Layered Double Hydroxide-Supported Nanoplatinum: An Efficient and Reusable Ligand-Free Catalyst for Heck and Stille Coupling of Iodoarenes

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Abstract: A layered double hydroxide-supported nanoplatinum catalyst is employed in the Heck and Stille cross-coupling of a wide range of iodoarenes to give the corresponding cross-coupled products in good to excellent yields. The catalyst is recovered by centrifugation and reused over a number of cycles with consistent activity.

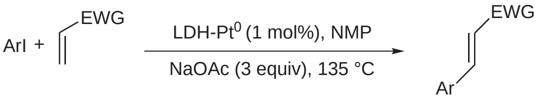
Key words: layered double hydroxides, nanoplatinum, Heck coupling, Stille coupling, iodoarenes

The palladium-catalyzed coupling of aryl halides by Heck, Suzuki, Sonogashira and Stille reactions is a well-established methodology in modern organic synthesis as the coupling products are important intermediates in materials, natural products, and bioactive compounds.[1] Mainly palladium salts with or without any ancillary ligand are used for these coupling reactions. Few reports appeared towards the development of catalysts involving the next member of the group, platinum, for Heck and related coupling reactions.[2] Dehalogenated product is major in the vinylation of aryl iodides by homogeneous platinum catalysts [2c] In case of Stille coupling, low yields of products were reported using $Pt(Ph_3)_4$ catalyst.[2b] Moreover, the non-reusability of the expensive platinum and use of costly and some times air sensitive ligands preclude the wide application of homogeneous platinum catalysts. So it is highly desirable to develop a reusable and ligand-free platinum catalyst for such coupling reactions. Recently, Horniacova et al. reported the functionalized mesoporous silica FSM-16-supported platinum complexes as effective heterogeneous catalysts for Heck reaction of aryl iodides,[2f] but the preparation and functionalization of mesoporous silica is tedious.

Layered double hydroxides (LDHs) of Mg and Al have recently received much attention in view of their potential usefulness as materials, anion exchangers, and more importantly as catalysts.[3] Moreover they can hold nanometal particles in the defect sites and provide adequate electron density to stabilize them.[4] Previously, we have prepared nanopalladium catalysts supported on LDH by exploiting its anion exchange capacity and effectively utilized the catalyst for Heck, Suzuki, Sonogashira and Stille-type coupling reactions of chloroarenes.[4] Recently following the same protocol, we have prepared a LDH-supported nanoplatinum catalyst (LDH-Pt^0) for efficient Suzuki coupling of aryl halides.[5] Herein, we wish to report the Heck and Stille cross-coupling of aryl iodides catalyzed by ligand-free heterogeneous LDH-Pt^0 catalyst.

The LDHs consists of alternating cationic $M(II)_{1-x}M(III)_x(OH)_2^{x+}$ and anionic $A^{n-}\cdot zH_2O$ layers. The positively charged layers contain edge-shared metal M(II) and M(III) hydroxide octahedra, with charges neutralized by A^{n-} anions located in the interlayer spacing or at the edge of the lamellae. Small hexagonal LDH crystals with $Mg_{1-x}Al_x(OH)_2(Cl)_x\cdot zH_2O$ composition were synthesized following the existing procedures (here, $x = 0.25$).[6] Hexachloroplatinate was exchanged onto chloride saturated LDH to obtain a light yellow colored LDH-Pt(IV) and subsequently reduced with hydrazine hydrate to give air-stable black LDH-Pt^0 catalyst. XRD patterns of initial LDH and LDH-Pt^0 hardly differ in the range $2\theta = 3–65°$. The observed d_{003} basal spacing of support that appeared at 7.8 Å remained unchanged after the anion exchange and subsequent reduction, which indicates that the $PtCl_6^{2-}$ and Pt^0 nanoparticles are mainly located at the edge-on surface in the respective samples.

Initially we have carried out the Heck reaction of iodobenzene with styrene under different conditions to optimize the reaction parameters. It was found that NMP was the best solvent among the different solvents screened.[7] Among the bases screened, NaOAc was found to be the best in terms of yield.[8] Reaction temperature was also playing a crucial role. Below 120 °C, there was no reaction. We got the best result in Heck reaction of iodobenzene and styrene by using 1 mol% LDH-Pt^0 in NMP with NaOAc base at 135 °C under nitrogen atmosphere. Under this optimized condition,[9] several other iodoarenes and a wide variety of activated alkenes were subjected to Heck coupling reaction (Scheme 1) and the results are summarized in Table 1.



