

Pd-catalyzed Dehalogenation of Aromatic Halides Under Solvent-free Conditions Using Hydrogen Balloon

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The dehalogenation of aromatic halides possesses great significance not only in the removal of halogenated organic contaminants but also in the development of synthetic methodologies.¹ Although several processes have already been well established to deal with toxic and even carcinogenic aryl halides, including adsorption and inactivation by oxidation and incineration methods, there is still a need for alternative treatments because conventional treatments unavoidably result in the production of highly deleterious by-products or huge amounts of waste materials.² Solvent-free (solvent-less) reactions have attracted much attention because they have several advantages over traditional reactions in organic liquid solvents: smaller reaction vessels, no organic medium to make less wastes, higher efficiency, easier operation, simpler purification and different product distribution.³ Chemical reductive dehalogenation, by means of the hydrogenolysis of the carbon-halogen bond to remove halogen atoms in molecules, has attracted attention from the field of both industry and academics.⁴

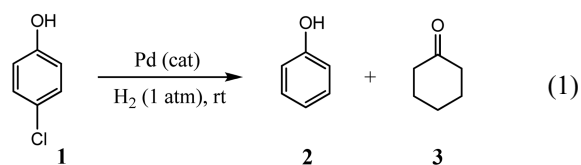
The reductive methods generally adopt transition metals as catalysts, such as nickel,^{5,6} palladium,^{7,8} rhodium,^{9,10} and platinum,^{11,12} among which palladium has been the most widely and intensively studied. Palladium (Pd) catalysts are technically important in accomplishing numerous organic transformations. Although commercial palladium sources, such as Pd/C and Pd/Al₂O₃, are extensively utilized as catalysts in synthetic chemistry,^{13,14} their efficiency and activity suffer greatly from wide distribution, poor dispersion of Pd particles deposited on the surface of supports, and the leaching of palladium when being processed. Hence, the preparation of unique Pd nanoparticles with unusually large surface has been intensively studied to catalyze the diverse reactions, especially the dehalogenations.¹⁵

Recently, a highly efficient heterogeneous Pd catalyst has been reported, which is composed of Pd nanoparticles entrapped in aluminum oxyhydroxide nanofibers [Pd/AlO(OH)]. It has been employed in various organic reactions such as the hydrogenation of alkenes and alkynes, the aerobic oxidation of alcohols, the alkylation of ketones with primary alcohols, the hydrogenolysis of epoxides, and *N*-alkylation of primary amines with benzyl alcohols.¹⁶ Most recently, we have also

reported that it could effectively catalyze the hydrogenation of alkenes and nitro-aromatics in solid state under solvent free conditions.¹⁷

To the best of our knowledge, only a few references are available for the dehalogenation of aromatic halides in solid state under solvent-free conditions using molecular hydrogen, which clearly has the advantages of non-toxicity and environmental efficiency,¹⁸ compared with other hydrogen sources such as formic acid and its salts, metal alkoxides, hydrosilanes, or Grignard reagents.²⁰ Herein, we report highly effective and environmentally benign process for the dehalogenation of solid aromatic halides: the reactions of various solid aromatic halides are readily catalyzed by Pd/AlO(OH) without any solvent at ambient temperature in the presence of atmospheric hydrogen, and no deactivation of the catalyst, Pd/AlO(OH), was observed for several times of recycle.

The reaction of 4-chlorophenol with molecular hydrogen initially produced phenol, the hydrogenolysis product of 4-chlorophenol (**1**).²⁰ Phenol (**2**) was further hydrogenated on aromatic rings under the same conditions and gave the cyclohexanone (**3**) with a very small amount of cyclohexanol (< 0.5%), showing a some activity of Pd/AlO(OH) for the hydrogenation of aromatic rings and a much lower activity for that of carbonyl groups (Eq. 1). The conversion of 4-chlorophenol increased with time, but the selectivity for phenol decreased with time to approximately 60% due to the further hydrogenation of the aromatic ring of phenol into cyclohexanone (Table 1, entry 1).



Comparative experiments were subsequently performed in normal organic solvents, and the catalytic efficiency of commercial palladium catalysts was also tested under solvent-free conditions (Table 1). Contrary to previous reports,²¹ hexane, a non-polar solvent, provided the best conversion among all solvents employed (Table 1, entries 2-5). The

Table 1. Dechlorination of 4-chlorophenol under various conditions^a

Entry	Catalyst	Solvent	Base	Conv. ^b (%)	2 ^b (%)	3 ^b (%)
1	Pd/AlO(OH)	No	No	82	63	38
2	Pd/AlO(OH)	hexane	No	82	91	9
3	Pd/AlO(OH)	MeOH	No	63	> 99	< 1
4	Pd/AlO(OH)	acetone	No	49	97	3
5	Pd/AlO(OH)	EA	No	68	98	2
6	Pd/C	No	No	9	85	15
7	Pd/Al ₂ O ₃	No	No	18	48	52
8	Pd/CaCO ₃	No	No	3	> 99	< 1
9	Pd/AlO(OH)	No	NaHCO ₃ ^c	95	83	17
10	Pd/AlO(OH)	No	Na ₂ CO ₃ ^c	90	81	19
11	Pd/AlO(OH)	No	K ₂ CO ₃ ^c	> 99	82	18
12	Pd/AlO(OH)	No	CS ₂ CO ₃ ^c	> 99	88	12
13	Pd/AlO(OH)	No	K ₂ HPO ₄ ^c	> 99	92	8

