; green chemistry; heterogeneous catalysis; palladium; supported catalyst

## Introduction

Polychlorinated biphenyls (PCBs), synthetic compounds of the 19th century, are known for their remarkable thermochemical stability and subsequent extensive use as additives in adhesives, casting agents, plasticizers and paints as well as fire retardants and insulators in electric appliances.<sup>[1]</sup> However, soon after the commercial production of PCBs, incidents including a mass poisoning due to Yushō disease in Japan<sup>[2]</sup> led to the prohibition of PCBs except for enclosed use in capacitors and transformers. By the 1970s, they were strictly banned for further production and subsequent use. PCBs are classified as some of the most toxic persistent organic pollutants,<sup>[3]</sup> with half-lives ranging from a few weeks to several years.<sup>[4]</sup> There have been serious concerns about PCBs remaining in the world.<sup>[5]</sup> It has been estimated that almost 31% of the total amount of PCBs has evaporated with 60% present in stored waste and 4% being decontaminated.<sup>[6]</sup> Owing to their high stability, long half-lives and lipophilicity for the plasma of living beings, they are considered to be toxic at the trans-generational level producing high risks of mental and motor deformities,<sup>[7]</sup> necrosis,<sup>[8]</sup> liver ulcers, dermatological infections, endocrine effects and carcinogenesis in humans.<sup>[9]</sup>

Therefore, there is an urgent need to get rid of these non-dioxin toxins so that living organisms can be protected from contamination. In the past, various measures have been adopted for the destruction, detoxification or elimination of PCBs including landfill capping, incineration, microbial degradation, solvent extraction, photocatalysis and chemical methods of PCB transformation including oxidative as well as reductive dechlorination. These methods have been reviewed and investigated.<sup>[10]</sup> However, they have limitations like the leaching out of PCBs in air or soil from land-fill storage, the need of a high temperature or production of hazard-ous chlorinated by-products in incineration and sluggish microbial remediation.<sup>[11]</sup> Reductive dechlorination seems to be an appropriate choice for the remediation of polychlorinated compounds with respect to efficiency, cost and green by-products. A brief and comprehensive review was conducted by Wu and co-workers in 2012<sup>[10]</sup> where various sources for reductive hydrogen starting from H<sub>2</sub> gas, to H<sub>2</sub>-saturated water, water, carboxylic acid, alcohol and hydrazine-like molecules are mentioned. Much of this research includes transition metal catalytic hydrodechlorination. The transition metals mostly employed for the task are iron, palladium and nickel<sup>[12]</sup> and their combination<sup>[13]</sup> or other metals like magnesium and aluminium.<sup>[14]</sup> This metal-catalyzed hydrodechlorination has advantages over other strategies employed for the detoxification of PCBs. However, there is still opportunity for improvement. Recent reports of Fe<sup>0</sup>/Ni<sup>0</sup> present a nice picture of hydrodechlorination but the aspect of recyclability of the catalyst is lacking.<sup>[15]</sup> Sometimes, the reaction temperature needs to be elevated in order to obtain optimized results<sup>[16]</sup> or the reaction time may become prolonged.[17] Some palladium nanoparticles have recently been reported as robust catalysts like those encapsulated by resin<sup>[18]</sup> anchored by dendrimer networks<sup>[19]</sup> and supported by carbon.<sup>[20]</sup> Hydrodechlorination is also reported to be catalyzed by palladium nanoparticles installed in micro-flow devices; however, despite excellent catalysis at the parts per million level, a report on the recyclability of the catalyst is missing.<sup>[21]</sup>

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Herein, we report an efficient, recyclable Pd(0) catalyst for the hydrogenolysis of the C–Cl bond in chlorinated arenes. Ammonium formate was employed as a hydrogen source as we explored previously.<sup>[22]</sup> The overall scheme of the catalysis is shown in Fig. 1.

# **Results and discussion**

Palladium nanoparticles are supported on an AG 1-X8 anion exchange resin, a copolymer of styrene and divinylbenzene units with quaternary ammonium ions attached to the aromatic skeleton and chloride counter anions as shown in Fig. 2. AG 1-X8 has been used for the sorption, exchange and separation of various anions.<sup>[23]</sup> In addition, it has strong affinity for the separation of various metals like Ni, Co, Cu, Zn, Mn and Fe from their respective solutions.<sup>[24]</sup> The evidence of strong interactions of AG 1-X8 resin with various metals led us to consider it as a support for palladium nanoparticles. The results are quite promising for the hydrodechlorination of chlorinated arenes.