Scheme 1

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Table 1 Heck Coupling Reaction of Iodoarenes and Alkenes Catalyzed by LDH-Pt^0 Catalyst[a]

Entry	Iodoarene	Olefin	Time (h)	Isolated yield (%)
1	Iodobenzene	Styrene	6	92, 90,[b] 88,[c] 90[d]
2	Iodobenzene	Methyl acrylate	6	90
3	Iodobenzene	4-Methyl styrene	6	86
4	4-Iodotoluene	Styrene	10	88
5	4-Iodoacetophenone	Styrene	4	94
6	4-Iodonitrobenzene	Styrene	4	93
7	2-Iodotoluene	Styrene	12	67
8	4-Iodoanisole	Styrene	16	90
9	Bromobenzene	Styrene	24	Trace

[a] Reaction conditions: iodoarene (0.5 mmol), alkene (0.75 mmol), LDH-Pt^0 (1 mol%), NaOAc (1.5 mmol), NMP (3 mL), 135 °C, nitrogen atmosphere.

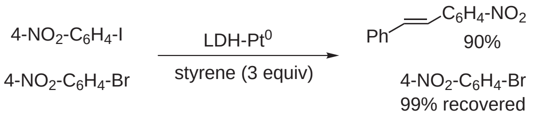
[b] LDH-Pt^0 (0.5 mol%), reaction time: 16 h.

[c] LDH-Pt^0 (0.1 mol%), reaction time: 48 h.

[d] Yield after 5th cycle.

It is observed that electron-rich iodoarenes were taking longer reaction time compared to electron-deficient iodoarenes but yields were comparable. Probably, the electron-withdrawing group present in the iodoarenes was facilitating the oxidative addition of iodoarenes.

Instead of 1 mol% catalyst, when 0.5 or 0.1 mol% catalyst was employed in the Heck reaction of iodobenzene with styrene, complete conversion of iodobenzene was observed although it took longer time (Table 1, entry 1). LDH-Pt^0 catalyst was found to be compatible with different functionalities like acetyl and nitro groups (Table 1, entries 5 and 6). 2-Iodotoluene was found to be less reactive and yield was moderate (Table 1, entry 7) which may be due to the steric hindrance. When bromoarenes were tested for Heck coupling using LDH-Pt^0 catalyst almost no product formation was observed. Based on this inertness towards bromoarenes, iodoarenes can be activated selectively in presence of bromoarenes by using LDH-Pt^0 catalyst (Scheme 2). This substrate selectivity could be useful in synthetic organic chemistry.



Scheme 2

The LDH-Pt^0 was separated from the reaction mixture by centrifugation, washed with water and acetone, dried and used in the next cycle. Almost consistent activity was noticed even after fifth cycle (Table 1, entry 1). Platinum content of the fresh and used (after 5th cycle) catalysts was found to be almost same (by ICP-AES). To check the heterogeneity of the catalyst, a reaction between iodobenzene and styrene was terminated at 16% conversion (after 30 min) and the catalyst was separated by a simple filtration. The reaction was continued for an additional 12 hours and the conversion almost remained unchanged. Moreover, the filtrate was tested for platinum by ICP-AES and no platinum was found. These studies clearly demonstrate that no leaching of platinum has taken place from the catalyst and through out the reaction platinum was bound to the support.

To widen the scope of LDH-Pt^0 catalyst in organic synthesis, it was employed in the Stille coupling reaction of iodoarenes with trialkyl tin reagents. Stille coupling of 4-iodoanisole with phenyltributyltin was carried out in NMP solvent at 100 °C using 1 mol% of catalyst loading without using any additive and 4-methoxybiphenyl (96%) was obtained with a small amount of biphenyl (7%). Then several other iodoarenes were also coupled with different trialkyltin reagents under this optimized condition[10] and results are summarized in Table 2. Here also, the catalyst was removed from the reaction mixture by simple centrifugation and washed with water followed by acetone and dried in air. The recovered catalyst was used for four consecutive cycles with consistent activity (Table 2, entry 1).

