Layered Double Hydroxide Supported Nanopalladium Catalyst for Heck-, Suzuki-, Sonogashira-, and Stille-Type Coupling Reactions of Chloroarenes

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Abstract: Layered double hydroxide and Merrifield resin supported nanopalladium(0) catalysts are prepared by an exchange of $PdCl_4^{2-}$ followed by reduction and well characterized for the first time. The ligand-free heterogeneous layered double hydroxide supported nanopalladium (LDH−Pd^0) catalyst using the basic LDH in place of basic ligands indeed exhibits higher activity and selectivity in the Heck olefination of electron-poor and electron-rich chloroarenes in nonaqueous ionic liquids (NAIL) over the homogeneous $PdCl_2$ system. Using microwave irradiation, the rate of the Heck olefination reaction is accelerated, manifold with the highest turnover frequency ever recorded in the case of both electron-poor and electron-rich chloroarenes. The basic LDH−Pd^0 shows a superior activity over a range of supported catalysts, from acidic to weakly basic Pd/C, Pd/SiO_2, Pd/Al_2O_3, and resin-$PdCl_4^{2-}$ in the Heck olefination of deactivated electron-rich 4-chloroanisole. The use of LDH−Pd^0 is extended to the Suzuki-, Sonogashira-, and Stille-type coupling reactions of chloroarenes in an effort to understand the scope and utility of the reaction. The catalyst is quantitatively recovered from the reaction by a simple filtration and reused for a number of cycles with almost consistent activity in all the coupling reactions. The heterogeneity studies provide an insight into mechanistic aspects of the Heck olefination reaction and evidence that the reaction proceeds on the surface of the nanopalladium particles of the heterogeneous catalyst. TEM images of the fresh and used catalyst indeed show that the nanostructured palladium supported on LDH remains unchanged at the end of the reaction, while the XPS and evolved gas detection by TGA−MS of the used catalyst identify ArPdX species on the heterogeneous surface. Thus, the ligand-free nanopalladium supported on LDH, synthesized by the simple protocol, displays superior activity over the other heterogeneous catalysts inclusive of nanopalladium in the C−C coupling reactions of chloroarenes.

Introduction

The palladium catalyzed coupling of bromo- and iodoarenes by Heck-, Suzuki-, Sonogashira-, and Stille-type reactions is a well-established methodology in modern organic synthesis. The coupling products find good applications as intermediates in the preparation of materials,[1] natural products,[2] and bioactive compounds.[3] Despite the synthetic elegance and high turnover number, these coupling reactions suffer from serious limitations of using the expensive bromo- and iodoarenes that precluded the wide use in industry.[4] The renaissance of the coupling reactions, one of the most important organic transformations in organic synthesis, stems from the recent discovery of the activation of chloroarenes, the easily and cheaply available feedstock catalyzed by palladium complexes composed of basic ligands.[5−8] The strong basic ligands devised to provide the requisite electron density on palladium to undergo oxidative addition of Pd^0 with chloroarenes indeed facilitate the coupling reactions successfully.[5,6] Further, the recent use of nonaqueous

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ionic liquids (NAIL) provides a high throughput, an improved thermal stability, and an increased lifetime over the conventional solvents[9] in the palladium catalyzed Heck olefination of haloarenes[10] in general and less reactive chloroarenes in particular.[6g,11] Whereas, the use of microwave irradiation, another option known to enhance the rate of the reaction because of localized superheating, affords high throughput in the Heck olefination reactions involving bromo- and iodoarenes.[12]

In efforts to develop a heterogeneous system[13] with the catalysts such as Pd/SiO$_2$,[13a] Pd/C,[13a,b] Pd complexes grafted on SiO$_2$,[13c,d] Pd complexes intercalated in montmorillonite,[13e,f] Pd/Al$_2$O$_3$,[13g] Pd/resin,[13g] and Pd-modified zeolites,[13h,i] a desired option for commercial realization affords poor to moderate conversions and selectivities in the Heck olefination of chloroarenes. The use of basic support, for example, Pd/MgO,[13j] in the Heck olefination resulted in high conversions albeit poor selectivity. The Suzuki coupling reactions mediated by a heterogeneous palladium catalyst are confined to bromo- and iodoarenes.[14] However, the Suzuki-, Sonogashira-,[13l] and Stille-type coupling reactions catalyzed by heterogeneous palladium involving chloroarenes are relatively unexplored.

Nanopalladium catalysts, as such or stabilized by poly-(vinylpyrrolidone), block copolymer micelles of polystyrene-*b*-poly-4-vinylpyridine, propylene carbonate, mesoporous MCM-41, and silica supported poly-γ-mercaptopropylsiloxane, exhibit higher catalytic activity in the Heck olefination of bromo- and iodoarenes because of the larger surface areas.[13p,15] The preparation of these stabilized colloids involves invariably difficult protocols using exotic reagents. However, to the best of our knowledge, there is no report available on the activation of the chloroarenes effectively for the coupling reactions using the nanopalladium particles stabilized on any support.
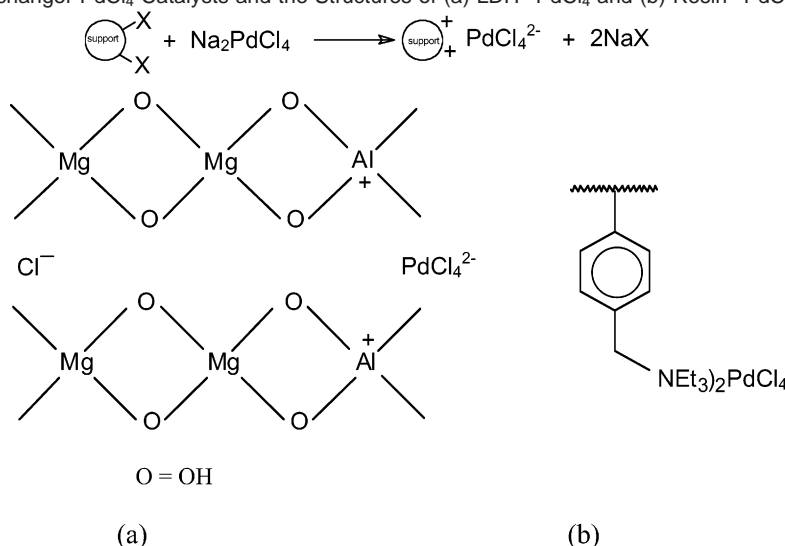
It is highly desirable to develop a phosphine-free new recyclable heterogeneous catalytic system to dispense the use of expensive and air-sensitive basic phosphines for palladium catalyzed coupling reactions of chloroarenes. We chose a basic support, Mg−Al layered double hydroxides (LDH), as the material of choice, not only to stabilize the nanopalladium particles but also to provide the adequate electron density to the anchored Pd^0 species to facilitate the oxidative addition of the deactivated electron-rich chloroarenes.