The AG 1-X8 resin has an open structure with crosslinked polymeric chains that can accommodate small molecules smoothly. The average mesh size range is 106–180  $\mu$ m with a round bead-type morphology as shown in the scanning electron microscopy (SEM) image in Fig. 3. It has been explored for applications including anion exchange and metal extraction; but herein, we report its novel application as a catalyst support.

The synthesis of the catalyst was carried out by applying a simple protocol of mechanical shaking at room temperature. Metal is tightly held by the coordination interactions with ammonium nitrogen.

 $Pd(OAc)_2$  is used to load Pd(II) on the resin in anhydrous tetrahydrofuran (THF) as a solvent at room temperature, followed by the reduction of Pd(II) using  $NaBH_4$  in methanol as a solvent. AG 1-X8 resin is of a light yellow color and undergoes a color change from light orange brown to black with coordination and reduction, respectively, accounting for Pd(II) and Pd(0) as shown in Fig. 1.

The catalyst developed was analyzed using inductively coupled plasma (ICP) analysis, SEM, transmission electron microscopy (TEM) and energy-dispersive analysis of X-rays (EDAX) to obtain better insight into the catalyst behavior. The TEM images provide a clear picture of palladium nanoparticles bonded with the resin support. From the analysis of the TEM images, the average size of palladium nanoparticles is 4 nm (Fig. 3) and the loading was







Figure 2. Structure of AG 1-X8 resin.







**Figure 3.** (a) SEM image of AG 1-X8 resin at resolution of 1.00 mm. TEM images of the catalyst showing Pd nanoparticles at resolutions of (b) 100 nm, (c) 50 nm and (d) 20 nm. (e) Palladium size distribution. (f) Energy-dispersive X-ray spectrum of the catalyst.

calculated to be 0.65 mmol Pd  $g^{-1}$  of resin on the basis of ICP analysis of the fresh catalyst.

The synthesized catalyst was used for the dechlorination of a range of mono-, di- and polychlorinated arenes. The reactions were carried under mild reaction conditions at room temperature using ammonium formate as an *in situ* hydrogen source and aqueous alcohol as the solvent. Similar conditions were investigated in a previous study.<sup>[25]</sup>

The catalytic system comprising Pd(0) supported on AG 1-X8 resin reacts efficiently with almost quantitative results (98–100% product yields) in a very short time, regardless of other functionalities present on the aromatic skeleton like hydroxyl, carboxyl, amino or ester groups (Table 1). This is strong support for the high efficiency of the developed catalytic system for various mono-, diand polychlorinated substrates.

The developed catalyst was evaluated by conducting recycling experiments for the hydrodechlorination of chlorinated substituted

 $\ensuremath{\text{Table 1.}}$  Substrates for the hydrodechlorination of mono-, di- and polychlorinated arenes  $\ensuremath{^a}$ 

$R \xrightarrow{X}_{Cl_{m}} \xrightarrow{Pd \text{ cat., HCOONH}_{4}} R \xrightarrow{X}_{T, \text{ IPA:H}_{2}O (9:1)} R$											
Entry	Substrate	Product	Time (h)	Yield (%) <sup>b</sup>							
1	Chlorobenzene	Benzene	3	Quant. <sup>c</sup>							
2	4-Chlorotoluene	Toluene	2	Quant. <sup>c</sup>							
3	(4-Chlorophenyl)methanol	Benzyl alcohol	2	98							
4	4-Chlorophenol	Phenol	2	99							
5	4-Chloroaniline	Aniline	2	99							
6	4-Chlorobenzoic acid	Benzoic acid	3	99							
7	4-Chlorobenzamide	Benzamide	3	99							
8	Methyl 4-chlorobenzoate	Methyl	2	99							
	benzoate										
9	3-Chloropyridine	Pyridine	2	99							
10	1,3-Dichlorobenzene	Benzene	2	Quant.							
11	2,4-Dichlorophenol	Phenol	4	99							
12	3,5-Dichlorophenol	Phenol	4	99							
13	2,4-Dichloroaniline	Aniline	4	99							
14	3,5-Dichloroaniline	Aniline	4	99							
15	2,4-Chlorobenzoic acid	Benzoic acid	3	99							
16	1,3,5-Trichlorobenzene	Benzene	5	Quant.							
17	2,4,5,6-Tetrachloroaniline	Aniline	12	99							
18	2,4,6-Trichlorophenol	Phenol	12	99							
19	Pentachloroaniline	Aniline	12	99							
<sup>a</sup> Reaction conditions: chloroarene (1 equiv., 1 mmol), ammonium											

