A new periodic mesoporous organosilica containing diimine-phloroglucinol, Pd(II)-grafting and its excellent catalytic activity and *trans*-selectivity in C–C coupling reactions[†]

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A new organosilane precursor has been designed *via* Vilsmeier–Haack formylation of phloroglucinol followed by its Schiff base condensation with 3-aminopropyl-triethoxysilane (APTES). A novel organic–inorganic hybrid periodic mesoporous organosilica (PMO) LHMS-3 containing the highly coordinating bis(propyliminomethyl)-phloroglucinol moiety inside the pore wall has been synthesized by using this precursor organosilane molecule. Phenolic-OH and imine-N donor sites present in this PMO material have been utilized to anchor Pd(II) species at the surface of the mesopores. Small angle neutron scattering, XRD, HR TEM, SEM, ¹³C and ²⁹Si solid state MAS NMR, UV-vis and FT IR spectroscopic tools are utilized to characterize the 2D-hexagonal mesophase and the presence of the bis(propyliminomethyl)-phloroglucinol moiety inside the pore wall. This Pd-anchored material Pd-LHMS-3 showed excellent catalytic activity and *trans*-selectivity in Heck C–C bond formation reactions for the synthesis of a series of value-added aromatic and aliphatic olefins.

Introduction

Since the first report of highly ordered mesoporous silica using the supramolecular templating approach,¹ a large variety of precursor molecules have been utilized for the synthesis of novel functionalized mesoporous materials to explore their applications in different frontier areas like sensing,² adsorption,³ catalysis,^{4,5} ion-exchange,⁶ optoelectronics,⁷ and so on. In order to functionalize the surface of mesoporous silica and induce hydrophobicity a large number of organosilanes have been used as precursors along with tetraethyl orthosilicate for the synthesis of organically modified mesoporous materials.^{8,9} Further, on loading of an active metal in the framework of these organically modified mesoporous materials showed much enhanced catalytic activity vis-à-vis pure mesoporous metallosilicates.¹⁰⁻¹² Thus designing active metal anchored mesoporous material having high surface area has huge potential to be exploited in catalytic reactions. In this context another versatile strategy has been developed for the synthesis of periodic mesoporous silicas (PMOs),¹³ where an organosilane compound [(R'O)₃Si-R- $Si(OR')_3$, $R = CH_2CH_2$, C_6H_4 , etc., $R' = CH_3$, C_2H_5 etc.] having two trialkoxysilyl groups connected by an organic bridge alone can be used as the precursor molecule for the synthesis of mesoporous materials.¹³⁻¹⁷ These PMOs have attracted widespread attention in recent times because of huge possibilities to tune the nature of organic functional group in the precursor organosilane compound and thereby controlling their physicochemical and related surface properties. Different functional organic moieties have been grafted inside the pore wall of these

PMO materials and the resulting materials have found exciting advanced applications in catalysis,¹⁸ biosensors,¹⁹ enantiomeric separation,²⁰ light harvesting,²¹ drug release²² and so on. Recently we have reported strong photoluminescence from a fluorophore grafted organic–inorganic hybrid mesoporous silica, synthesized through Schiff base condensation between an aromatic dialdehyde and aminopropyl-trimethoxysilane (APTES).²³ Due to the presence of highly coordinating phenolic-OH and imine-N donor groups in the framework these fluorophore grafted materials^{23,24} showed excellent metal ion sensing properties.

On the other hand, the Pd-containing catalysts have gained increasing attention over the years in a series of C-C coupling reactions especially in Heck²⁵ and Suzuki²⁶ reactions for the synthesis of value-added organic compounds.²⁷ For homogeneous systems these Pd-containing catalysts suffer the drawback of complicated catalyst recovery and difficult regeneration processes. Very recently Pd-containing heterogeneous catalytic systems have been intensively studied in Heck reactions, where the Pd species is anchored inside the pore walls of mesoporous material.²⁸⁻³⁰ However, the nature of binding of Pd species to the pore-wall, which essentially determines the stability of metalanchoring and thus reducing the possibility to leach the Pd species during the catalytic reaction at elevated temperature still remains a challenge today over Pd-functionalized materials under liquid phase catalytic reaction conditions. The presence of multiple imine-N and phenolic-OH groups in the bis(propyliminomethyl)-phloroglucinol moiety in the mesopore wall could anchor Pd(II) species more strongly in the mesopore surface and thus minimizing the possibility to leach-out the Pd species during the reaction. Herein, we first report a new organic-inorganic hybrid periodic mesoporous organosilica (LHMS-3) containing a highly coordinating diimine-phloroglucinol moiety (designed through Vilsmeier-Haack formylation reaction of phloroglucinol followed by its Schiff base condensation with 3-aminopropyl-trimethoxysilane) inside the pore wall, which can