^aSubstrates (0.20 mmol) and Pd (4×10^{-3} mmol) under 1 atm H₂ at room temperature. ^bEstimated by GC and ¹H NMR. ^c0.15 mmol of bases was used.

selectivity of the reaction in hexane was better than that under solvent-free conditions. The dechlorination of 4-chlorophenol using Pd/AlO(OH) offered a high conversion (82%, entry 1), those using commercial palladium catalysts, such as Pd/C, Pd/Al₂O₃ and Pd/CaCO₃, showed low conversions (< 20%, entries 6-8). Aramendia and co-workers reported that HCl produced from dechlorination tends to be adsorbed on the activated carbon, leading to a progressive poisoning of Pd/C.²² Based on this observation, we assumed that it would be efficient to add some bases for the removal of HCl, a critical catalyst poison. Among several tested bases, K₂CO₃ was employed in subsequent experiments due to its easy availability (see Table 1, entries 9-13). Our solvent-free dechlorination reactions seem to proceed in a fused state, as we recently reported for the hydrogenation of solid aromatics using the same catalyst.¹⁷

To establish the generality of the catalyst system, various solid aromatic halides were subjected under the solvent-free conditions (Table 2). A simple haloarene, bromobiphenyl was dehalogenated selectively into biphenyl in almost quantitative yield (entry 1). The major products were phenols in the reactions of halophenols (entries 2-5); in the case of 1-bromonaphthalen-2-ol the corresponding dehalogenated product was obtained in quantitative yield (entry 5). Our catalyst system was highly efficient for the dehalogenation of halobenzonitriles to give the corresponding benzonitriles (entries 6 and 7). Nitro group was also hydrogenated in the reactions of halonitroarenes (entries 8 and 9). Hydrogenolysis products were obtained in the reaction of benzylhalides (entries 10 and 11). Carbonyl groups were also hydrogenated under our conditions (entries 12 and 13). Particularly, a significant amount of a hydrogenolysis product, diphenylmethane was formed in the reaction of 4-chlorobenzophenone (entry 13).²³

Finally, it is worth reporting that the Pd/AlO(OH) catalyst could be recycled after simply washing it with water and

Table 2. Dehalogenation of various aryl halides under solvent-free conditions^a

$\text{R}-\text{C}_6\text{H}_4-\text{X} \xrightarrow[\text{H}_2 (1 \text{ atm}), \text{rt}]{\text{Pd/Al(O)OH (cat), No Solvent}} \text{R}-\text{C}_6\text{H}_4-\text{H}$ X = F, Cl, Br					
Entry	Substrate	Product	Time (h)	Conv. (%) ^b	Product (%)
1			4	96	> 99
2			4	80	78
3			1	> 99	81
4			3	98	77
5			2	> 99	> 99
6			0.5	> 99	> 99
7			0.5	> 99	> 99
8			1	> 99	99
9			1	96	> 99
10			2	> 99	> 99
11			2	> 99	98
12			1	> 99	98 ^c
13			2	> 99	60 ^d

^aA mixture of a solid substrate (0.20 mmol), Pd/AlO(OH) (2 mol % of Pd) and K₂CO₃ (0.15 mmol) was ground finely in a mortar and was allowed to react with H₂ (1 atm) under ambient conditions. ^bMeasured by GC and ¹H NMR. ^cA trace amount of toluene was detected. ^dA significant amount (40%) of 1,1-diphenylmethane was detected.

Table 3. Reusability of Pd/AlO(OH) by using 4-chlorophenol as a substrate^a

Recycle	1	2	3	4	5	6
Total conversion (%) ^b	> 99	> 99	98	> 99	> 99	> 99

^aUnless otherwise stated, 4-chlorophenol (0.2 mmol) was used in every entry together with Pd/AlO(OH) (Pd 4×10^{-3} mmol) and K₂CO₃ (0.15 mmol) under 1 atm H₂ environment at room temperature. ^bTotal conversion was confirmed by GC.

acetone, and then drying under vacuum. Our palladium catalyst could be used at least six times for the dechlorination of 4-chlorophenol without any loss of activity, similar to the our previous report.¹⁷

In summary, we explored the environmentally benign dehalogenation of solid aromatic halides using Pd/AlO(OH) and hydrogen balloon under solvent-free conditions. All

substrates in this study were efficiently converted into less toxic compounds with high conversions in short reaction time. In addition, the operation was accomplished in a simple way.

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20. All reactions were carried out in a small (10 mL) and flame-dried glassware. Pd/AIO(OH) (1.00 wt %) was prepared by the literature method.^{16a} GC analysis was performed on an ACME 6000 GC equipped with THERMO TR-WaxMS column (30 m × 0.25 mm ID × 0.25 μm) and FID detector. Typical procedure of solvent-free dehalogenation of 4-chlorophenol is described as follows: the mixture of solid 4-chlorophenol (0.2 mmol) and Pd/AIO(OH) (2.0 mol % of Pd) was ground finely with a mortar and pestle at ambient temperature before use, and then put into a glassware equipped with a rubber septa, followed by sealing with parafilm. Nitrogen gas was charged into the reactor for several times to expel air and then expelled by atmospheric pressure of hydrogen. The mixture was allowed to react for a desired time without controlling the temperature in the vessel. After filtering the catalyst, the product analyses were performed using GC and ¹H NMR by comparing to the authentic samples. Dehalogenation in organic solvents: the mixture of 4-chlorophenol and Pd/AIO(OH) (2.0 mol % of Pd) in organic solvent (3 mL) was exposed to atmospheric hydrogen environment at room temperature. After reaction, the analysis procedure was the same as described above.
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