

Layered double hydroxides supported nanoplatinum catalyst for Suzuki coupling of aryl halides

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Abstract

Layered double hydroxides (LDH) supported nanoplatinum catalyst was prepared and employed for Suzuki cross coupling of aryl halides (iodides and bromides) with a broad range of arylboronic to afford the corresponding biaryls in good to excellent yields without using any external ligand. The catalyst is reused for several cycles with consistent activity.

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Keywords: Layered double hydroxides; Nanoplatinum; Suzuki; Aryl halides; Reusable catalyst

1. Introduction

Suzuki [1] reaction, coupling of aryl halides with arylboronic acids, is one of the most powerful methods for the synthesis of biaryl compounds, important intermediates for pharmaceuticals, herbicides and natural products. Although several reports using palladium and nickel complexes [2] are available, a few examples using platinum, the next group member is cited for Suzuki cross coupling [3]. It is most probable that the slow rate of reductive elimination of biaryl group from platinum complexes compared with the rate for the analogous palladium complex is responsible for the less reactivity of platinum. Bedford et al. [3a] and Oh et al. [3b] reported Suzuki biaryl coupling reactions of aryl bromides and aryl iodides, respectively, using Pt complexes. In view of the non-reusability of the expensive platinum catalyst and use of costly ligands, it is highly desirable to develop a reusable and recoverable platinum catalytic system without using any external ligand. Previously we have reported layered double hydroxides (LDH) supported nano-Pd⁰ [4] cata-

lyst, which can activate aryl chlorides also. Herein we report Suzuki cross coupling reaction catalyzed by a heterogeneous layered double hydroxides supported nanoplatinum catalyst (Scheme 1).

2. Experimental

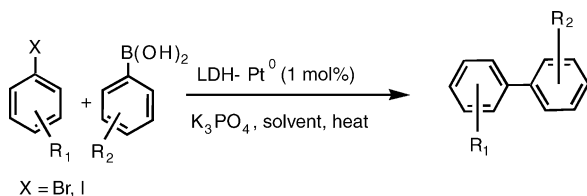
2.1. Materials and methods

FTIR spectra were recorded on a Perkin-Elmer spectrophotometer. ¹H NMR spectra were recorded on Bruker (300 MHz) spectrophotometer using CDCl₃ as solvent and TMS as the internal standard. X-ray photoelectron spectroscopy (XPS) spectra were recorded on a KRATOS AXIS 165 with a dual anode (Mg and Al) apparatus using the Mg K α anode. X-ray powder diffraction (XRD) data were collected on a Simens/D-5000 diffractometer using Cu K α radiation. The particle size and external morphology of the samples were observed on a JEOL JEM-100CX transmission electron microscopy (TEM). SEM-EDX was performed on a Hitachi SEM S-520, EDX-Oxford Link ISIS-300 instrument. All known compounds were characterized by comparing their physical data with those in the literature. Solvents used for

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Scheme 1. LDH-Pt⁰ catalyzed Suzuki cross coupling of aryl halides and arylboronic acids.

experiments were dried and distilled according to literature procedures. All the reactants were commercially available and used without purification.

2.2. Preparation of LDH-PtCl₆

LDH-Cl (Mg:Al = 3:1) was prepared according to the literature [5]. LDH-Cl (2 g, Mg:Al = 3:1) was suspended in 150 ml of aqueous K₂PtCl₆ (0.388 g, 0.8 mmol) solution and stirred at 25 °C for 24 h under N₂ atmosphere. The solid catalyst was filtered, washed thoroughly with 500 ml of water and vacuum-dried to obtain LDH-PtCl₆.

2.3. Preparation of LDH-Pt⁰

LDH-PtCl₆ (1 g) was reduced with hydrazine hydrate (1 g, 20 mmol) in ethanol (10 ml) for 3 h under nitrogen atmosphere, filtered and washed with ethanol to give an air stable black powder (0.374 mmol of Pt per gram of the catalyst).

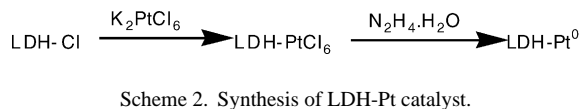
2.4. General experimental procedure

In an oven dried 10 ml round-bottom flask aryl halide (1 mmol), arylboronic acid (1.5 mmol), K₃PO₄ (2 mmol), LDH-Pt⁰ (1 mol%), and dioxane:water [5:1] (2 ml) were taken and stirred at 100 °C under N₂ atmosphere. After the completion of the reaction, monitored by TLC, the catalyst was filtered. The filtrate was diluted with ethyl acetate and washed with 10% aqueous NaOH solution and finally with saturated aqueous NaCl solution. The organic layer was dried with Na₂SO₄ and concentrated to get the crude product. The crude product was column chromatographed using hexane and ethyl acetate mixture as an eluent. All products were characterized by NMR and mass spectroscopy.

