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Layered-double-hydroxide-supported $Pd(TPPTS)_2Cl_2$: a new heterogeneous catalyst for Heck arylation of olefins

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The $Pd(TPPTS)_2Cl_2$ (TPPTS: triphenylphosphine trisulfonate, sodium salt) complex is immobilized on layered double hydroxides by the ion-exchange method. This heterogeneous catalyst is successfully used in Heck arylation of olefins. The catalyst can be recycled several times with almost consistent activity.

KEY WORDS: palladium; TPPTS; layered double hydroxide; Heck reaction.

1. Introduction

Industrial interest spurred by the introduction of a biphasic counterpart of the rhodium-catalyzed hydroformylation in the early 1980s using water-soluble ligands such as triphenylphosphine trisulfonate, sodium salt (TPPTS), TPPDS, TPPMS and innovative developments also served to reinvigorate academic interest in overcoming the technological limitations of the powerful catalysts available [1]. Numerous water-soluble complexes are also reported for various organic reactions. Hydroformylations [1], hydrogenations [2], oxidations [3], Heck arylation of various olefins [4] and amination of haloarenes [5] are some of the reactions that have been carried out under homogeneous aqueous biphasic conditions using water-soluble complexes. Although biphasic reactions have proved to be a successful solution for easy recovery of the catalyst and recharge for several cycles in some cases, these reactions have limited scope and applicability, because the catalyst, which resides in the aqueous phase, has a limited interface with the substrates that are totally insoluble in the aqueous phase to react with such substrates to afford good conversions and yields.

Heterogenization of these water-soluble metal complexes on solid supports is an alternative procedure to recover and reuse these metal complexes in the process. The supported aqueous phase (SAP) technique [6] has been developed, effecting the immobilization of water-soluble metal complexes such as Rh/TPPTS, Co/TPPTS, Ru/TPPTS, Pt/TPPTS and Pd/TPPTS on aqueous phase or ethylene glycol phase using solid supports like silica and porous glass beads, which are used for various organic transformations like hydroformylation of alkenes [7], hydrogenation [8] and Heck reactions [9]. But this technique seriously suffers from the leaching of precious metal from the support and thus limits its applicability as truly heterogeneous catalysts. Therefore it is felt that there is a need to develop a truly heterogeneous catalyst with these metal complexes and exploit their inherent advantages in heterogeneous catalysis for fine chemical production.

The C–C bond-forming reactions find several applications, such as in the synthesis of taxol, antitumor antibiotic CC-1065, drug intermediates, UV absorbers and antioxidants [10]. The $Pd(TPPTS)_2Cl_2$ complex is used in C–C and C–heteroatom coupling reactions to generate widely used intermediates in organic synthesis [4,5]. We choose and design the heterogenization of these metal complexes on solid supports like layered double hydroxides (LDH) to overcome the problems manifested in homogeneous biphase and supported aqueous-phase catalytic reactions as discussed. We report here the heterogenization of the water-soluble complex $Pd(TPPTS)_2Cl_2$ on the LDH by the ion-exchange process (scheme 1) and the application of these LDH complexes in Heck arylation of olefins to afford excellent yields and high trans-selectivity.

The LDH consists of alternating cationic $M(II)_{1-x}M(III)_x(OH)_2^{x+}$ and anionic $A^{n-}\cdot nH_2O$ layers [11]. 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 edges of the lamellae. LDHs have recently received much attention in view of their potential usefulness as adsorbents, anion exchangers and more importantly as catalysts [12,13].

2. Experimental

Diffuse reflectance UV spectra for samples as KBr pellets were recorded on a GBC Cintra 10e UV–vis

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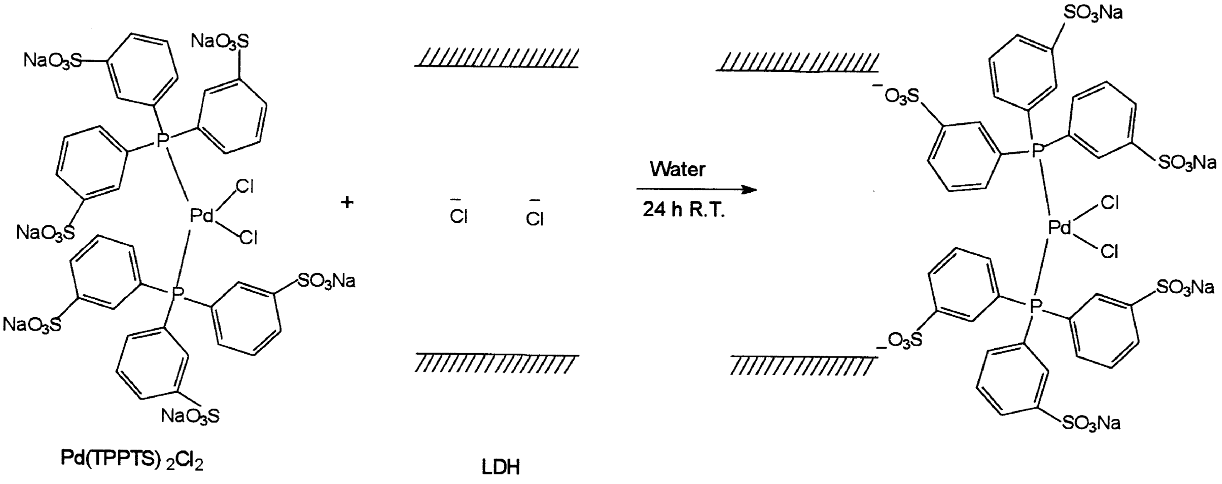