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effectively anchor $Pd(\pi)$ species strongly on its mesopore surface, and thereby show excellent catalytic activity and *trans*-selectivity in the Heck C–C bond formation reaction between aryl halides and alkenes (both aromatic and aliphatic) for the synthesis of value-added organics.

Experimental

Synthesis of diformylphloroglucinol

Diformylphloroglucinol was synthesized through Vilsmeier-Haack formylation³¹ of phloroglucinol (Scheme 1). In a typical synthesis 1.0 g (0.008 mol) phloroglucinol (Merck) was dissolved in 10 ml distilled dioxane (Merck) under rapid stirring and mild heating. In another beaker 1.75 gm DMF (0.024 mol, Merck) was taken and then 3.67 gm phosphorous oxychloride (0.024 mol, Lobie Chemie) was added drop-wise maintaining the temperature of the mixture at about 303 K through mild heating. During this addition a highly viscous and reactive yellow liquid was formed. Then this yellow iminium salt was added very slowly to the phloroglucinol solution under rapid stirring maintaining the temperature at ca. 313–318 K. After complete addition, the reactant mixture was stirred for several hours until a yellow crystalline solid is formed. Then the solid was dissolved in the minimum amount of distilled water and then twice extracted with ethyl acetate. The organic layer was washed with Brine solution and then dried in sodium sulfate for about 30 min. After removing ethyl acetate using a rotary evaporator, an orange vellow solid was recovered. The solid was further heated at 363 K until it was completely solvent free. Then it was re-crystallized from ethylacetate-petroleum ether (1:5) and characterized by solid state ¹H NMR (300 MHz, DMSO-d₆: δ 12.49 (br, 3H, OH), 9.992 (s, 2H, CHO), 5.88 (s, 1H, Ar-H) ppm), ¹³C NMR (75 MHz, DMSO-d₆: $\delta = 94.5$ (CH), 104.2 (C), 169.9 (C), 191.85 (CH) ppm) and FT IR (KBr: $\nu = 2890$, 1641.2, 2599, 2783.4, 1402.9, 1260, 1196.8, 1097 cm⁻¹).

Synthesis of Schiff base bridged organosilane precursor I

3-Aminopropyl triethoxysilane (APTES, Adrich) was used as Si source for its condensation with the aromatic aldehyde moiety of diformylphloroglucinol (Scheme 1). For the synthesis of this Schiff base, a solution of diformylphloroglucinol (1.0 g, 0.0054 mol) in dry ethanol (20 ml) was placed under argon in



Scheme 1 Synthesis of I: Vilsmeier–Haack hydroformylation followed by Schiff base condensation.

a two-neck round-bottom flask equipped with a condenser and an addition funnel. A solution of APTES (2.38 g, 0.0108 mol) in dry ethanol (5 ml) was added drop-wise over 30 min. Within 5 min after initiating the addition, the reaction became mildly exothermic. The reaction mixture was kept at reflux for 2 h after the complete addition of APTES. The mixture was allowed to cool to room temperature and evaporated using a rotary evaporator, leaving behind a very viscous dark red gel, which dried in air to yield a dark red solid. This red solid was characterized by solid state ¹³C (Fig. 1, $\delta = 9.6$ (2C), 18.0 (2C), 23.8 (6C), 52.2 (2C), 58.2 (6C), 99.6 (1C), 105.5 (2C), 157.8 (2C), 167.3 (3C) ppm) and ²⁹Si (Fig. 2: $\delta = -51.2$ ppm) MAS NMR spectroscopy.