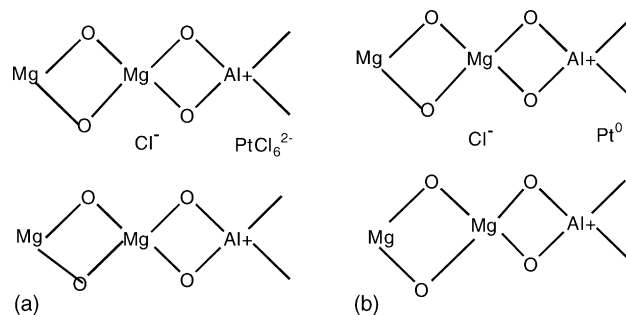
3. Results and discussion

3.1. Preparation of LDH-Pt⁰

Hexachloroplatinate was exchanged onto chloride saturated LDH to obtain a light yellow colored LDH-Pt(IV) and then reduced with hydrazine hydrate to give air stable black colored LDH-Pt⁰ catalyst (Scheme 1). The possible structures for the catalysts are depicted in Schemes 2 and 3.



Scheme 2. Synthesis of LDH-Pt catalyst.



Scheme 3. The structures of catalysts (a) LDH-PtCl₆ and (b) LDH-Pt⁰.

3.2. Characterization of the LDH-Pt⁰ catalyst

3.2.1. X-ray powder diffraction

Patterns of initial LDH and LDH-Pt⁰ hardly differ in the range $2\theta = 3^\circ\text{--}65^\circ$. The observed d_{003} basal spacing of support that appeared at 7.9 Å remained unchanged after the anion exchange and subsequent reduction, which indicates that the PtCl₆²⁻ and Pt⁰ nano particles are mainly located at the edge-on surface in the respective samples (Fig. 1).

3.2.2. X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopic investigation of LDH-Pt⁰ (Fig. 2) at Pt 4f level shows a 4f_{7/2} line at 72.87 eV and 4f_{5/2} at 75.19 eV, which clearly indicates that the metal is in the reduced form [6].

3.2.3. Transmission electron microscopy

TEM image of the LDH-Pt⁰ catalyst shows that the average sizes of nanoplatinum particles are in the range of 4–6 nm. The TEM images of the used catalyst indicate that the size

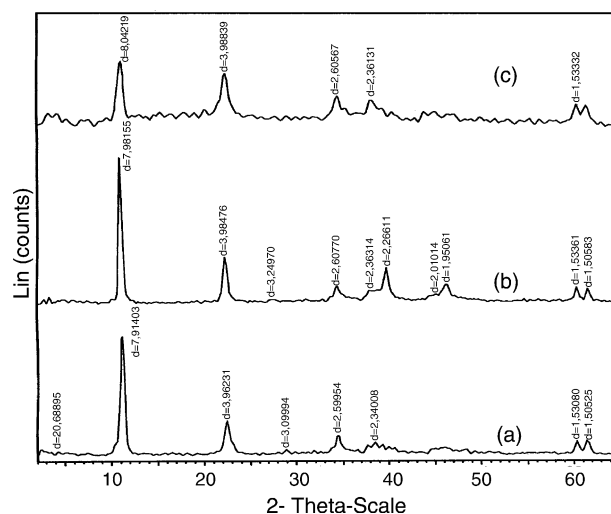


Fig. 1. XRD of: (a) LDH-Cl; (b) LDH-Pt⁰; (c) LDH-PtCl₆.

and morphology of the nanoplatinum remains unchanged in the used catalyst.


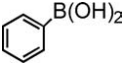
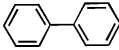

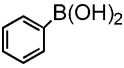
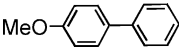

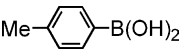
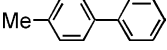
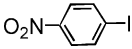
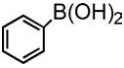
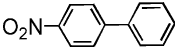
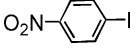
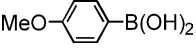
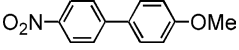
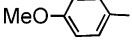
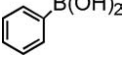
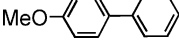
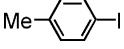
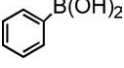
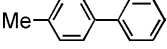

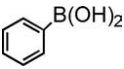
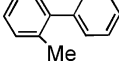
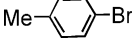
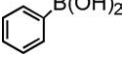
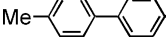
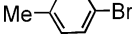
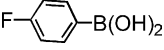
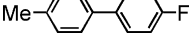

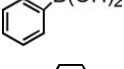
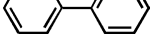

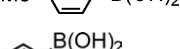
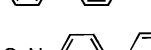
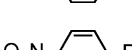
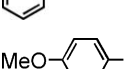
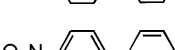
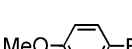
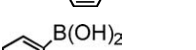
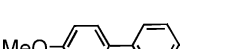
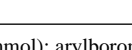
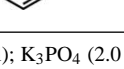
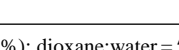
3.3. Catalytic Suzuki coupling of aryl halides

A variety of aryl iodides and bromides reacted in the presence of 1.0 mol% LDH-Pt⁰ with different arylboronic acids at 100 °C temperature affording the corresponding cross coupling biphenyl product in very good to excellent yields. The results are summarized in Table 1.