In conclusion, we have developed an efficient and simple protocol for Heck and Stille coupling of aryl iodides using LDH-Pt^0 catalyst. Moreover, the catalyst can be easily recovered by simple centrifugation and reused with consistent activity.

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Table 2 Stille Coupling of Iodoarenes with Trialkyltin Using LDH-Pt^0 Catalyst[a]

Entry	Iodoarene	Trialkyltin	Time (h)	Isolated yield (%)
1	Iodobenzene	Phenyl tributyltin	4	90, 88[b]
2	Iodobenzene	Vinyl tributyltin	6	92
3	4-Iodonitrobenzene	Phenyl tributyltin	4	95
4	4-Iodonitrobenzene	Vinyl tributyltin	4	92
5	4-Iodotoluene	Phenyl tributyltin	8	90
6	4-Iodotoluene	Vinyl tributyltin	8	88
7	4-Iodoacetophenone	Phenyl tributyltin	4	92
8	4-Iodoanisole	Phenyl tributyltin	12	94
9	2-Iodotoluene	Phenyl tributyltin	12	67

[a] Reaction conditions: iodoarene (0.5 mmol), trialkyltin reagent (0.75 mmol), LDH-Pt^0 (1 mol%), NMP (3 mL), 100 °C, nitrogen atmosphere.
[b] Yield after 5th cycle.

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(7) For Heck reaction of iodobenzene with styrene in presence of LDH-Pt^0 (1.0 mol%) using NaOAc as base at 135 °C for 6 h yield of *trans*-stilbene: 92% (NMP), 88% (DMF), 89% (DMAc), 10% (MeCN), 0% (xylene).

(8) For Heck reaction of iodobenzene with styrene in presence of LDH-Pt^0 (1.0 mol%) in NMP solvent at 135 °C for 6 h yield of *trans*-stilbene: 92% (NaOAc), 78% (K_2CO_3), 35% (NaOH), no reaction (Bu_3N).

(9) For preparation and characterization of LDH-Pt^0 catalyst see ref. 5. Loading of Pt in LDH-Pt^0 is 0.374 mmol of Pt per gram of catalyst. In a typical procedure for Heck coupling using LDH-Pt^0 as catalyst: in an oven-dried 10-mL round-bottomed flask, iodobenzene (0.5 mmol), styrene (0.75 mmol), NaOAc (1.5 mmol), LDH-Pt^0 (1.0 mol%), and NMP (3 mL) were taken and stirred at 135 °C under N_2 atmosphere and the reaction was monitored by TLC. After the completion of the reaction, the catalyst was centrifuged and reused. The centrifugate was diluted with Et_2O and washed with sat. aq NaCl solution. The organic layer was dried with Na_2SO_4 and concentrated to get the crude product. Then it was subjected to column chromatography to get the pure product. Isolated yield of *trans*-stilbene was 92%.
^{1}H NMR: $\delta = 7.11$ (s, 2 H), 7.21–7.30 (m, 2 H), 7.31–7.41 (t, 4 H, $J = 7.54$ Hz), 7.47–7.56 (d, 4 H, $J = 7.54$ Hz).

(10) **Typical Procedure for Stille Coupling Using LDH-Pt^0 as Catalyst.**
In an oven-dried 10-mL round-bottomed flask, 4-iodoanisole (0.5 mmol), phenyltributyl tin (0.75 mmol), LDH-Pt^0 (1.0 mol%), and NMP (3 mL) were taken and stirred at 100 °C under nitrogen atmosphere and the reaction was monitored by TLC. After the completion of the reaction, the catalyst was centrifuged and reused. The centrifugate was diluted with Et_2O and washed twice with aq 20% KF solution followed by sat. aq NaCl solution. The organic layer was dried with Na_2SO_4 and concentrated to get the crude product. Then it was subjected to column chromatography to get the pure product. Isolated yield of 4-methoxybiphenyl was 94%.
^{1}H NMR: $\delta = 3.85$ (s, 3 H), 6.93 (d, 2 H, $J = 8.9$ Hz), 7.20–7.31 (m, 1 H), 7.33–7.44 (t, 2 H, $J = 7.4$ Hz), 7.46–7.56 (m, 4 H).