Synthesis of LHMS-3

I was used as organosilane source along with tetraethyl-orthosilicate (TEOS, Aldrich) in 1 : 3 molar ratio for the synthesis of LHMS-3. Cetyl pyridinium chloride (CPC, Loba Chemie) was used as a structure-directing agent and tartaric acid (TA, Loba Chemie) was used to adjust the initial pH of the synthesis mixture. In a typical synthesis 3.58 g (0.01 mol) of CPC was dissolved in an aqueous solution of TA (0.6 g in 70 g H₂O) under vigorous stirring. To this 1.2 g Brij-35 ($C_{12}H_{25}$ -($OC_{2}H_{4}$)₂₃-OH, co-surfactant, Loba Chemie) was added. The resulting mixture was stirred for about 30 min to obtain a clear solution. Then the



Fig. 1 ¹³C CP MAS NMR spectrum of the precursor I.



Fig. 2 ²⁹Si MAS NMR spectrum of the precursor I.

viscous gel was poured into the premixed surfactant solution and stirred vigorously for about 2 h. After 2 h stirring, 2M NaOH solution was added drop-wise into the mixture until the pH reached ca. 12.0. The resulting solution was kept under stirring for another 14 h at room temperature and then hydrothermally treated at 353 K for 72 h under static conditions. The red powder was recovered under filtration, washed several times with water and dried under vacuum. Surfactant CPC was removed from the as-synthesized solid by two repeating ethanol-HCl extraction at room temperature and this sample is designated as LHMS-3. For Pd-loading 1 g of LHMS-3 was suspended in acetic acid solution (15 ml) of palladium(II) acetate (0.75 g) and the suspension was refluxed for 24 h at 393 K, the dark red mesoporous material slowly changed color to deep brown and no further change in color was observed on further reflux. The resulting mesoporous material was filtered and washed thoroughly with tetrahydrofuran and methanol and dried under vacuum to obtain Pd-LHMS-3.

For a typical catalytic reaction under nitrogen, an oven-dried two-necked round-bottom flask containing a stirring bar was charged with an organic halide (1.00 mmol), olefin (1.00 mmol), Pd-LHMS-3 catalyst (0.05 g) and triethanolamine (5.0 ml). The mixture was refluxed at 373 K for *ca*. 12–14 h under vigorous stirring. Then the mixture was allowed to cool to room temperature and filtered immediately to separate the catalyst from the residual mixture. The filtrate was diluted by addition of diethyl ether (15 ml) and then it was extracted using ethyl acetate. The combined organic layers were washed with water and brine and then dried with MgSO₄ and concentrated under reduced pressure to obtain either a solid residue or a viscous liquid. The product was finally purified through re-crystalization in an ethylacetate– hexane mixture to obtain the yield.

Instrumentation

¹H and ¹³C NMR experiments (liquid state) were carried out on a Bruker DPX-300 NMR spectrometer. Mass spectrometric data were acquired using the electron spray ionization (ESI) technique at 25-70 eV in a Micromass Q-tof-Micro Quadruple mass spectrophotometer. Carbon, hydrogen and nitrogen contents were analyzed using a Perkin Elmer 2400 Series II CHN analyzer. X-Ray diffraction patterns of the powder samples were obtained with a Bruker AXS D8 Advanced SWAX diffractometer using Cu K α ($\lambda = 0.15406$ nm) radiation. Using small-angle neutron scattering (SANS), we measured the scattering intensity I(Q) as a function of wave vector transfer $Q = 4\pi \times \sin\theta/\lambda$, where λ is the wavelength of the incident neutrons and 2θ is the scattering angle). The measurements were performed on the SANS instrument at the Guide Tube Laboratory, Dhruva reactor, BARC, India. This diffractometer uses a polycrystalline BeO filter as a monochromator and the mean wavelength of the incident neutron beam is 5.2 Å with a resolution $(\Delta \lambda / \lambda)$ of about 15%. The angular distribution of the scattered neutron was recorded using a linear 1 m long He3 position sensitive detector. The data were recorded in the accessible Q range of 0.017– 0.35 Å⁻¹. The measured SANS data were corrected for the background and the empty cell contributions.

