



Note

Preparation of polymer-bound palladium catalyst and its application to the reduction of nitro arenes and the hydrodehalogenation of aryl halides



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ARTICLE INFO

Article history:

Received 8 December 2013

Received in revised form

29 December 2013

Accepted 31 December 2013

Keywords:

Palladium

Reduction

Hydrodehalogenation

Nitro arenes

Aryl halides

ABSTRACT

Polymer-bound palladium catalyst was prepared as PdO nanoparticles bound on the surface of polystyrene beads. This catalytic system showed good activities in the reduction of nitro arenes and the hydrodehalogenation of aryl halides. When the nitro arenes were reacted with 10 mol% PdO and K₃PO₄ (1.5 equiv.) in DMF/cyclohexanol at 110 °C, the corresponding amino arenes were formed in good yields. In addition, these reaction conditions afforded hydrodehalogenated products from aryl iodides, bromides, and chlorides.

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1. Introduction

Palladium-catalyzed transformations have been intensively used in synthetic organic chemistry applications, as well as in the pharmaceutical and material fields [1]. The catalytic activity of palladium highly depends on the nature of the ligand used in terms of electronic and steric properties, and this trend is exhibited in the homogenous catalytic system. Although it is easy to tune the catalytic activity by using a number of different ligands in the homogenous catalyst, it requires much more effort in the separation of catalyst and purification of product than those needed for a heterogenous catalyst. To address these issues, it has been reported that the catalyst has been linked or supported on recoverable materials such as polymers [2–4], carbon nanotubes [5–7] and graphene [8]. Polymer-supported catalytic systems require a process for the introduction of heteroatoms such as phosphorus and nitro groups, which could coordinate and hold the palladium catalyst. This additional process gives rise to problems with cost and time. This inspired us to develop a simple and easy preparation

method for obtaining a recoverable palladium catalyst. We then attempted to apply this system to the reduction of nitro group to amine and to the hydrodehalogenation of aryl halides.

The reduction of nitro group to amine is one of the most important transformations in organic synthesis. The amine group is often found in nature and exhibits a wide range of bioactivities [9–11]. In addition, it is a key functional group for the architecture of molecules in the medicinal and in material chemistry. A variety of methods have been reported, including metal-catalyzed hydrogenation with molecular hydrogen or reducing agents and reduction with stoichiometric reducing agents [12–19]. Among them, palladium-catalyzed hydrogenation with H₂ gas has widely been used in the reduction of nitro compounds. However, this method suffers from problems with the handling of gas. Therefore, a non-gas reduction system is needed [20–23].

In addition, hydrodehalogenation, which involves the conversion of aryl halides to non-toxic reagents, is a very important process in green chemistry fields, and numerous methods have been developed [24–31]. Recently, we reported on the hydrodehalogenation of aryl halides by using a palladium/phosphite catalytic system and paraformaldehyde as the hydride source [32,33]. Although these showed good activities, they were hard to recover due to the fact that their catalytic systems are all homogeneous.

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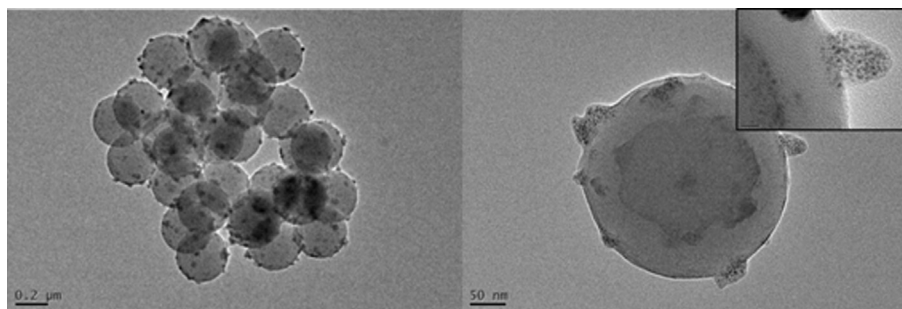


Fig. 1. TEM images of PdO bound on PS beads.