<sup>a</sup>Reaction conditions: chloroarene (1 equiv., 1 mmol), ammonium formate (3 equiv. per chlorine atom), Pd catalyst (5 mol%, 0.05 mmol, 0.077 g), isopropanol– $H_2O$  (9:1 ratio), reaction conc. 0.5 M. <sup>b</sup>Isolated yield. <sup>c</sup>GC yield.

arenes. The first recycle followed the general procedure of the hydrodechlorination. The subsequent reactions were carried out using the catalyst recovered from the previous recycle experiment. This process was carried out for over nine recycles and the product was obtained in virtually quantitative yields (95–100%). The product yield decreases from quantitative to 95% but we believe that it is a handling error as recycling does not affect the results of the first to sixth cycles and the later seventh to ninth cycles (Table 2). This proposition was supported from the ICP analysis of the reaction mixture giving a Pd content less than 10 ppm.

The present system was also investigated for its application in real systems such as the hydrodechlorination of PCBs with average chlorine number (ACN) ranging from ca 3 to 5,<sup>[17]</sup> commercially available as aroclors. Aroclors are complex mixtures of various

Table 2.      Hydrodechlorination of 4-chlorobenzoic acid to benzoic acid <sup>a</sup>												
HOOC $-$ CI $\xrightarrow{\text{Pd cat., HCOONH}_4}$ HOOC $-$ HOOC $-$												
Recycle Yield (%) <sup>b</sup>	1 99	2 99	3 98	4 100	5 99	6 100	7 95	8 95	9 96			
<sup>a</sup> Reaction conditions: 4-chlorobenzoic acid (1 equiv., 1 mmol, 0.156 g), ammonium formate (3 equiv., 3 mmol, 0.189 g), Pd catalyst (5 mol%, 0.05 mmol, 0.077 g), isopropanol–H <sub>2</sub> O (9:1 ratio), 3 h, reaction conc. 0.5 M. <sup>b</sup> Isolated yield.												

congeners of PCBs. They are named based on the average number of carbon atoms in the compounds (e.g. 12 (biphenyl)) and the weight percentage of chlorine in the mixture.

For the hydrodechlorination of aroclors, a set of experiments was conducted using excess (20 equiv. ammonium formate) at room temperature. With respect to the average chlorine number of a particular aroclor, the palladium catalyst used was 5 mol% of the aroclor substrate. The reaction progress was monitored every hour by GC-MS, as shown for aroclor 1254 in Fig. 4. The mixture of PCB congeners can be seen for three aroclor samples as shown in Fig. 5. With the progress of the reaction, the aroclor starts converting to the only biphenyl product and eventually a sole biphenyl peak can be seen after 3 h (Fig. 4(d)). Similarly, the hydrodechlorination of aroclors 1248 and 1242 proceeds smoothly with quantitative yields of biphenyl after 1 and 5 h, respectively (Table 3).

At first, a comparison of the progress of the reaction among the aroclors was made on the basis of average chlorine number. Hydrodechlorination of aroclor 1242 was expected to complete in shorter reaction time as compared to aroclor 1254. However, the results are contrary to the prediction. A study conducted on hydrodechlorination pathways for Fe<sub>3</sub>O<sub>4</sub> reaction system showed that the reaction is not equally facile for *ortho-*, *meta-* and *para*-substituted aroclors.<sup>[26]</sup> We propose the reaction of aroclor 1242 to be not as facile as that of aroclor 1254 on the basis of the substitution pattern of the most abundant PCB congener in the mixture. Therefore, the percentage of chlorine in the aroclor as well as the substitution pattern of chlorine on the biphenyl ring are estimated to be crucial parameters for the hydrodechlorination of aroclors.<sup>[27]</sup>

A new and efficient catalytic system was developed for the hydrodechlorination of chlorinated arenes. Initially, palladium nanoparticles were supported on an anion exchange resin and application of the system for dechlorination was explored using ammonium formate for in situ hydrogen donation to the substrate. The catalyst is found to be active not only for the hydrodechlorination of chlorinated arenes but also for the complete detoxification of commercially available samples of PCB congeners by dechlorination. Palladium at 5 mol% is been shown to be sufficient to yield quantitative results and the catalyst can be recycled for use again in subsequent reaction runs. The reaction is conducted under very mild conditions at room temperature and the use of ammonium formate as hydrogen source overcomes the gas management and safety issues encountered when using hydrogen gas. Application of the developed system for the detoxification of commercially available PCBs and its recyclability are the two eminent features of the catalyst.