High resolution transmission electron microscopy images are recorded on a JEOL 2010 TEM operated at 200 kV. Nitrogen

adsorption/desorption isotherms are obtained using a Bel Japan Inc. Belsorp-HP at 77 K. Prior to gas adsorption, samples were degassed for 4 h at 393 K under high vacuum conditions. ¹³C and ²⁹Si solid state MAS NMR measurements were performed on a Bruker Avance 500 MHz NMR spectrometer using a 4 mm MAS probe under static conditions. The 90° pulse lengths used for ¹³C in the experiments were typically 3.0 µs and a recycle time of 5 s. The chemical shifts for ²⁹Si spectra are referenced to TMS at 0 ppm. Thermogravimetry (TG) and differential thermal analyses (DTA) of the samples were carried out using a TGA Instruments thermal analyzer TA-SDT Q-600. Atomic absorption spectroscopic (AAS) measurements were carried-out by using a Shimadzu AA-6300 AAS spectrometer fitted with a double beam monochromator. UV-visible diffuse reflectance spectra were recorded on a Shimadzu UV 2401PC with an integrating sphere attachment. BaSO₄ was used as background standard. FT IR spectra of these samples were recorded using a Nicolet MAGNA-FT IR 750 Spectrometer Series II.

Results and discussion

Nanostructure

Fig. 3 shows the SANS data of the template-free LHMS-3 sample. The scattering intensity clearly depicts a Bragg peak at Q = 0.151 Å⁻¹ corresponding to the ordered mesoporous structure in the sample. The Bragg peak occurs at $Q = 2\pi/d$, where d is the repeating distance between the pores. From this figure we obtain value of d = 4.16 nm, which agrees very well with small angle powder XRD data ($d_{100} = 4.1$ nm, Fig. 4b). The powder X-ray diffraction patterns for as-synthesized and templateextracted LHMS-3 samples are shown in Fig. 4. The materials are highly ordered, showing three strong diffractions for the 100, 110, 200 planes corresponding to 2D-hexagonal mesophase.¹ A representative TEM image of LHMS-3 is shown in Fig. 5. In this image low electron density spots (pores) can be seen throughout the specimen and these are arranged in a honey-comb like hexagonal array.^{1,13,23} A closer look into this image suggested the dimension of the pores to be ca. 2.8 nm. This was further confirmed from the FFT pattern shown in the inset of Fig. 5.



Fig. 3 Small angle neutron scattering pattern of LHMS-3.



Fig. 4 Small angle XRD patterns of as-synthesized (a) and templateextracted (b) LHMS-3 samples.



Fig. 5 Transmission electron micrograph of LHMS-3. Fast Fourier Transform (FFT) pattern is shown in the inset.

Bright diffraction spots and their hexagonal arrangements are quite clear.

Mesoporosity and pore dimension

The N₂ sorption isotherms of template-free LHMS-3 are shown in Fig. 6. These isotherms are classified as type IV, characteristic of the mesoporous materials.¹ The sharp increase in N₂ uptake for adsorption is observed at $P/P_0 = 0.28-0.36$, clearly indicating that the mesopores are uniform in size. Pore size distribution of these samples estimated by employing the BJH method is shown in the inset of Fig. 6, suggesting uniform pores with dimensions of *ca.* 2.78 nm in this material. Unit cell for the 2D-hexagonal structure of LHMS-3: a = 4.73 nm and wall thickness $t = (2d_{100}/$ $\sqrt{3}$ – pore diameter) 1.95 nm, agrees very well with HR TEM results. The BET surface area and pore volume of LHMS-3 were $478 \text{ m}^2 \text{ g}^{-1}$ and 0.37 cc g⁻¹, respectively. Pores of dimension of *ca.* 2.8 nm are good for loading Pd(II) on the surface and carrying out the Heck C–C coupling reaction of the bulky organic reactants.



Fig. 6 N_2 adsorption/desorption isotherms of LHMS-3 77 K. Adsorption points are marked by filled circles and desorption points by empty circles. Pore size distribution is shown in the inset.

