



Recyclable palladium catalyst for facile synthesis of imines from benzyl alcohols and nitroarenes

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ARTICLE INFO

Article history:

Received 24 July 2013

Received in revised form 15 October 2013

Accepted 21 October 2013

Available online 26 October 2013

Keywords:

Imine synthesis

One-pot reaction

Palladium

Heterogeneous catalysis

Nitrobenzene

ABSTRACT

Using a supported palladium catalytic system, the reaction of nitroarenes with benzyl alcohols occurred smoothly via hydrogen transfer to produce imines in an atom-economical manner. The palladium species were dispersed well on hydrotalcite (HT) support and palladium nanoparticles with size of about 3.5 nm were formed during reaction. Both of the small size of palladium nanoparticles and the rich hydroxyl groups on HT surface enhanced the catalytic performance of Pd/HT. The catalytic system is recyclable and amenable to a variety of aromatic alcohols and nitro compounds.

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1. Introduction

The reduction of nitro compounds by acid/metal (e.g. Fe, Zn or Sn) or via transition-metal catalyzed hydrogenation is commonly used access to amines, an important class of organic compounds. However, these traditional processes usually proceed under high pressure of hydrogen and/or use stoichiometric acids and metals with a lot of toxic wastes released. From the standpoint of sustainable development, an atom-economic, “green” and operationally convenient method for the synthesis of amines from nitro compounds is highly desirable. In this regard, the borrowing-hydrogen methodology [1–3], which transfers hydrogen from readily available alcohols to nitro compounds to produce amines as well as valuable aldehyde, provides a promising alternative to the existing method for reduction of nitro compounds.

Till date, many efforts have been made to contribute the development of the borrowing-hydrogen methodology. *N*-functionalized compounds (secondary and tertiary amines mainly) syntheses starting with nitroarenes and alcohols without any other reductants have been established over homogeneous catalysts (mostly Ru) [1], heterogeneous catalysts [2] and TiO₂-based photocatalysts [3]. Notably, outstanding catalytic activities have been obtained from the Au recyclable heterogeneous catalysts [2a,b] that overcame the inherent drawbacks of homogeneous ones such as the dependence on toxic and costly ligands and the difficulties in

separating and reusing expensive catalysts from reaction mixture. The transfer of hydrogen from alcohols to nitro compounds allows generating amines and aldehydes and because the two products can easily condense into imines, these hydrogen-transfer reactions would yield imines as the final products. In certain cases, the amines can even formed due to further hydrogenation of the imines [1b,c,d,e,2b,c,d].

Supported-palladium catalysts are classical heterogeneous catalysts for oxidations and reductions. Among various heterogeneous catalysts [4], palladium-based catalysts have shown excellent performances for the dehydrogenation of alcohols [4f]. In this sense, we speculated that supported-palladium catalyst would promote the reduction of nitro compounds with alcohols as a hydrogen source if the palladium-hydride species from palladium-mediated dehydrogenation of alcohol could deliver hydrogen to nitro compounds.

Herein, we reported an easy-to-handle heterogeneous palladium catalytic system for the selective production of imines, a class of versatile synthetic intermediates for dyes, fragrances, pharmaceuticals, fungicides, optical material and agricultural chemicals [5], using hydrogen-transfer strategy between nitroarenes and benzyl alcohols. To the best of our knowledge, only one palladium heterogeneous catalysis has been reported recently for this kind of transformation, however strong base was required in that case [2e].

2. Experimental

2.1. Catalyst preparation

The hydrotalcites used in this work with the composition of Mg₆Al₂(OH)₁₆CO₃ were prepared according to an established

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method [6]. Two aqueous solutions were ready at first. $\text{AlCl}_3 \cdot 9\text{H}_2\text{O}$ (50 mmol) and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (150 mmol) were dissolved in 100 mL of deionized water (solution **a**). Na_2CO_3 (60 mmol) and NaOH (210 mmol) were dissolved in 60 mL of deionized water (solution **b**). Solution **a** was slowly added into solution **b** and the emulsion was heated at 65°C for 18 h with vigorous stirring. Thereafter, the white slurry was cooled to room temperature. The solids were filtered and washed with about 1.6 L deionized water, finally dried at 120°C overnight.

Pd/C was purchased from Aladdin Reagent Corporation. The rest supported-palladium catalysts were synthesized by the impregnation method. The support was immersed into a fresh aqueous solution of PdCl_4^{2-} , and the mixture was stirred for 4 h. Thereafter the mixture was allowed to stand for 6 h and then dried at 60°C under stirring. The powdery sample was dried at 120°C over night and calcined at 300°C for 0.5 h. For a hydrotalcite supported catalyst, the calcination was not carried out in order to keep the special layer-to-layer structure. XRD patterns confirmed the hydrotalcite structure on Pd/HT.