In this article, we report the nanopalladium immobilized layered double hydroxide (LDH−Pd^0) catalyzed Heck olefination of chloroarenes in NAIL media and microwave conditions for the first time with excellent yields and high turnover frequency. When the catalytic system is applied for Suzuki-, Sonogashira-, and Stille-type coupling reactions, the reaction affords excellent yields. The studies on the heterogeneity of the best-evolved catalyst, LDH−Pd^0 in the Heck olefination of deactivated electron-rich 4-chloroanisole, provides strong evidence that the reaction proceeds in a heterogeneous way. Incidentally, this forms the first report of heterogeneous palladium catalyst employed in the Suzuki- and Stille-type coupling reactions.

Results and Discussion

Preparation of Exchanger-Pd^0. LDHs have recently received much attention in view of their potential usefulness as materials,[16] anion exchangers, and more importantly as catalysts.[17,18] The LDHs consist of alternating cationic M(II)$_{1-x}$M(III)$_x$

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Scheme 1. Synthesis of Exchanger-PdCl$_4$ Catalysts and the Structures of (a) LDH−PdCl$_4$ and (b) Resin−PdCl$_4$

$$(\text{support})\overset{\text{X}}{\underset{\text{X}}{<}} + Na_2PdCl_4 \longrightarrow (\text{support})^{+}_{+} \; PdCl_4^{2-} + 2NaX$$

O = OH

(a)   (b)

(OH)$_2$$^{x+}$ and anionic A^{n-}.zH$_2$O layers.[19] The positively charged layers contain edge-shared metal M(II) and M(III) hydroxide octahedra, with charges neutralized by A^{n-} anions located in the interlayer spacing or at the edges of the lamellae. Small hexagonal LDH crystals with Mg$_{1-x}$Al$_x$(OH)$_2$(Cl)$_x$.zH$_2$O composition were synthesized following the existing procedures (here x = 0.25).[18c] Tetrachloropalladate (PdCl$_4$$^{2-}$) was exchanged onto chloride saturated LDH to obtain a dark brown colored LDH−Pd^{II} (Scheme 1). Resins are another class of polymeric supports originating from organic precursors,[20] which are widely employed as catalyst carriers and also in solid-phase organic synthesis. PdCl$_4$$^{2-}$ was also exchanged onto quaternary ammonium groups covalently bound to organic resin to obtain a maroon colored resin−Pd^{II}. The supported palladium salts were then reduced with hydrazine hydrate, giving air stable black powder of nanopalladium catalysts.

Characterization of Catalysts. (a) UV−vis/Diffuse Reflectance Spectroscopy. The complete reduction of palladium in LDH−Pd^0 was confirmed by UV−Vis/DRS, in which the peak at 280 nm corresponding to PdCl$_4$$^{2-}$ disappeared upon reduction (Figure 1). Further, the absorption in the visible region increases, indicating that the Pd^0 nanoparticles are formed.[15f] Similarly, the formation of nanopalladium particles is also observed in resin−Pd^0 (Figure 1).

(b) X-ray Powder Diffraction. X-ray powder diffraction patterns of the LDH, LDH−Pd^{II}, and LDH−Pd^0 hardly differ

in the range 2θ = 3°−65°. The observed d$_{003}$ basal spacing of the support that appeared at 7.8 Å remained unchanged after the anion exchange and reduction, which indicates that the PdCl$_4$$^{2-}$ and Pd^0 nanoparticles are mainly located at the edge-on surface in the respective samples.

(c) X-ray Photoelectron Spectroscopy (XPS). An X-ray photoelectron spectroscopic investigation of LDH−PdCl$_4$ at the Pd 3d level shows a 3d$_{5/2}$ line at 337.1 eV that is closer to the binding energy (337.9 eV) reported for PdCl$_4$$^{2-}$ impregnated on γ-alumina.[21] The chloride signal is also observed at 198.1 eV, which indicates that palladium is in the metal chloride form. Resin−PdCl$_4$ also exhibits identical binding energies for Pd and Cl. The XPS investigations of LDH−Pd^0 and resin−Pd^0 at the Pd 3d level show 3d$_{5/2,3/2}$ lines at 335.3 and 340.6 eV, respectively, which clearly indicates that the palladium is in the reduced form.[22]

(d) Transmission Electron Microscopy (TEM). As the LDH−Pd^0 is found to be the best catalyst, the results of the further characterization of fresh and used LDH−Pd^0 are presented here to establish a correlation between the structure and reactivity of the catalyst. The average sizes of nanopalladium particles in the fresh and used LDH−Pd^0 were measured from TEM images and found to be in the range 4−6 nm.

(e) BET Analysis. The BET surface areas of LDH, LDH−Pd^{II}, and LDH−Pd^0 are found to be 47, 58, and 64 m^2/g, respectively.

Coupling Reactions: (a) Heck Olefination of Chloroarenes. The LDH−Pd^0 nanoparticle catalyst thus synthesized was subjected to Heck olefination of chloroarenes. LDH−Pd^0 (3 mol %), chlorobenzene, and styrene were treated with Bu$_3$N in *N*-methyl pyrrolidinone (NMP) under stirring at 130 °C for 48 h, which afforded poor yields of *trans*-stilbene (10%). However, on using a nonaqueous ionic liquid, tetra-*n*-butylammonium
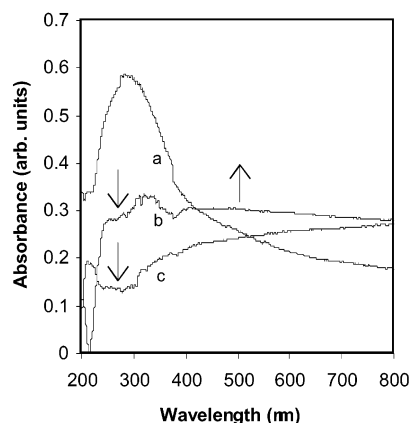
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Table 1. LDH−Pd^0 Catalyzed Heck Olefinations of Chloroarenes[a]

entry	chloroarene	olefin	microwave irradiation[b]		thermal heating[c]	
			time (h)	yield (%)	time (h)	yield (%)
1	chlorobenzene	=Ph	0.5	95	30	98
2	O$_2$N–C$_6$H$_4$–Cl	=Ph	0.5	96	10	95
3	MeOC–C$_6$H$_4$–Cl	=Ph	0.5	93	15	97
4	OHC–C$_6$H$_4$–Cl	=Ph	0.5	95	15	98
5	PhOC–C$_6$H$_4$–Cl	=Ph	0.5	91	15	93
6	MeO–C$_6$H$_4$–Cl	=C(O)OnBu	1	85	40	86
7	MeO–C$_6$H$_4$–Cl	=Ph	1	80	40	76(5)[d]
8	Me–C$_6$H$_4$–Cl	=Ph	0.5	92	30	96(55)[d]
9	HOH$_2$C–C$_6$H$_4$–Cl	=Ph	0.5	90	30	92(51)[d]

[a] Chloroarene (1 mmol), olefin (1.2 mmol), LDH−Pd^0 (3 mol %), [NBu$_4$]Br (10 mmol), and tri-*n*-butylamine (1.2 mmol). [b] Microwave power 400 W and temperature 130 °C. [c] Reactions are conducted at 130 °C. [d] The values in parentheses refer to the homogeneous reaction conducted with PdCl$_2$ under identical conditions.