Considering the importance of recyclable catalytic systems and our previous results, the simple preparation of reusable palladium catalyst might solve these issues. The immobilization of palladium species on polymer supports has been performed through several categorized techniques using ligand-anchored polymer supports [34], incarceration in a polymer matrix [35], and palladium nanoparticles captured during the polymerization step [36]. Although these approaches were useful in various Pd-catalyzed reactions, barriers to practical use still remain due to multiple labor-intensive steps in the catalyst preparation and limitations in reusability. Thus, in this work, we provide a general method for obtaining immobilized palladium catalyst, which might be easily reproducible using routine resources and equipment within a short period of time in normal chemistry laboratories. We report on the preparation of polymer-bound palladium catalyst and its application for the reduction and hydrodehalogenation.

2. Results and discussion

Polymer-bound palladium catalyst was prepared as PdO nanoparticles bound on the surface of cross-linked polystyrene (PS) beads with 250-nm diameter (Fig. 1). The PdO was formed in oxidation conditions using NaClO, where PS beads were suspended in aqueous PdCl₂ solution. PdO nanoparticles were precipitated and grown to 20-nm particles on PS surfaces at 50 °C for 1 h. The TEM

Table 1
The optimization of the reduction of nitrobenzene with palladium catalyst.^a

Entry	PdO	Base	Solvent ^b	Temp (°C)	Conv ^c (%)	Yield ^c (%)
1	5	K ₃ PO ₄	DMF/MeOH	80	33	30
2	5	K ₃ PO ₄	DMF/ <i>i</i> -PrOH	80	10	8
3	5	K ₃ PO ₄	DMF/H ₂ O	80	12	10
4	5	K ₃ PO ₄	DMF/cyclohexanol	80	39	38
5	5	K ₃ PO ₄	DMF/cyclohexanol	110	57	48
6	10	K ₃ PO ₄	DMF/cyclohexanol	110	92	86
7	10	K ₃ PO ₄	Cyclohexanol	110	67	42
8	10	K ₃ PO ₄	DMF/glycerol	110	100	49
9	10	K ₃ PO ₄	DMF/tetraethylene glycol	110	100	58
10	10	K ₂ HPO ₄	DMF/cyclohexanol	110	10	12
11	10	K ₂ CO ₃	DMF/cyclohexanol	110	34	36
12	10	Cs ₂ CO ₃	DMF/cyclohexanol	110	80	52(10) ^d

^a Reaction conditions: nitrobenzene (0.3 mmol), PdO (5 or 10 mol%) and base (1.5 equiv.) were reacted in the solvent for 12 h.

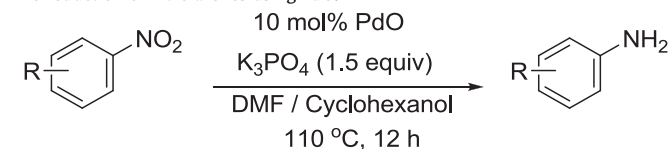
^b The ratio of solvent mixtures is 1/1.

^c Determined by GC with internal standard.

^d Diphenyldiazene was formed.

images of PdO particles on PS were observed as aggregates of 2-nm particles of PdO to form 20-nm flakes. The content of Pd in the PdO/PS composites was determined by ICP-AES, indicating 14.3 wt% Pd

Table 2
The reduction of nitro arenes using PdO.^a



Entry	ArNO ₂	Product	Yield (%) ^b
1			75
2			84
3			75
4			80
5			61
6			91
7			– ^c (66) ^d

^a Reaction conditions: nitro arene (4.0 mmol), PdO (10 mol%) and K₃PO₄ (6.0 mmol) were reacted in DMF (6.0 mL) and cyclohexanol (6.0 mL) for 12 h at 110 °C.

^b Isolated yield.

^c 4-Bromoaniline was not detected.

^d Yield of aniline.

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