Scheme 1.

spectrometer. ^1H NMR spectra were recorded on a Varian Gemini 200 MHz spectrometer. The chemical shifts (δ) are reported in ppm using TMS as an internal standard and $CDCl_3$ as solvent. X-ray photoelectron spectra (XPS) were recorded on a Kratos Axis 165 with dual anode (Mg and Al) apparatus using the Mg K_α anode. The pressure in the spectrometer was about 10^{-9} Torr. For energy calibration we have used the carbon 1s photoelectron line. The carbon 1s binding energy was taken to be 285.0 eV. X-ray powder diffraction (XRD) data were collected on a Siemens D-5000 diffractometer using Cu K_α radiation ($\lambda = 1.5405$ Å). Scanning electron microscopy–energy dispersive X-ray analysis (SEM-EDX) was performed on a Hitachi SEM S-520, EDX-Oxford Link ISIS 300 instrument. Thin-layer chromatography was performed on Merck precoated silica gel 60–F_{254} plates.

$MgCl_2 \cdot 6H_2O$ and $AlCl_3 \cdot 6H_2O$ were purchased from Aldrich. Styrene and all other starting materials were purchased from commercial sources and used as received.

2.1. Preparation of the catalyst: LDH–Pd(TPPTS)$_2$Cl$_2$

LDH (Mg–Al–Cl) [12], TPPTS ligand [14] and $Pd(TPPTS)_2Cl_2$ [15] were prepared according to reported procedures. In a typical procedure, 0.2 mmol of the $Pd(TPPTS)_2Cl_2$ was dissolved in 100 ml of decarbonated water and stirred with 1 g of LDH (Mg–Al–Cl) under nitrogen atmosphere for 24 h. The resultant solid was filtered and washed with decarbonated water (200 ml) and thoroughly vacuum dried to give LDH–$Pd(TPPTS)_2Cl_2$ (**1**) (0.18 mmol of Pd per gram).

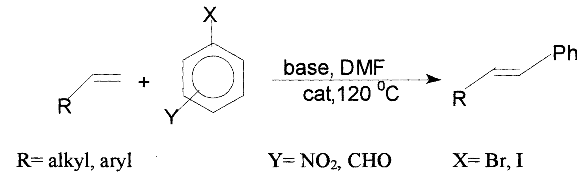
2.2. Procedure for the Heck arylation reaction

An olefin (1.1 mmol), haloarene (1 mmol), LDH–$Pd(TPPTS)_2Cl_2$ (1) (25 mg, 0.0045 mmol), tributylamine (2 mmol) and DMF (10 ml) were taken in a round-bottomed flask and stirred at 120 °C under nitrogen atmosphere. After completion of the reaction (as monitored by TLC) the reaction mixture was filtered and washed with ethyl acetate. The combined organics were washed with water and concentrated to get crude product. The mixture was subsequently chromatographed on silica gel with hexane/ethyl acetate as an eluent to afford the corresponding olefin. The products were characterized by ^1H NMR and mass spectroscopy.

3. Results and discussion

Small hexagonal LDH crystals with $Mg_{1-x}Al_x(OH)_2(Cl)_x \cdot nH_2O$ composition are synthesized following the existing procedures ($x = 0.25$) [12]. LDH-$Pd(TPPTS)_2Cl_2$ (**1**) was prepared by ion-exchange of $Pd(TPPTS)_2Cl_2$ with LDH–(Mg–Al–Cl) in water (scheme 1). The X-ray powder diffraction patterns of the initial LDH and LDH–$Pd(TPPTS)_2Cl_2$ hardly differ in the range $2\theta = 3$–65°. The observed d_{003} basal spacing of the support that appeared at 7.8 Å remained unchanged after the anion exchange, which indicates that $Pd(TPPTS)_2Cl_2$ is mainly located on the edge of LDH. The X-ray photoelectron spectroscopy (XPS) analysis of catalyst (**1**) (Pd $3d_{5/2}$ 337.2 eV) indicates that the Pd is present in the +2 oxidation state and chlorine binding energy (197.8 eV) reveals that it is in metal chloride form. The UV–DRS spectrum of the catalyst (**1**) shows the absorption maxima at 270 nm similar to the homogeneous complex, indicating that there is no change in the coordination of the complex upon heterogenization on LDH.