Scheme 2. Heck Olefination of Chloroarenes with Olefins Using LDH−Pd^0
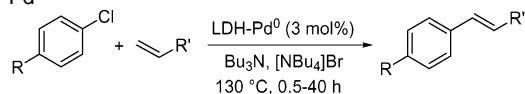
bromide as a solvent in place of NMP, the reaction under identical conditions gave *trans*-stilbene in quantitative yields within 30 h (Scheme 2).

To extend the scope of the reaction, we examined the Heck olefination of various substituted chloroarenes and olefins under NAIL conditions (Table 1). Although the products are obtained with excellent yields and >99% *trans*-selectivity, the reactions required longer duration (10−40 h). The olefination of the deactivated electron-rich chloroarenes took longer hours (Table 1, entries 6 and 7), while the reactions with the activated electron-poor chloroarenes were accomplished within 10−15 h (Table 1, entries 2−5). In the case of electron-neutral chlorobenzene, the reaction was completed in 30 h (Table 1, entry 1). Thus, the reactivity of these chloroarenes in the coupling reactions, which is in the order activated electron-poor chloroarenes > nonactivated electron-neutral chlorobenzene > deactivated electron-rich chloroarenes, is correlated to the nucleophilicity of the aromatic ring.

To realize a high turnover frequency, the Heck olefination reactions were conducted under microwave irradiation with identical reactive ingredients, and the results are very impressive (Table 1). It is significant to note that the duration of this reaction was dramatically reduced under microwave conditions from 10−40 h to 0.5−1 h without sacrificing the yields and selectivity. The nanocatalyst displays a higher turnover frequency for chlorobenzene (Table 1, entry 1), an increase by 2.76-fold under thermal conditions (1.08 h^{-1}) and 162-fold under microwave conditions (63.3 h^{-1}) when compared to the results

obtained using PdCl$_2$ and the nonaqueous ionic liquids in homogeneous conditions (0.39 h^{-1}).[6g] These results are quite impressive when compared to the other nanopalladium catalysts either supported or unsupported.[15]

The LDH−Pd^0 also displays enhanced rates in the Heck olefination, especially in the case of electron-neutral 4-chlorotoluene and 4-chlorobenzyl alcohol over the homogeneous reaction conducted with PdCl$_2$ under identical conditions (Table 1, entries 8 and 9). The effect is more pronounced with resilient 4-chloroanisole in the nonaqueous ionic liquid under thermal and microwave heating (Table 1, entry 7) to afford 76% yield in 40 h and 80% yield in 1 h, respectively, when compared to the 5% yield in 40 h obtained using PdCl$_2$ under the identical homogeneous thermal conditions.[6g] In the arylation of styrene with 4-chloroanisole, the turnover frequency is enhanced by 15.7 and 665 times under the thermal and microwave conditions, respectively, over the results obtained using PdCl$_2$ under the nonaqueous homogeneous conditions.[6g] The turnover frequency (25.3 h^{-1}) obtained under microwave conditions, to the best of our knowledge, is the highest ever recorded by any palladium catalyst for the deactivated electron-rich chloroarenes. For industrial and pharmaceutical applications of the Heck olefination reaction, the lifetime of the heterogeneous catalyst and its reusability must be high. The catalyst was recycled for five cycles in the Heck olefination of 4-chloroanisole with styrene under microwave and thermal conditions to record a TON of 160 in total (Figure 2). After the completion of the reaction, the catalyst was recovered by filtration and subsequently washed with water followed by dichloromethane. Alternatively, the heterogeneous catalyst and NAIL were also recovered after the vacuum distillation of the reactants and products at the end of each reaction. The higher efficacy, as displayed in the non-
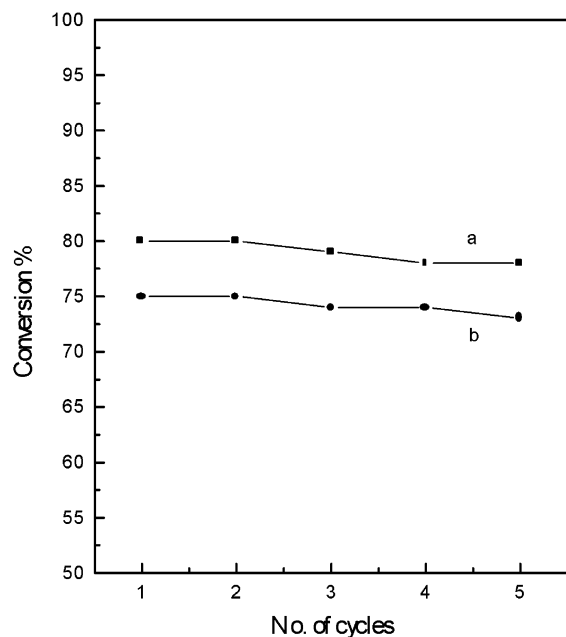
Figure 2. Recycling experiments with LDH−Pd^0 for 4-chloroanisole (a) under microwave conditions and (b) under thermal conditions.

Table 2. Heck Olefinations of 4-Chloroanisole with Styrene Using Various Palladium Catalysts[a]

entry	catalyst	yield (%)
1	LDH−Pd^0	76
2	resin−Pd^0	29
3	Pd/C	28
4	Pd/Al$_2$O$_3$	22
5	Pd/SiO$_2$	15
6	PdCl$_2$	5

[a] 4-chloroanisole (1 mmol), olefin (1.2 mmol), palladium catalyst (3 mol %), [NBu$_4$]Br (10 mmol), and tributylamine (1.2 mmol) were stirred at 130 °C for 40 h.

aqueous ionic liquid under the microwave conditions, is ascribed to the ionic conductance.

In an effort to compare the reactivity of LDH−Pd^0 with those of other heterogeneous catalysts, namely Pd/C, Pd/SiO$_2$, resin−Pd^0, and Pd/Al$_2$O$_3$, in the Heck olefination, separate experiments were conducted under identical conditions with the same ingredients, and the results are summarized in Table 2. The activity of various catalysts in the Heck olefination of 4-chloroanisole is found to be in the order: LDH−Pd^0 > resin-Pd^0 > Pd/C > Pd/Al$_2$O$_3$ > Pd/SiO$_2$. These results indicate that the basic support, LDH, facilitates the oxidative addition of Pd^0 with 4-chloroanisole and eventually the Heck olefination reaction.

For comparison, we also performed Heck olefinations of bromo- and iodoarenes using the LDH−Pd^0, and expectedly, higher conversions and >99% *trans*-selectivities are obtained over the homogeneous systems, thus supporting our devise of basic support in place of basic ligands.