Solid state NMR and chemical environment

¹³C and ²⁹Si MAS NMR experiments often provide useful information regarding the chemical environment around the C and Si nuclei and the presence of organic functional groups in the hybrid frameworks. In Fig. 7 a ¹³C CP MAS NMR spectrum for template-extracted LHMS-3 is shown. The spectrum exhibits strong signals at 9.6, 13.9, 22.8, 52.2, 99.6, 104.8, 158.2 and 160 ppm, which resembles different carbon atoms of I as shown in Fig. 1. Respective peaks of I species are marked in the inset. This result indicates that the diimine fragment (I) is covalently grafted inside the pore walls of LHMS-3. Further, very small signals at 173.5 and 189 ppm suggested the presence of some unreacted aldehyde species in LHMS-3 material also. ²⁹Si MAS NMR spectra of LHMS-3 sample (Fig. 8) shows downfield chemical shifts at -57.3 and -51.9 ppm, which could be



Fig. 7 ¹³C CP MAS NMR spectrum of LHMS-3.



attributed to the T² ((OH)₂(OSi)Si–R–Si(OSi)₂(OH)) and T¹ ((OH)₂(OSi)Si–R–Si(OSi)(OH)₂) species, respectively^{13,23} in addition to peaks at -103.8 (Q³) and -95.0 ppm (Q²) further suggesting the presence of species I (Scheme 1) in the framework.

UV-vis absorption

UV-visible spectroscopy was used to characterize the optical absorbance of the bis(propyliminomethyl)-phloroglucinol moiety present in the pore walls of the LHMS-3 and Pd-LHMS-3 samples. LHMS-3 (as-synthesized and template-free forms) and Pd(π)-exchanged samples exhibited major UV-visible absorption bands in the range of 200 to 600 nm (Fig. 9). Three strong absorption bands appeared at 255, 350 and 446 nm for the template-free LHMS-3 sample. The Pd-LHMS-3 material exhibits large absorption in the higher wavelength region in

(tiun (arb) 200 300 400 500 600 700 800 Wavelength (nm)

Fig. 9 UV-vis diffuse reflectance spectra of as-synthesized (a) and surfactant-free LHMS-3 (b), and Pd-LHMS-3 (c).



Scheme 2 Binding sites of Pd(II) in Pd-LHMS-3.

addition to the broad absorption maximums due to the bis(propyliminomethyl)-phloroglucinol moiety. This could be attributed to the ligand chelation, which leads to ligand-to-metal charge transfer (LMCT) bands in addition to the $\pi \rightarrow \pi^*$ transitions due to the phenolic and diimine moieties.³² In the presence of Pd(II) the imine-N and phenolic-OH donors form strong coordination and covalent bonds (Scheme 2). This leads to low energy absorption. On grafting of Pd(II) through bonding with the imine-N and phenolic–OH donor sites of the pore walls of LHMS-3 could stabilize *via* six-membered rings as shown in Scheme 2.³³ Hence this spectroscopic result further suggested that the bridged organosilane moiety I is present inside the pore walls of the LHMS-3 framework.

Framework and bonding

Both the functionalized PMO material LHMS-3 and Pd-LHMS-3 exhibit FT IR peaks (Fig. 10) in the region 3650–3300 (v O–H), $3100-2800 \text{ cm}^{-1}$ (ν C–H), ~1620, ~1512 and 1452 cm⁻¹ (skeletal vibrations). Apart from the C-H vibrations at 2930 and 2850 cm⁻¹ N-C vibrations at ca. 800 cm⁻¹ are observed for the template-free LHMS-3 samples. The formation of Schiff base in LHMS-3 has been confirmed by the appearance of a sharp peak at 1621 cm⁻¹ ($\nu > C = N$ -). In the palladium(II) anchored mesoporous material Pd-LHMS-3, the $\nu > C = N$ peak is quite broad, the $\nu > C = N$ - (free) band at 1621 cm⁻¹ has been shifted at 1606 cm⁻¹ for $\nu > C=N-$ (coordinated). Mild shifts in three medium intensity peaks to 1606, 1512 and 1452 cm⁻¹ for the Pd-LHMS-3 sample suggested metalation.²⁶ This spectral evidence suggests the presence of the bis(propyliminomethyl)-phloroglucinol moiety in LHMS-3 and palladium(II) species are strongly anchored to the mesopore surface via covalent bridges.