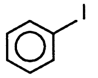
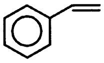
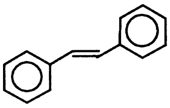
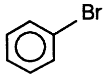
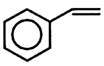
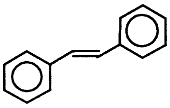
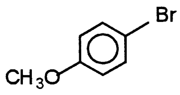
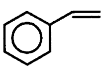
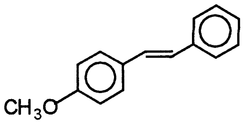
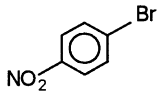
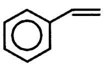
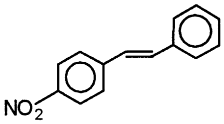
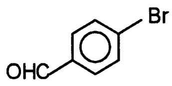
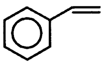
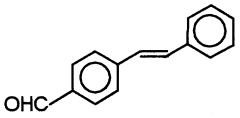
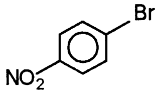
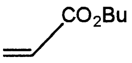
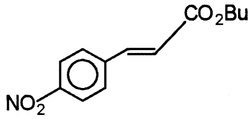
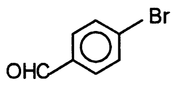
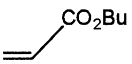
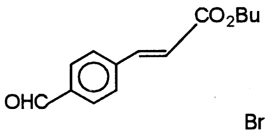
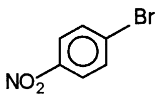
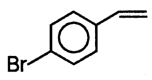
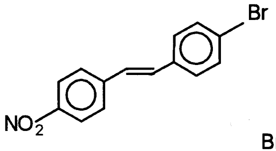
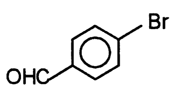
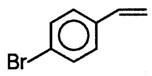
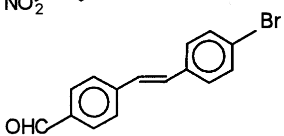
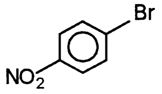
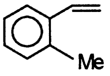
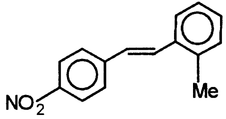
The LDH–$Pd(TPPTS)Cl_2$ (**1**) catalyst thus prepared was evaluated in Heck arylation (scheme 2) of olefins using both bromobenzenes and iodobenzenes as arylating agents using DMF as a solvent and tributylamine as base at 120 °C under nitrogen atmosphere to give aryl olefins with excellent yields and high *trans*-selectivity (table 1).



Scheme 2.

No corresponding *cis*-aryl olefin is detected in the proton NMR of the crude product. The catalyst (**1**) displays a higher rate of activity with bromoarene-bearing electron-withdrawing groups (entries 4 and 5), while the reaction is slow with bromoarenes having electron-donating substituents (entry 3). The catalyst (**1**) displays a turnover frequency of 6.25 h^{-1} in the arylation of styrene with bromobenzene in DMF using tributylamine as

Table 1
LDH–$PdCl_2(TPPTS)_2$ catalyzed Heck arylation of olefins

Entry	Haloarene	Olefin	Product	Time (h)	Yield (%)[a]
1				16	98 (95)[b]
2				32	93 (90)[b] (60)[c]
3				28	87
4				20	92
5				22	91
6				4	94
7				4	92
8				6	90
9				7	92
10				8	94

[a] Yields based on ^1H NMR; the rest is unreacted haloarenes. Olefin (1.1 mmol), haloarene (1 mmol), cat (25 mg, 0.0045 mmol of Pd), tributylamine (2 mmol) and DMF (10 ml) at 120 °C under nitrogen atmosphere.

[b] Isolated yields.

[c] $PdCl_2(TPPTS)_2$ (0.025 mmol), olefin (5.5 mmol), haloarene (5.0 mmol), tributylamine (5.5 mmol) and DMF (10 ml) were stirred at 120 °C under nitrogen atmosphere.