1. Heterogeneity of LDH−Pd^0. There are two divergent schools of thought as to the how Heck olefination reaction is mediated by the heterogeneous catalysts. Blackmond[15d] and Reetz[15e] disclose that the reaction occurs at the heterogeneous surface, involving nanopalladium particles. On the other hand, Arai[13a] and Biffis[13g] independently made detailed studies recently on the heterogeneity of the palladium supported systems
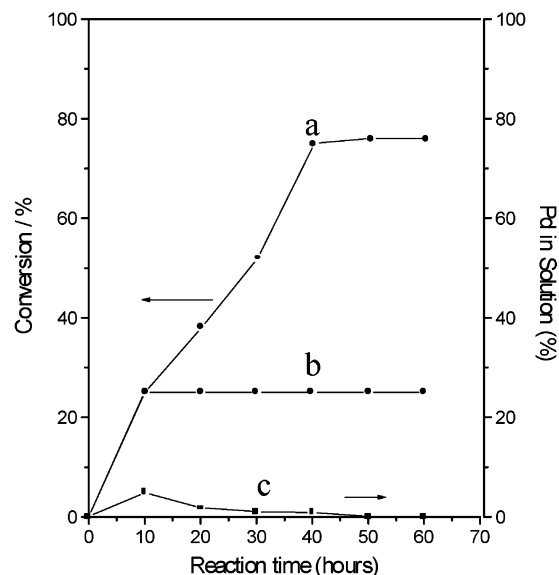

Figure 3. Activity profile for 4-chloroanisole (left-hand side scale) (a) with catalyst and (b) with filtrate and (c) the amount of palladium present in solution (right-hand side scale).

and found that the reactivity is proportional to the leached palladium, which indicates that the heterogeneous palladium is the source of homogeneous palladium species[13g] that actually performed the catalytic homogeneous reactions.

Since iodobenzene undergoes Heck olefination reactions in both heterogeneous and homogeneous phases, it is difficult to pinpoint unambiguously whether the reaction proceeds exclusively on the heterogeneous surface, in the homogeneous phase, or partly on the heterogeneous surface /homogeneous phase. Such an ambiguity could be best resolved with the present example, wherein the LDH−Pd^0 is found to give excellent yields in the Heck olefination of 4-chloroanisole with olefin, while the corresponding homogeneous reaction conducted under the identical conditions by us and others gives poor yields (5−8%).

To address this issue, two parallel experiments were carried out for the Heck olefination of highly resilient 4-chloroanisole with styrene using the LDH−Pd^0 as catalyst (3 mol %) and Bu$_3$N as base in the NAIL. The first experiment was conducted until the completion of the reaction, and the reactivity profile versus time is shown in Figure 3. Analyzing the clear supernatant solutions at different time intervals during the reaction by Atomic Absorption Spectroscopy (AAS), we obtained a leaching profile of the active palladium species from the LDH support as a function of time (Figure 3). Palladium found in the solution at the end of the reaction corresponds to <1% of the total palladium.

The second experiment was terminated after 10 h, and the conversion was found to be 25%. At this juncture, the catalyst was separated from the solution by a simple filtration and the resultant filtrate was tested for palladium by AAS to show that 4.5% of the total palladium leached into the solution. The reaction was continued with the filtrate for an additional 40 h, and the conversion almost remained unchanged. These studies, as summarized in the Figure 3, demonstrate that the palladium bound to LDH during the reaction is only active and the reaction proceeds on the heterogeneous surface. There is no change in the size and morphology of the nanopalladium particles of the used catalyst, as is evident from the TEM.
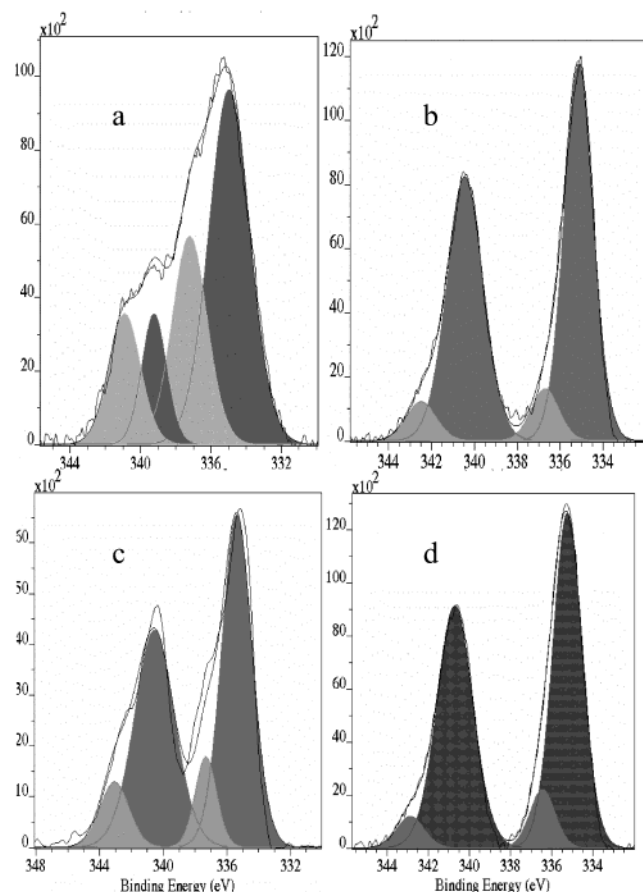
Figure 4. XPS deconvolutions of palladium in used and reacted catalysts (a) LDH−Pd^{0}BU, (b) LDH−Pd^{0}AU, (c) LDH−Pd^{0}BR, and (d) LDH−Pd^0-AR.

Figure 5. XPS survey scan of LDH−Pd^{0}AU along with (a) C 1s of LDH−Cl (carbon impurity), (b) C1s of LDH−Pd^{0}AR, (c) Cl 2p of LDH−Cl, and (d) Cl 2p of LDH−Pd^{0}AU.

The samples of used catalysts in the Heck olefination of 4-chloroanisole (denoted as LDH−Pd^{0}AU) and iodobenzene (LDH−Pd^{0}BU) and the samples obtained by the reaction between LDH−Pd^0 and 4-chloroanisole (denoted as LDH−Pd^0-AR) or iodobenzene (LDH−Pd^{0}BR) were then subjected for the XPS analysis in order to provide further proof of the heterogeneity. The XPS of the used catalyst and the catalyst reacted with the haloarenes only show almost identical patterns for Pd, Cl, and I. However, the carbon XPS of the used catalysts, LDH−Pd^{0}AU and LDH−Pd^{0}BU, show extra lines that can be accounted for by other intermediates, arising out of a subsequent olefin interaction. The XPS of Pd 3d$_{5/2}$ of the LDH−Pd^0 used in the olefination of 4-chloroanisole and iodobenzene with styrene, as well as catalysts reacted with 4-chloroanisole and iodobenzene resolved by a deconvolution process using a curve resolver, show the lines at 337.3 eV for PdCl and 337.1 eV for PdI, respectively (Figure 4).