Fig. 10 FT IR spectra of surfactant-free LHMS-3 (a) and Pd-LHMS-3 (b).

The AAS spectroscopic tool was employed to determine the amount of palladium(II) loading in this mesoporous surface and it was found that Pd-LHMS-3 contains 7.4 wt% Pd, which is sufficient to carry out liquid phase catalytic reactions.

Catalysis

In Table 1 we have summarized our results for Pd-LHMS-3 catalyzed Heck reactions of aryl halides with aromatic (styrene) as well as aliphatic olefins (acrylic acid). The reaction pathway is schematically presented in Scheme 3. As seen from Table 1,



Scheme 3 Heck C–C bond formation reaction catalyzed by Pd-LHMS-3.

Table 1 Heck coupling reactions catalyzed by Pd-LHMS-3

Entry	R	x	Olefin	Time (h)	Yield (%) ^a	Reference (see ESI)
1	Н	Ι	Styrene	10	85	S1
2	4-OCH ₃	Ι	Styrene	12	80	S2
3	4-NO ₂	Ι	Styrene	10	80	S3
4	ΗĨ	Br	Styrene	14	75	S4
5	-CHO	4-Br	Styrene	12	75	S5
6	Н	Ι	Acrylic acid	10	80	S6
7	4-OCH ₃	Ι	Acrylic acid	12	75	S 7
8	$4-NO_2$	Ι	Acrylic acid	10	85	S8
9	Н	Br	Acrylic acid	12	75	S9
10	$4-CH_3$	Ι	Acrylic acid	12	75	S10

 $^{\prime\prime}$ Yields refer to those of purified products characterized by 1H and ^{13}C NMR data.

Pd-LHMS-3 showed excellent catalytic activity (yield 75–85%) for the C–C coupling of aryl halides with a series of styrene and acrylic acid functionalities. After the fourth catalytic cycle, the yield for *trans*-stilbene is *ca*. 81%, suggesting high catalytic efficiency and *trans*-selectivity for Pd-LHMS-3.

Proof of heterogeneity of the catalyst (hot filtration test)

We have chosen the Heck reaction between styrene and iodobenzene to examine whether Pd is being leached out from the catalyst to the solution. The hot filtration test was conducted in a reaction mixture consisting of 1.0 mmol of iodobenzene, 1.0 mmol of styrene, 0.05 g Pd-LHMS-3 catalyst and 5 ml of triethanolamine. The solution was refluxed in a round-bottom flask at 110 °C under inert an atmosphere placed in a temperature controlled oil bath. After 5 h, the reaction mixture was allowed to cool to room temperature and the viscous solution was diluted with water and then filtered. Atomic absorption spectrometric analysis was carried out with the filtrate and no Pd was detected. This result clearly suggests that no Pd is being leached out from the catalyst during the course of this reaction. For another part of the hot reaction mixture for this same experiment (after 5 h reaction) the catalyst was filtered out immediately and the rest of the coupling reaction was continued in the absence of the catalyst for another 5 h. Conversion remained the same (46.2 and 46.7 mol% after and before the hot filtration test, respectively). It is noteworthy that the solution remains completely colorless after the Heck coupling reaction, in the presence of the Pd-catalyst. All of these experimental observations suggest that our novel Pdloaded PMO catalyst is truly heterogeneous in nature for this Heck C-C coupling reaction.

Recycling of the catalyst

The recycling of the catalyst is an important issue in heterogeneous catalysis. Thus we have turned our attention to prove the reusability of our Pd-PMO catalyst. We have recycled the catalyst four times for the reaction between iodobenzene and styrene. The catalyst was recovered and reused by the following steps. After the reaction was completed, the mixture was allowed to cool to room temperature and diluted with water. The catalyst was filtered, washed extensively with water, ethyl acetate, hexane, acetone until GC analysis of the filtrate indicated no detectable amount of reagents or products. Then the catalyst was dried under high vacuum overnight at 120 °C. It was then reused in the next run without changing the reaction conditions. After carrying out the reactions for the fourth catalytic cycles the catalyst showed consistent catalytic activity as shown in Table 2.