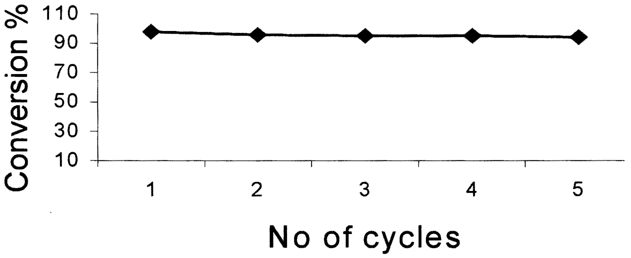
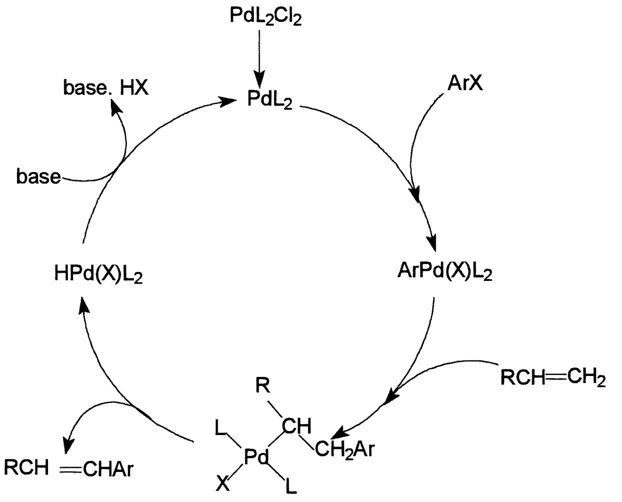


Figure 1. Reusability of the catalyst for five cycles. Reaction conditions: olefin (1.1 mmol), haloarene (1 mmol), catalyst (25 mg, 0.0045 mmol of Pd), tributylamine (2 mmol) and DMF (10 ml) at 120 °C under nitrogen atmosphere.

base at 120 °C (entry 2). It is significant to note that there are no studies made using bromoarenes as arylating agents with the analogues, water-soluble Pd$(TPPTS)_2Cl_2$ and heterogenized SAP–Pd$(TPPTS)_2Cl_2$. However, in the arylation of styrene with bromobenzene conducted under our reaction conditions as detailed above with the homogeneous analogue, Pd$(TPPTS)_2Cl_2$, the yield of arylation product is only 60% and the turnover frequency is $3.75\,h^{-1}$. The catalyst (**1**) is recovered after the arylation of styrene with iodobenzene reaction conducted in DMF solvent using tributylamine base at 120 °C (entry 1) by a simple filtration, and is reused successfully for five cycles with almost consistent activity (figure 1) under identical conditions as described. A very small amount of palladium (<0.5%) was leached out of the total palladium present in the catalyst (**1**) at the end of the reaction, as is evident by SEM-EDX studies. The results are very impressive when compared with the heterogeneous catalysts Pd on activated carbon [16a,b] and silica [16b], and heterogenized ethylene glycol phase on silica–Pd$(TPPTS)_2Cl_2$ [17a], glass–Pd$(TPPTS)_2Cl_2$ [9], and silica–Ni/TPPTS [17b], wherein the leaching of the Pd into the solution from the support is noticed.

The catalytic cycle in a plausible mechanism described in scheme 3 initiates with the formation of LDH–Pd(0)L_2 (L = TPPTS) from LDH–PdL_2Cl_2 by reduction. The redox cycle, Pd(0)/Pd(II), mainly comprises the oxidative addition of haloarenes to Pd(0) and reductive elimination to form Pd(0). The XPS analysis of the used catalyst shows a binding energy of Pd ($3d_{5/2}$) at 335.6 eV corresponding to Pd(0). The higher activity using iodobenzene and bromobenzene as arylating agent is ascribed to the effect of layered double hydroxide (LDH), a basic support, which facilitates the redox cycle, Pd(0)/Pd(II). The large positive electrical potential and spatial organization of the LDH–Pd(0)L_2 may be responsible for the superior performance. This result is in consonance with LDH–WO_4 catalyzed oxidative bromination [13a] and LDH–OsO_4 catalyzed asymmetric dihydroxylation [12d].

In summary, the Pd$(TPPTS)_2Cl_2$ complex supported on LDH is designed and developed by the ion-exchange technique and used for Heck arylation of olefins to afford high activity. The higher activity, simple workup procedure and reusability of catalyst makes a potential candidate for commercial exploitation in industry.



L = triphenylphosphine trisulfonated, sodium salt (TPPTS)

Scheme 3. Plausible reaction mechanism.

Acknowledgments

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