The increased ratio of Pd^{II}/Pd^0 in the used catalyst (LDH−Pd^{0}BU) in the olefination of iodobenzene with styrene, when compared to that of the olefination of 4-chloroanisole with styrene (Figure 4), is ascribed to the higher reactivity of iodobenzene that resulted in the higher number of surface (presumably phenyl and iodide) species

The XPS survey scan of LDH−Pd^{0}AU and narrow scans of the XPS of the carbon 1s in the LDH−Cl (carbon impurity due to pump oil) and LDH− Pd^{0}AR (inset) and chloride in LDH−Cl and LDH−Pd^{0}AU (inset) are shown in the Figure 5. The XPS spectra of Cl 2p of the used catalyst, LDH−Pd^{0}AU, exhibit
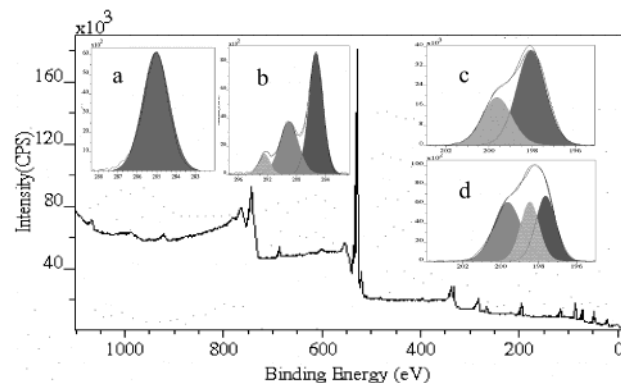
three lines on deconvolution at 197.6, 198.4, and 199.6 eV (Figure 5d) that are assigned to the interlayers LDH−Cl, Pd−Cl, and chloride present as impurities, respectively, in contrast to the two lines present in the LDH−Cl (Figure 5c). The C 1s of the deconvoluted XPS spectrum of the LDH−Pd^{0}AR displays two extra lines at 288.8 and 292.4 eV (Figure 5b) over the LDH−Cl. As the specific assignment is difficult, we then subjected this sample to TGA−MS analysis to detect the evolved gases as a function of temperature. The m/z values are 15, 31, 76, and 107 amu corresponding to Me, OMe, C$_6$H$_4$, and MeOC$_6$H$_4$, respectively (please see Supporting Information, Figures A and B). It is significant to note that the m/z value corresponding to 4-chloroanisole is not detected, which suggests that the mass fragments of the sample LDH−Pd^{0}AR are the pyrolysis products of ArPdCl.

The XPS survey scan of LDH−Pd^{0}BR and narrow scans of I 3d and C 1s are shown in Figure 6. The XPS spectra of I 3d$_{5/2,3/2}$ in LDH−Pd^{0}BR are 619.1 and 630.5 eV, respectively, which are assigned to the Pd−I bond.[23] The curve resolver also indicates the presence of other iodide in minor quantities, which may be due to an iodide exchanged on to the LDH during the reaction process. The XPS spectra of C 1s in LDH−Pd^{0}BR exhibit two lines centered at 285.2 and 288.6 eV, which may be due to a carbon impurity and Pd−C, respectively. As no such data is available in the literature to our knowledge for Pd−C, we then subjected the samples for evolved gas detection, which indeed gives m/z values 77 and 127 amu corresponding to phenyl and iodide species, respectively (please see Supporting Information, Figure C). The m/z value corresponding to iodobenzene is not observed, which indicates that the pyrolysis products are obtained from the PhPdI.

During the olefination of iodobenzene with styrene, palladium is present in minor amounts in solution rather than in the solid catalysts, as observed by us (please see Supporting Information, Figure D) and Arai.[13a] Identification of the intermediate species on the used catalyst (LDH−Pd^{0}BU) as well as the catalyst reacted (LDH−Pd^{0}BR) with iodobenzene suggests that the reaction indeed occurs predominantly at the heterogeneous surface. The reaction proceeding in the homogeneous medium albeit a minor one cannot be ruled out, since the Pd^0 is known to undergo oxidative addition with iodobenzene, even in the

(23) (a) Kim, K. S.; Gossmann, A. F.; Winograd, N. *Anal. Chem.* **1974**, *46*, 197. (b) Moulder, J. F.; Stickle, W. F.; Sobol, P. E.; Bomden, K. D. *Handbook of X-ray photoelectron Spectroscopy*; Perkin-Elmer Corp.: MN, 1992.

Scheme 3. Plausible Mechanism for the LDH−Pd[0] Catalyzed Heck Olefination of Chloroarenes
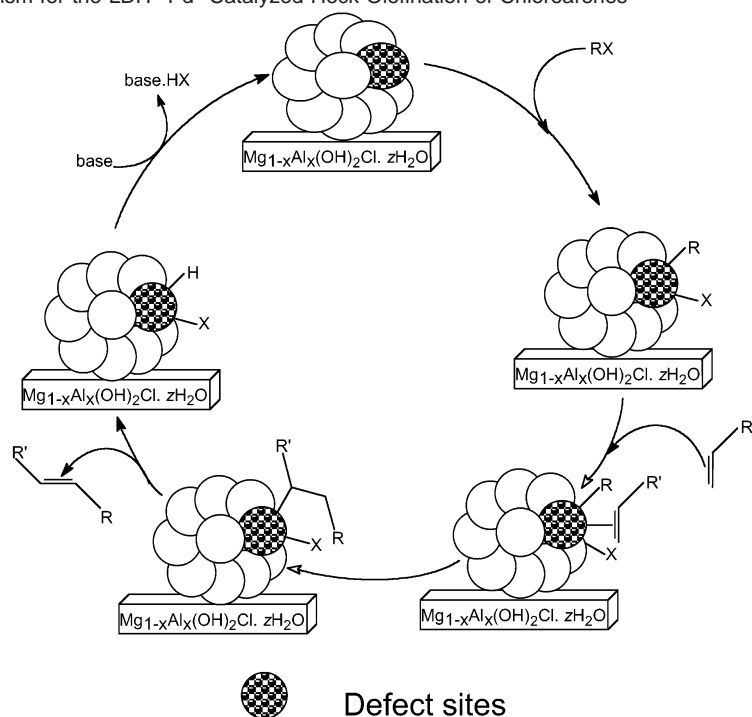
🔘 Defect sites

homogeneous conditions.[15a] All these results further reinforce that the Heck olefination of 4-chloroanisole occurs exclusively and with iodobenzene predominantly on the surface of the nanopalladium particle presumably at defect sites. These are in good agreement with the earlier results.[15d,e]

The plausible mechanism proceeds similarly as that in the homogeneous phase involving the Pd[0]/Pd[II] cycle (Scheme 3). The nanopalladium undergoes oxidative addition with haloarenes to afford ArPdX, as is evident from XPS and TGA-MS studies. The C 1s XPS spectra of the used catalysts show extra lines accounting the other possible intermediates.

Thus, palladium stabilized on the basic support of LDH activates even the deactivated chloroarenes. The basic LDH surface increases the electron density of the Pd center to promote the oxidative addition of chlorobenzene to the Pd[0], which is responsible for higher activity. This is in consonance to the earlier observation that O[2−] of MgO increases electron density on the palladium.[13j, 24]

Buoyed with the impressive results obtained in the Heck olefination reaction, we further examined the LDH−Pd[0] for

Figure 6. XPS survey scan of LDH−Pd[0]BR and deconvolutions (inset) of (a) C 1s of LDH−Cl (carbon impurity), (b) C1s of LDH−Pd[0]BR, and (c) I 3d of LDH−Pd[0]BR.

different cross-coupling reactions of chloroarenes using aryl-boronic acids (Suzuki coupling), terminal alkynes (Sonogashira coupling), and trialkyltin hydrides (Stille-type coupling). Since there is no perceptible increase in the rate of the reaction when NAIL is used in the coupling reactions, as is evident from the results summarized in the Tables 3−5, the reactions were conducted using common solvents in all the coupling reactions.