From Table 1, it is clear that aryl iodides are more reactive than the aryl bromides in the Suzuki coupling with aryl-

boronic acids as expected. The presence of electron donating groups in the aryl halide system retards the reaction, whereas electron-withdrawing group enhance the reaction. Here proper choice of solvent plays a crucial role for effective reaction. Without water, no reaction took place under identical condition. In dry dioxane, acetonitrile, DMF, toluene the yields were very poor (5–10%). It may be due to the poor solubility of inorganic bases in the organic solvents. Among the bases screened [7] K₃PO₄ was found to be the best but NaOH, KF were also good alternatives. Instead of LDH-Pt⁰, LDH-PtCl₆ can also catalyze the cross coupling reaction of aryl iodides with arylboronic acids in good yields but in case

Table 1
Catalytic Suzuki coupling^a of aryl halides and arylboronic acids using LDH-Pt⁰

Entry	Aryl halide	Arylboronic acid	Biaryl	Isolated yield (%)
1				90, 88 ^b , 85 ^c , trace ^d
2				95
3				92
4				98
5				98
6				88
7				90
8				78
9				82, 80 ^b , 55 ^c
10				82
11				90
12				85
13				95
14				95
15				60

^a Aryl halide (1.0 mmol); arylboronic acid (1.5 mmol); K₃PO₄ (2.0 mmol); LDH-Pt⁰ (1 mol%); dioxane:water = 5:1 (3 ml) 100 °C; reaction time = 12 h (for iodides) and 24 h (bromides).

^b Yield after fifth cycle.

^c LDH-PtCl₆ (1.0 mol%) used as a catalyst.

^d K₂PtCl₆ (1.0 mol%) used as a catalyst.

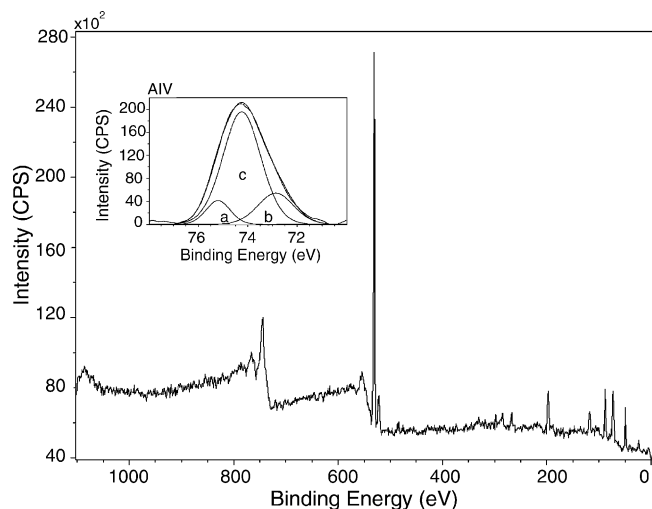


Fig. 2. XPS scan of LDH-Pt⁰, in inset narrow scan for Pt (a and b) and Al (c).

of aryl bromides the results are poor (Table 1, entries 1 and 9). The homogeneous precursor of the LDH-Pt catalyst, K₂PtCl₆ is not at all effective even for aryl iodides (Table 1, entry 1).

3.4. Reusability of the catalyst

The catalyst was recovered by simple filtration and washed with acetone and oven dried. The recovered catalyst was reused and consistent activity was noticed even after the fourth cycle (Table 1, entries 1 and 9). When a fresh reaction was conducted with the filtrate obtained at the end of the Suzuki reaction, no product formation was observed. Moreover, the absence of Pt in the filtrate was determined by AAS. The platinum content of the catalyst was found to be almost same in the fresh catalyst and in the used catalyst after the fifth cycle by SEM–EDX. These results show that after the reaction no platinum is observed in the filtrate however, the possibility of dissolution of platinum during the reaction and re-precipitation after the completion of reaction cannot be excluded as this phenomenon is already observed in case of palladium catalyzed reactions [8].

4. Conclusion

In summary, layered double hydroxides supported nanoplatinum was prepared and employed for Suzuki cross coupling of aryl halides (iodides and bromides) with a broad range of arylboronic acids to afford the corresponding biaryls in good to excellent yields without using any external ligand. The simple procedure, easy recovery, and reusable catalytic systems are expected to contribute to the development of benign chemical process and products.

Acknowledgements

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