Table 2 Catalytic activity in different cycles over Pd-LHMS-3 in thereaction between iodobenzene and styrene^a

Number of reaction cycles	Product yield (%)		
1	85.6		
2	85.0		
3	83.4		
4	82.1		

^{*a*} Reactions were carried out at 110 $^{\circ}$ C and under a N₂ atmosphere in the presence of triethanolamine solvent under rapid stirring.

From this table it is clear that our novel mesoporous Pdcontaining PMO material Pd-LHMS-3 has been successfully utilized in Heck coupling reactions and the catalyst can be easily filtered and reused for four catalytic cycles without any significant decrease in its catalytic activity.

Salient features of our Pd-LHMS-3 catalytic system in Heck C-C coupling reaction are (i) recycling ability of the solvent triethanol amine (TEA), (ii) dual role of TEA: both as base as well as solvent, in addition to this it can stabilize the active metal species due to its significant ligand character, (iii) this C-C coupling can be performed very effectively without the addition of triphenylphosphine,³⁴ which is conventionally used in the Heck coupling reaction and is environmentally toxic. Thus final work-up can be done easily here in an environmentally friendly way. Although Heck reaction between aryl halides and butyl acrylate catalyzed by Pd(II) complexes³⁵⁻³⁷ gives good catalytic activity for activated aryl halides, recycling of the catalyst is a major drawback in such cases. Pd-functionalized silica surfaces,^{38–40} where the Pd(II) moiety is grafted at the surface of the material have the additional advantage of high recycling efficiency in the Heck C-C coupling reaction.

High concentration of phenolic-OH groups due to the presence of the phloroglucinol in the pore wall of Pd-LHMS-3 material may support the anion ligated palladium(0) mechanism for Heck coupling as proposed by Amatore and Jutand.⁴¹ In Scheme 4 we have proposed a catalytic cycle for this C–C bond formation reaction over Pd-LHMS-3. In the first step of this cycle, Pd⁺² is reduced to Pd⁰ by the solvent TEA⁴² at the surface of the mesopores. Pd⁰ is the active species of this reaction, which could be stabilized by the neighboring imine-N donor sites of the PMO and also by the solvent triethanolamine (TEA). The next



Scheme 4 Proposed reaction pathway for the Heck reaction over Pd-LHMS-3.

step is the oxidative addition of an aryl halide to this 14-electron Pd⁰ species to yield Ar-Pd-X species.³⁹ The third step is the syn addition of an alkyl or aryl vinyl group to the Ar-Pd-X species to generate the intermediate adduct. The fourth step has been accomplished by β -H elimination to obtain the desired alkene with high selectivity (E/Z).³⁵ In the final step TEA abstracts a proton from H-Pd-X to regenerate the catalyst for further reaction. Thus the Pd-LHMS-3 heterogeneous catalyst containing the bis(propyliminomethyl)-phloroglucinol moiety inside the pore wall has a strong ability to trap Pd²⁺ ions on the surface of the mesopores through metal legation to generate a highly active heterogeneous catalyst for C-C coupling reaction. The active species (Pd⁰) of the Heck coupling reaction has been stabilized by strongly coordinating with neutral imine-N donor sites at the surface of the mesopores, which circumvents the leaching of Pd⁰ from the catalyst surface. Thus, due to the presence of a large number of accessible donor sites, this material can serve as an excellent scaffold for metal-mediated catalytic reactions.

Conclusions

From our above experimental results we can conclude that a new organic-inorganic hybrid PMO material can be synthesized by designing an organosilane precursor prepared through Vilsmeier-Haack hydroformylation of phloroglucinol followed by its Schiff base condensation with 3-aminopropyl-trimethoxysilane. The highly donating bis(propyliminomethyl)-phloroglucinol moiety in the pore wall of this PMO material is responsible for anchoring Pd(II) ions, and the resulting Pd-LHMS-3 showed excellent catalytic activity and trans-selectivity in the Heck C-C bond formation reaction between aryl halides and alkenes in the synthesis of value-added organics. Thus the ability to functionalize the pore wall of a mesoporous material with a highly coordinating species for a metal ion scavenger together with uniform systems of mesopores and visible absorption could open-up new avenues in designing functionalized PMO materials for fine chemical synthesis via green chemical routes.

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