(b) Suzuki Coupling. The Suzuki coupling of chloroarenes with arylboronic acids in the presence of the LDH−Pd[0] nanoparticle catalyst (1 mol %) using KF as a base in 1,4-dioxane/water (5:1) under stirring at 100 °C for 10 h afforded good yields of corresponding biaryls (Scheme 4).

The nanocatalyst displays a high turnover number for 4-chloroanisole (Table 3, entry 7), an increase by 2.3-fold when compared to the results obtained with the palladacycle under the homogeneous conditions.[7e] The catalyst is reused for five cycles, which shows almost consistent activity and selectivity (Figure 7b) in the coupling reaction involving phenylboronic acid and chlorobenzene (Table 3, entry 1). Although the successful use of palladium heterogeneous catalysts[14a,14b] and palladium nanoparticles stabilized by polymers[15f] is reported for the Suzuki coupling reactions involving bromo- and io-doarenes, there is no such report with the chloroarenes using the heterogeneous palladium catalyst.

Different solvent systems, such as polar and nonpolar solvents, were used for the Suzuki coupling reaction using LDH−Pd[0] catalyst. Low yields were obtained with nonpolar solvents such as toluene and *o*-xylene, while polar solvents such as THF, 1,4-dioxane, and 1,4-dioxane/water (5:1) gave good yields. The latter one shows higher activity when compared to those of other polar solvents.

(c) Sonogashira Coupling. The Sonogashira coupling reaction of chloroarenes with terminal acetylenes using the LDH−
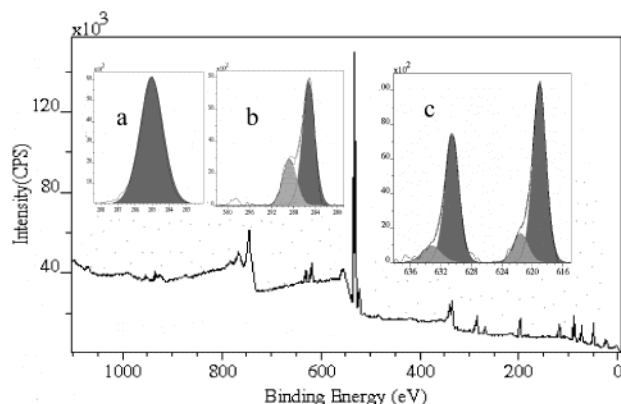
(24) Dossi, C.; Fusi, A.; Recchia, S.; Anghileri, M.; Psaro, R. *J. Chem. Soc., Chem. Commun.* **1994**, 1245.

**Table 3.** Suzuki Coupling Reactions of Chloroarenes with Arylboronic Acids[a]

entry	chloroarene	arylboronic acid	yield (%)
1	Cl-phenyl	phenyl-B(OH)$_2$	93(92)[b]
2	Cl-phenyl	3-NO$_2$-phenyl-B(OH)$_2$	90
3	Cl-phenyl	4-Me-phenyl-B(OH)$_2$	60
4	Cl-phenyl	naphthyl-B(OH)$_2$	80
5	Cl-phenyl	4-F-phenyl-B(OH)$_2$	70
6	4-MeOC-Cl-phenyl	phenyl-B(OH)$_2$	60
7	4-MeO-Cl-phenyl	phenyl-B(OH)$_2$	90
8	4-MeOC-Cl-phenyl	4-Me-phenyl-B(OH)$_2$	88

[a] Chloroarene (1 mmol), arylboronic acid (1.5 mmol), LDH–Pd[0] (1 mol %), and KF (3 mmol) were stirred at 100 °C for 10 h. All the reactions were carried out with 1,4-dioxane/water (5:1, 5 mL) as solvent. [b] Under NAIL conditions, 8 h.
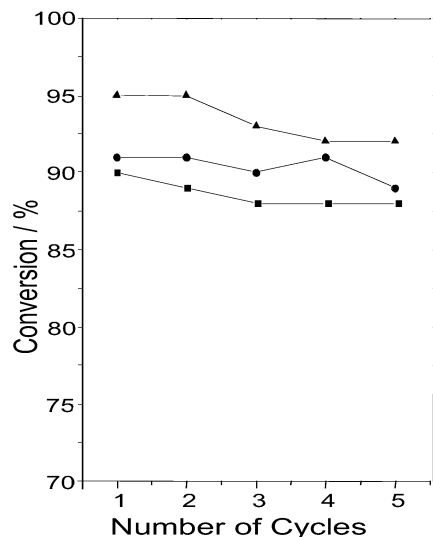
Figure 7. Recycling experiments using LDH–Pd[0] catalyst for (a) Sonogashira coupling, (b) Suzuki coupling, and (c) Stille-type coupling (downward).

Scheme 4 Suzuki Coupling Reactions of Chloroarenes with Arylboronic Acids Using LDH–Pd[0] Catalyst
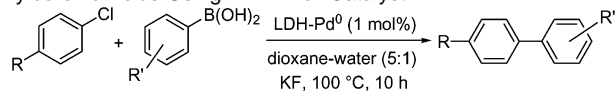

Pd[0] nanoparticle catalyst (1 mol %) and Et$_3$N as a base in THF/water (1:1, 8 mL) under stirring at 80 °C for 30–48 h afforded good yields (Scheme 5) of diphenylacetylenes.

The reaction is quite impressive when extended to deactivated electron-rich chlorides (Table 4, entry 2). Although the heterogeneous-polymer-anchored bis(pyrimidine)-based palladium catalyst induced Sonogashira coupling using chlorobenzene with impressive turnover frequency (TOF = 205 h^{-1}), it was not tried for electron-rich chloroarenes.[131] The LDH–Pd[0] catalyst

Scheme 5. Sonogashira Coupling of Chloroarenes with Phenylacetylene
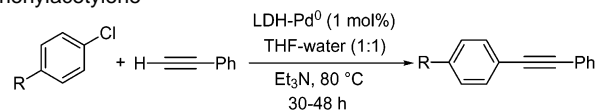
Table 4. Cross-Coupling Reactions between Phenylacetylene and Chloroarenes[a]

entry	chloroarene	alkyne	time (h)	yield (%)
1	Cl-phenyl	H—≡—Ph	30	95
			27	95[b]
2	4-MeO-Cl-phenyl	H—≡—Ph	48	60
3	4-O$_2$N-Cl-phenyl	H—≡—Ph	40	82

[a] Chloroarene (1 mmol), phenylacetylene (1.1 mmol), LDH–Pd[0] (1 mol %), Et$_3$N (1.5 mmol), 80 °C. All reactions were carried out with THF/water (1:1, 8 mL) as the solvent system. [b] Under NAIL conditions.