2.2. Catalyst characterization

The specific surface area of varied supports were determined by micropore analyzer ASAP 2020. The palladium loading in the catalysts before and after reaction were determined by inductively coupled plasma OES spectrometer (ICP) using a Jobin Yvon Ultima 2. Transmission electron microscope (TEM) measurements were performed on a JEM 2010 electron microscope operated at an acceleration voltage of 200 kV. Samples for TEM measurements were suspended in ethanol and dispersed ultrasonically. Drops of the suspensions were applied on a copper grid coated with carbon.

3. Catalytic test

All reactions were performed under nitrogen atmosphere using Schlenk techniques. The reagents used in the experiments were purchased from Sigma-Aldrich Co., Acros Organics, Avocado and Alfa Aesar and used as received.

Table 1
Direct synthesis of imine from nitrobenzene and benzyl alcohol on various catalysts^a.

Entry	Catalyst ^b	Conv. of 2a (%) ^c	Conv. of 1a (%) ^c	Yield (%) ^c 3a	4a	5a
1	2 wt% Pd/ γ - Al_2O_3	83	20	8	2	0
2	2 wt% Pd/ TiO_2	91	20	3	15	0
3	10 wt% Pd/C	51	25	18	2	2
4	2 wt% Pd/HAP	44	22	5	4	0
5	2 wt% Pd/MgO	43	15	2	9	0
6	2 wt% Pd/HT	>99	>99	93	7	0
7 ^d	2 wt% Pd/HT	>99	97	88	7	0
8 ^e	1 wt% Pd/HT	47	32	23	5	1
9	1 wt% Pd/HT	97	94	79	13	1
10	1 wt% Pd/CoAl-HT	23	19	12	5	2
11	HT	23	6	0	0	0
12 ^f	1 wt% Pd/HT	81	75	63	6	2
13 ^g	2 wt% Pd/HT	–	35	19	7	0

^a Reaction conditions: nitrobenzene (0.5 mmol), benzyl alcohol (1.5 mmol), toluene (2 mL), and catalyst (metal: 2 mol%), 130°C , 24 h.

^b Pd/C was purchased from Aladdin Reagent Corporation. The other catalysts were prepared by wet impregnation methods (see the supporting information).

^c Yield was based on nitrobenzene conversion, determined by GC using *n*-dodecane as the internal standard.

^d 12 h.

^e The catalyst was calcined at 300°C for 0.5 h.

^f The palladium precursor was $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$.

^g Nitrobenzene (0.3 mmol), benzaldehyde (0.9 mmol), toluene (2 mL), and catalyst (Pd 2 mol%) with the substitution of about 1 mmol H_2 for N_2 at an atmospheric pressure.

In a typical reaction, 2 wt% Pd/HT catalyst (0.05 g, 2 mol% Pd relative to nitrobenzene) was added to a pressure tube (25 mL) equipped with a stir bar. The tube was sealed with a rubber septum, and vacuumed for several times. Substrates nitrobenzene (0.5 mmol, 50 μL), benzyl alcohol (1.5 mmol, 150 μL), and solvent toluene (2 mL) were added into the tube through the rubber septum using syringes, and then the septum was replaced by a Teflon screwcap under a nitrogen flow. The tube was sealed and the mixture was allowed to stir in a preheated oil bath at 130°C for 24 h. After the reaction was completed, a GC internal standard dodecane (10 μL) was added to the mixture. The mixture was diluted with ethyl acetate and filtered through a pad of silica gel. The pad of the silica gel was washed again with small amount of ethyl acetate and the final volume of the clear solution was marked up to 25 mL. The liquid products were then analyzed using a gas chromatography equipment (Agilent 7820A).

For the cycling performance test when the reaction mixture was cooled down, the solid catalyst was separated by centrifuge, washed with ethanol several times and dried at 120°C . Then the recycle catalyst was ready for the next reaction. After the reaction the solid catalyst was filtered, and the filtrate was analyzed for palladium by ICP. And the palladium loading in the 2 wt% Pd/HT catalyst was also determined by ICP.

For the analysis of the nitrobenzene and benzyl alcohol derivatives, an aliquot (2 mL) was removed from the reaction mixture in the pressure tube, and it was concentrated under reduced pressure. NMR internal standard paraldehyde was added to it. The product was then determined by ^1H NMR spectroscopy.

4. Results and discussion

4.1. Optimization of catalytic systems and recycling of catalysts

The optimization study was first performed on a series of palladium catalysts loaded on various supports (Table 1). The reaction of nitrobenzene (**1a**) with 3 equiv. of benzyl alcohol (**2a**) was chosen as the model system, in which the 1:3 ratio of **1a** to **2a** was calculated on the basis of the minimum theoretical amount of hydrogen needed for the nitrobenzene reduction. Among the palladium

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