# Experimental

## **Catalyst preparation**

To coordinate Pd(II) with the AG 1X8 resin, a mixture of 2.0 g of resin and 0.22 g of Pd(OAc)<sub>2</sub> in 25 ml of deoxygenated anhydrous THF was subjected to vigorous mechanical shaking (15 rpm) at room temperature for 12 h. An orange-brown-colored product of Pd(II) supported on resin was collected from the mixture after filtration and dried under vacuum at 40°C.

The collected Pd(II) complex was reduced using 0.11 g of NaBH<sub>4</sub> in 25 ml of anhydrous methanol in a shaker. After 12 h of vigorous shaking, black-colored catalyst was collected after filtration, washed with methanol and dried in a vacuum oven at 40°C. The catalyst loading was found to be 0.65 mmol of Pd per gram of the catalyst.

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Figure 4. GC-MS monitoring of the hydrodechlorination of aroclor 1254: (a) start; (b) 1 h; (c) 2 h; (d) 3 h.

Figure 5. GC-MS analysis of aroclor congeners 1242, 1248 and 1254.

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## General procedure for hydrodechlorination of substituted benzenes

For a typical experiment of hydrodechlorination, chloroarene (1 mmol) and Pd(0) catalyst (0.077 g, 5 mol%) were added to a 10 ml round-bottom flask containing 1.8 ml of isopropanol. The reaction mixture was stirred at room temperature, followed by the addition of ammonium formate (0.189 g, 3 mmol) solution in 0.2 ml of water. The progress of the reaction was monitored by GC until completion (3 h). Upon completion, the reaction mixture was diluted with ethyl acetate. The catalyst was filtered and the filtrate was analyzed using ICP analysis. The reaction mixture was washed with water, extracted with ethyl acetate and analyzed using GC.

#### **Characterization and analysis**

SEM and EDAX measurements were performed with a highresolution Jeol electron microscope at an acceleration of 300 kV while TEM experiments were carried out using a Jeol JEM 2100F field emission electron microscope. The loading of Pd nanoparticles in the catalyst was estimated using ICP analysis with a JY Ultima 2C (Jobin Yuon, France). ICP analysis was also used to check for leaching out after recycle testing. <sup>1</sup>H NMR spectra were recorded with a Bruker 400 MHz instrument using CDCl<sub>3</sub> solvent and tetramethylsilane as an internal standard. GC and GC-MS analyses were performed with an Agilent 7890A GC system and 5975C MSD, respectively.

#### Hydrodechlorination of aroclors

Hydrodechlorination of 25 mg of aroclor was carried out using the general procedure described for chlorinated arenes. The reactions were monitored by GC-MS.

## **Recycling experiments**

Hydrodechlorination of 4-chlorobenzoic acid was carried out following the general procedure described before. The catalyst was recovered after the reaction, washed with methanol and dried. It was then reused again in the next recycle test.