Scheme 6. Stille-Type Coupling Reactions of Chloroarenes
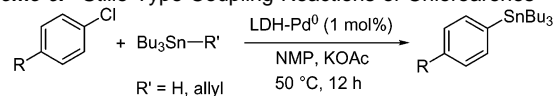
is reused for five cycles and shows consistent activity and selectivity in the coupling reaction of phenylacetylene and chlorobenzene (Table 4, entry 1, Figure 7a).

(d) Stille-Type Coupling. Here, we are reporting, for the first time, couplings of deactivated chloroarenes with trialkyltin reagents[25] with the heterogeneous nanopalladium catalyst. Various chloroarenes were coupled with 2 equiv of tributyltin hydride in the presence of a catalytic amount of the LDH–Pd[0] nanoparticle catalyst (1 mol %) using potassium acetate as a base in NMP solvent under stirring at 50 °C for 16 h to afford the corresponding trialkylarylstannanes selectively (Scheme 6). The use of potassium acetate as a base retards the formation of the biaryl, a byproduct.
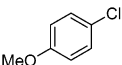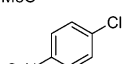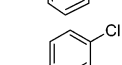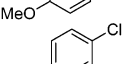
The catalyst was reused for five cycles, which shows almost consistent activity and selectivity in the coupling reaction of chlorobenzene and tributyltin hydride (Table 5, entry 1, Figure 7c).

Conclusions

In summary, the recyclable nanopalladium particles supported on LDH, designed and developed by the simple ion-exchange technique followed by reduction, are used in Heck-, Suzuki-, Sonogashira-, and Stille-type coupling reactions of chloroarenes to afford good to excellent yields of coupling products. The superior activity, as reflected in high turnover frequency achieved using nanopalladium catalyst in the Heck olefination under microwave irradiation coupled with nonaqueous ionic liquids, certainly helps in creating a combinatorial library expeditiously. The oxidative addition of Pd[0] with the resilient electron-rich chloroarenes to facilitate the Heck olefination and other coupling reactions is ascribed to the basic LDH support, as is evident from the heterogeneity studies. The heterogeneity studies also disclose that the reaction occurs at the heterogeneous surface of the nanopalladium particle. The catalyst was quan-

(25) (a) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508. (b) Murata, M.; Watanabe, S.; Masuda, Y. *Synlett* **2000**, 1043.

Table 5. Stannylations of Haloarenes with LDH−Pd⁰ Catalyst[a]

entry	chloroarene	tin reagent	yield (%)
1	chlorobenzene (Cl)	Bu_3Sn-H	90(91)[b]
2	4-chloroanisole (MeO, Cl)	Bu_3Sn-H	80
3	4-chloronitrobenzene (O_2N, Cl)	Bu_3Sn-H	90
4	chlorobenzene (Cl)	Bu_3Sn allyl	80
5	4-chloroanisole (MeO, Cl)	Bu_3Sn allyl	65
6	4-chloronitrobenzene (O_2N, Cl)	Bu_3Sn allyl	70

[a] Chloroarene (1 mmol), trialkyltin reagent (2 mmol), potassium acetate (3 mmol), and LDH−Pd⁰ (2 mol %). All the reactions were carried out with NMP as solvent at 50 °C for 16 h. [b] Under NAIL conditions, 12 h.

titatively recovered from the reaction by simple filtration and reused for a number of runs with consistent activity in all the coupling reactions. The TONs observed here using the LDH−Pd⁰ in the Heck-, Suzuki-, Sonogashira-, and Stille-type coupling reactions of chloroarenes are superior over those of the best homogeneous ligand-free $PdCl_2$ catalyst system as well as heterogeneous and nanopalladium supported systems. However, the TONs are not as impressive as those in homogeneous systems using the palladium basic phosphine complexes for Heck and other coupling reactions of chloroarenes.[5g] Nevertheless, the catalyst reported here can be regarded as an important step toward a simple system with the potential for commercial exploitation of heterogeneous catalysts in the coupling reactions.

Experimental Section

General. UV−vis/Diffuse Reflectance spectra for samples as KBr pellets were recorded on a GBC Cintra 10e UV−Vis spectrometer in the range 200−800 nm with the scan speed 400 nm/min. 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 the solvent. The particle size and external morphology of the samples were observed on a JEOL JEM-100CX transmission electron microscope (TEM). The samples were mounted on a copper grid by ultrasonification. X-ray photoemission spectra were recorded on a KRATOS AXIS 165 with a dual anode (Mg and Al) apparatus using the Mg Kα 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. Spectra were deconvoluted using the Sun Solaris based Vision 2 curve resolver. The location and the full width at half-maximum (fwhm) for a species was first determined using the spectrum of a pure sample. The location and fwhm of the products, which were not obtained as pure species, were adjusted until the best fit was obtained. Symmetric Gaussian shapes were used in all cases. Binding energies for identical samples were, in general, reproducible to within ±0.1 eV. TGA−MS thermograms were recorded on a Mettler-Toledo TGA/SDTA 821e instrument coupled to a Balzers Thermostar GSD 300T in the temperature range 25−1000 °C with a heating rate of 10 °C/min in a nitrogen atmosphere. Atomic absorption spectroscopy (AAS) analysis was carried out using palladium standards (Perkin-Elmer make) on a Perkin-Elmer AAanalyst 300. X-ray powder diffraction (XRD) data were collected on a Siemens/D-5000 diffractometer using Cu Kα radiation ($\lambda = 1.5405$ Å). Specific surface areas are calculated from BET nitrogen isotherms determined at −196 °C (Micromeritics ASAP

2000) on samples degassed at 250 °C for 12 h before the experiment. SEM-EDX (scanning electron microscopy energy−dispersive X-ray analysis) 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-F₂₅₄ plates. Microwave experiments were carried out in a closed Teflon vessel, and samples were irradiated in a Miele Electronic M270 microwave oven at 400 W and 130 °C for 0.5−1 h. The reactor was filled not exceeding one-fourth of the total volume of the tube, thereby allowing headspace for pressure buildup during the microwave treatment. All the reactions in the microwave oven were conducted in the absence of stirring. The tube was allowed to cool before being opened carefully in a fume cupboard. Tetra-*n*-butylammonium bromide, NAIL purchased from CDH, was dried and degassed by exposing the melt to vacuum/nitrogen for at least 2 h prior to use. $MgCl_2·6H_2O$ and $AlCl_3·6H_2O$ were purchased from Aldrich. Arylboronic acids, tin reagents, and phenylacetylene were purchased from Fluka. All other chemicals were procured from commercial sources and used as such without further purification. All the solvents procured from commercial sources were distilled before use.

Preparation of Catalysts. (a) Preparation of Mg−Al−Cl (LDH) Support. The preparation of LDH (Mg−Al−Cl)[18c] and Na₂PdCl₄[26] were based on literature procedures.

(b) Preparation of LDH−PdCl₄. Mg−Al−Cl (1.5 g) was suspended in 150 mL of aqueous Na₂PdCl₄ (0.441 g, 1.5 mmol) solution and stirred at 25 °C for 12 h under a nitrogen atmosphere. The solid catalyst was filtered, washed thoroughly with 500 mL of water, and vacuum-dried to obtain 1.752 g of LDH−PdCl₄ (0.86 mmol of Pd/g).

(c) Preparation of LDH−Pd⁰. LDH−PdCl₄ (1 g) was reduced with hydrazine hydrate (1 g, 20 mmol) in ethanol (10 mL) for 3 h at room temperature, filtered, and washed with ethanol to give an air stable black powder (0.95 mmol of Pd/g).

(d) Preparation of Resin−PdCl₄. Quaternary ammonium resin was prepared as described earlier.[17e] The resin (1 g) was suspended in 100 mL of (0.294 g, 1 mmol) aqueous Na₂PdCl₄ solution and stirred at 25 °C for 12 h under a nitrogen atmosphere. The solid catalyst was filtered, washed thoroughly with water (300 mL), and vacuum-dried to obtain resin−PdCl₄ (0.8 mmol of Pd/g).

(e) Preparation of Resin−Pd⁰. Resin−PdCl₄ (1 g) was reduced with hydrazine hydrate (1 g, 20 mmol) in ethanol (10 mL) for 3 h at room temperature, filtered, and washed with ethanol to give air stable black beads (0.87 mmol of Pd/g).

Experimental Procedure for Heck Olefination of Chloroarenes. In a 100-mL Schlenk flask, the NAIL (3.23 g, 10 mmol) was heated to melt (130 °C) and degassed with nitrogen and vacuum prior to the addition of other reagents. After cooling the NAIL to room temperature, LDH−Pd⁰ (3 mol %) and tri-*n*-butylamine (222 mg, 1.2 mmol) were added. The olefin (1.2 mmol) and chloroarene (1 mmol) were then added, and the reaction was heated to 130 °C and stirred for 10−40 h under a nitrogen atmosphere. After completion of the reaction, the LDH−Pd⁰ catalyst was filtered and washed with water and dichloromethane. After the removal the solvent, the crude material was chromatographed on silica gel or recrystallized from ethanol to afford the corresponding *trans*-olefin.

(*E*)-*n*-Butyl 4-Methoxycinnamate. (Table 1, entry 6). ¹H NMR: δ 0.98 (t, 3H), 1.40−1.46 (m, 2H), 1.62−1.67 (m, 2H), 3.82 (s, 3H), 4.19 (t, 2H), 6.24 (d, 1H), 6.86 (d, 2H), 7.48 (d, 2H), 7.60 (d, 1H).

Experimental Procedure for Heck Olefination of Chloroarenes under Microwaves. An olefin (1.2 mmol), chloroarene (1 mmol), LDH−Pd⁰ (3 mol %), tri-*n*-butylamine (222 mg, 1.2 mmol), and Bu₄NBr (3.23 g, 10 mmol) were taken in a Teflon vessel, enclosed, and irradiated in a Miele Electronic M270 microwave oven at 400 W and 130 °C for 0.5−1 h. After completion of the reaction, the LDH−Pd⁰ catalyst was filtered and washed with water and dichloromethane. After

(26) *Encyclopedia of Reagents for Organic Synthesis;* John Wiley & Sons: Chichester, U.K., 1992; Vol. 4, p 2301.

the removal the solvent, the crude material was chromatographed on silica gel to afford the corresponding *trans*-olefin.

Used and Reacted Catalysts for XPS and TGA−MS Analysis. The catalysts recovered after the completion of the Heck olefination of 4-chloroanisole and iodobenzene are designated as LDH−Pd⁰AU and LDH−Pd⁰BU, respectively. Similarly, the samples obtained by heating LDH−Pd⁰ at 130 °C with 4-chloroanisole in the NAIL for 40 h and at 75 °C with iodobenzene for 3 h as such without the addition of olefin are designated as LDH−Pd⁰AR and LDH−Pd⁰BR, respectively.

Experimental Procedure for Suzuki Coupling. Chloroarene (1 mmol), arylboronic acid (1.5 mmol), potassium fluoride (3 mmol), LDH−Pd⁰ (1 mol %), and 1,4-dioxane/water (5:1, 5 mL) were charged in a round-bottomed flask. Reactions were carried out at 100 °C for 10 h. After completion of the reaction (monitored by TLC), the catalyst was filtered and the reaction mixture was poured into water; the aqueous phase was extracted with ether. After drying, the corresponding product was purified by crystallization from diethyl ether/pentane.

4-Methyl-4′-acetylbiphenyl. (Table 3, entry 8). ^{1}H NMR: δ 2.39 (s, 3H), 2.59 (s, 3H), 7.2 (d, 2H), 7.46 (d, 2H), 7.60 (d, 2H), 7.94 (d, 2H).

Experimental Procedure for Sonogashira Coupling. To a stirred slurry of chloroarene (1 mmol), cuprous iodide (7.6 mg, 0.04 mmol), and LDH−Pd⁰ (1 mol %) in THF (2 mL) and water (4 mL) was added triethylamine (152 mg, 1.5 mmol). A solution of 1.1 mmol of phenylacetylene in THF (2 mL) was then added over 2 h and stirred at 80 °C. After completion of the reaction (monitored by TLC), the solvent was evaporated, and the residue was treated with pentane. The solution was filtered to obtain the catalyst, and evaporation of the solvent gave the coupling product.

Experimental Procedure for Stille-Type Coupling. A round-bottomed flask was charged with LDH−Pd⁰ (1 mol %), potassium acetate (294 mg, 3 mmol), and NMP (4 mL). To this chloroarene (1 mmol) and tributyltin reagent (2 mmol) were added successively, and the mixture was stirred at 50 °C for 16 h. The reaction mixture was diluted with benzene and washed with water, and the evaporation of the solvent gave the coupling product.

Heterogeneity Tests: Experimental Evidence for the Leaching and Redeposition of Palladium. (a) Experiment 1. LDH−Pd⁰ (3 mol %), 4-chloroanisole (142 mg, 1 mmol), styrene (124 mg, 1.2 mmol), tri-*n*-butylamine (222 mg, 1.2 mmol), and NAIL (3.23 g, 10 mmol) were taken in a round-bottomed flask and stirred at 130 °C for 10 h under a nitrogen atmosphere. At this stage (25% conversion), the catalyst was filtered off and the experiment was continued with the filtrate for another 40 h. There was no increase in the product concentration, as is evident from the GC analysis.

(b) Experiment 2. LDH−Pd⁰ (0.2 mol %), iodobenzene (5 mmol), styrene (5 mmol), and triethylamine (5.5 mmol) were taken in a round-bottomed flask and stirred at 75 °C for 3.5 h under a nitrogen atmosphere without any solvent, and the leached palladium in solution was analyzed by AAS at time intervals.

Supporting Information Available: TG−DTA thermograms for LDH−Pd⁰AR and LDH−Pd⁰BR, mass fragments for methyl, methoxy (Figure A), C_6H_4, $MeOC_6H_4$ (Figure B), phenyl, and iodo (Figure C), and an activity profile for the Heck reaction of iodobenzene (Figure D). This material is available free of charge via the Internet at http://pubs.acs.org.

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