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## References

- [1] M. D. Erickson, R. G. Kaley, II, Environ. Sci. Pollut. Res. Int. 2011, 18, 135–151.
- [2] a) K. Fujiwara, Sci. Tot. Environ. 1975, 4, 219–247. b) Y. Aoki, Environ. Res.
  2001, 86, 2–11. c) G. Umeda, Ambio 1972, 1, 132–134.
- [3] M. S. El-Shahawi, A. Hamza, A. S. Bashammakh, W. T. Al-Saggaf, *Talanta* 2010, *80*, 1587–1597.
- [4] a) D. L. Phillips, A. B. Smith, V. W. Burse, G. K. Steele, L. L. Needham,
  W. H. Hannon, Arch. Environ. Health 1989, 44, 351–354. b)
  S. Sinkkonen, J. Paasivirta, Chemosphere 2000, 40, 943–949.
- [5] a) G. Brambilla, V. Abate, A. di Domenico, M. Esposito, A. R. Fulgenzi, N. lacovella, F. P. Serpe, M. Tassinari, *Food Addit. Contam.* 2015, *32*, 864–873. b) R. Herrick, J. Stewart, J. Allen, *Environ. Sci. Pollut. Res.* 2015, *22*, 1–11. c) M. A. Khairy, D. C. Muir, C. Teixeira, R. Lohmann, *Environ. Sci. Technol.* 2015, *49*, 13787–13797. d) R. Fuoco, M. P. Colombini, A. Ceccarini, C. Abete, *Microchem. J.* 1996, *54*, 384–390.
- [6] S. Tanabe, Environ. Pollut. **1988**, 50, 5–28.
- [7] N. El Majidi, M. Bouchard, G. Carrier, *Regul. Toxicol. Pharmacol.* 2013, 66, 130–146.
- [8] V. Abella, A. Santoro, M. Scotece, J. Conde, V. López-López, V. Lazzaro, J. J. Gómez-Reino, R. Meli, O. Gualillo, *Toxicol. Lett.* **2015**, *234*, 13–19.
- [9] S. Safe, Environ. Health Perspect. **1993**, 100, 259–268.
- [10] B. Z. Wu, H. Y. Chen, S. J. Wang, C. M. Wai, W. Liao, K. Chiu, Chemosphere 2012, 88, 757–768.
- [11] a) T. Y. I. Gorbunova, V. I. Saloutin, O. N. Chupakhin, *Russian Chem. Rev.* **2010**, *79*, 511–530. b) D. F. Laine, I. F. Cheng, *Microchem. J.* **2007**, *85*, 183–193.
- [12] H.-M. Choi, B. Veriansyah, J. Kim, J.-D. Kim, Y.-W. Lee, J. Environ. Sci. Health 2009, 44, 494–501.
- [13] a) X. Chen, X. Yao, C. Yu, X. Su, C. Shen, C. Chen, R. Huang, X. Xu, *Environ. Sci. Pollut. Res.* 2014, *21*, 5201–5210. b) R. Abazari, F. Heshmatpour, S. Balalaie, *ACS Catal.* 2013, *3*, 139–149.
- [14] a) A. Ido, S. Ishihara, A. Kume, T. Nakanishi, Y. Monguchi, H. Sajiki, H. Nagase, *Chemosphere* **2013**, *90*, 57–64. b) P. Maloney, R. DeVor, S. Novaes-Card, E. Saitta, J. Quinn, C. A. Clausen, C. L. Geiger, *J. Hazard. Mater.* **2011**, *187*, 235–240.
- [15] a) Q. Zhang, Y. Guo, M. Huang, H. Li, C. Gu, *Chem. Eng. J.* **2015**, *276*, 122–129. b) S. Mallampati, Y. Mitoma, T. Okuda, S. Sakita, C. Simion, Environ. Sci. Pollut. Res. **2014**, *21*, 9270–9277.
- [16] a) W. Wu, J. Xu, H. Zhao, Q. Zhang, S. Liao, *Chemosphere* **2005**, *60*, 944–950. b) N. Lingaiah, M. A. Uddin, A. Muto, Y. Sakata, *Chem. Commun.* **1999**, 1657–1658.
- [17] L. Lassova, H. K. Lee, T. S. A. Hor, J. Org. Chem. **1998**, 63, 3538–3543.
- [18] H. Kaur, D. Shah, U. Pal, Catal. Commun. 2011, 12, 1384–1388.
- [19] E. A. Karakhanov, A. L. Maksimov, E. M. Zakharian, Y. S. Kardasheva, S. V. Savilov, N. I. Truhmanova, A. O. Ivanov, V. A. Vinokurov, J. Mol. Catal. 2015, 397, 1–18.
- [20] A. B. Dongil, L. Pastor-Pérez, J. L. G. Fierro, N. Escalona, A. Sepúlveda-Escribano, *Catal. Commun.* 2016, 75, 55–59.
- [21] Y. M. A. Yamada, T. Watanabe, A. Ohno, Y. Uozumi, *ChemSusChem* **2012**, *5*, 293–299.
- [22] a) R. Nakao, H. Rhee, Y. Uozumi, Org. Lett. 2005, 7, 163–165. b) S. Rajagopal, A. F. Spatola, J. Org. Chem. 1995, 60, 1347–1355.
- [23] T. Sangvanich, W. Ngamcherdtrakul, R. Lee, J. Morry, D. Castro, G. E. Fryxell, W. Yantasee, J. Nanomed. Nanotechnol. 2014, 5, 222.
- [24] a) F. W. E. Strelow, Anal. Chem. 1978, 50, 1359–1361. b) J. Korkisch,
  H. Krivanec, Anal. Chim. Acta 1976, 83, 111–118. c) K. A. Kraus,
  G. E. Moore, J. Am. Chem. Soc. 1953, 75, 1460–1462. d) A. J. Mason,
  G. M. Henderson, A. Vaks, Geostand. Geoanal. Res. 2013, 37, 261–275.
- [25] Y. Uozumi, R. Nakao, H. Rhee, J. Organometal. Chem. 2007, 692, 420–427.
- [26] L. Huang, G. Su, A. Zhang, Y. Shi, C. Xia, H. Lu, L. Li, S. Liu, M. Zheng, J. Hazard. Mater. 2013, 261, 451–462.
- [27] J. G. Rodri guez, A. Lafuente, Tetrahedron Lett. 2002, 43, 9581–9583.

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