New aliphatic C-metallated palladacycle in the pores of 3-hydroxypropyl triethoxysilane functionalized MCM-41

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A new aliphatic C-metallated palladacycle has been prepared in the pores of 3-hydroxypropyl triethoxysilane functionalized MCM-41 and has been found to be a superior recyclable catalyst for Heck reaction. The thermal stability of the palladated material was found to be higher than that of the nonpalladated starting material.

KEY WORDS: palladium catalyst; heterogeneous catalyst; MCM-41; palladacycle; Heck reaction.

1. Introduction

After the discovery of MCM-41 by Mobil researchers, there have been vast current researches focused on the synthesis and applications of modified mesoporous MCM-41 [1]. Modification via host–guest interactions with organo silane and anchoring of homogeneous ligands onto the pores making discrete and uniform catalytic sites on the inner walls of the porous system is of current interest [2,3]. Palladium catalyzed carbon–carbon bond formation, Heck reaction, represents one of the most versatile tools in modern synthetic chemistry and has its own potential for industrial applications [4]. Heterogeneous catalytic systems, which include polymer/dentrimer, supported palladium catalysts [5,6], palladium on carbon [7,8], palladium-supported metal oxides [9], clays [10], molecular sieves [11,12] and metal complexes of Ni, Co, Cu, Mn [13], have been studied well. Palladacycle catalysts in which ligand coordinates to the metal center through both a donor atom and metallated carbon have shown considerable promise [14–16]. Palladium grafted mesoporous MCM-41 material prepared by vapor grafting has been reported for Heck catalysis [17]. Reetz *et al.* have prepared nanostructured Pd clusters either electrochemically using sacrificial Pd anode or by thermolysis of Pd $(OAc)_2$, stabilized in propylene carbonate even at 140–155 °C and studied for Heck reactions [18]. Li *et al.* have reported the use of palladium on porous glass for catalytic coupling reactions [19]. Cammidge *et al.* have prepared heterogeneous Pd catalyst assemblies by the molecular imprinting method and proved them to be recyclable catalysts [20]. Recently, silica-supported imine-based palladacycle catalysts have been studied as an excellent mechanistic probe in the Suzuki reaction [21]. Kosslick *et al.* have studied the anchoring of alkylsilylsulfonic acid to Al-MCM-41 to stabilize the catalytic active palladium complex formed during the course of reaction [22]. Here we report the synthesis and characterization of a new, active and recyclable aliphatic C-metallated palladacycle in the pores of 3-hydroxypropyl triethoxysilane functionalized MCM-41 that exhibits excellent activity toward nonactivated haloarene substrate in the Heck reaction.

2. Experimental

Tetraethyl orthosilicate (TEOS, Aldrich, USA), 3-chloropropyl triethoxysilane (3-ClPTS, Aldrich, USA), cetyltrimethylammonium bromide (CTMAB, Loba Chemie, India), tetramethylammonium hydroxide (TMAOH 25% solution in water, Aldrich, USA), palladium chloride, lithium chloride, methanol and sodium acetate (Loba Chemie, India) were used as the reagents for the synthesis of catalysts. Typically, the molar composition of the synthesis mixture was as follows:

$$1\,SiO_2 : 0 \cdot 24\ CTMAB : 0 \cdot 3\ TMAOH : 120\ H_2O$$

TEOS (tetraethyl orthosilicate) and 3-ClPTS (3-chloropropyl triethoxysilane) in methanol were taken in the molar ratio of 0.8 : 0.2, respectively. The catalyst was prepared as outlined in scheme 1. The Cl-MCM-41 (scheme 1(a)) was prepared by the modified synthesis procedure [23]. The synthesis mixture was stirred for 3 h at room temperature and refluxed at 373 K for 48 h. The final product (Cl-MCM-41) was filtered and dried at 373 K overnight. The template was extracted by refluxing with acidified methanol (100 ml MeOH + 5 ml conc. HCl per gram of solid). The Cl-MCM-41 was treated

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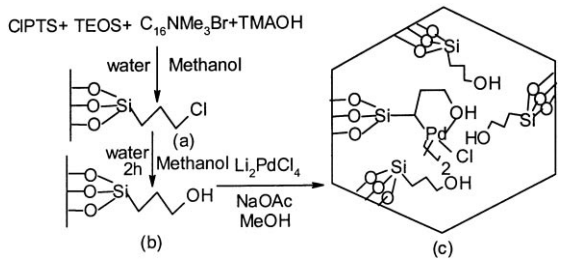
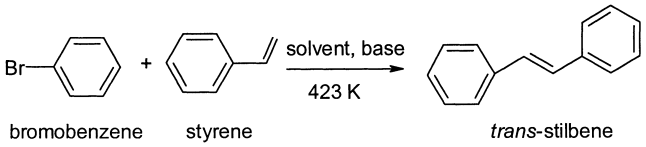


Scheme 1.



Scheme 2.

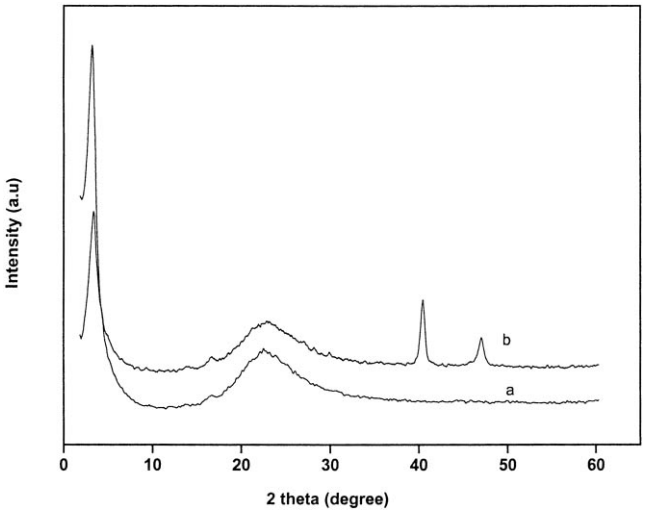


Figure 1. X-ray diffractograms of OH-MCM-41 and Pd-OMS; a: OH-MCM-41 and b: Pd-OMS.

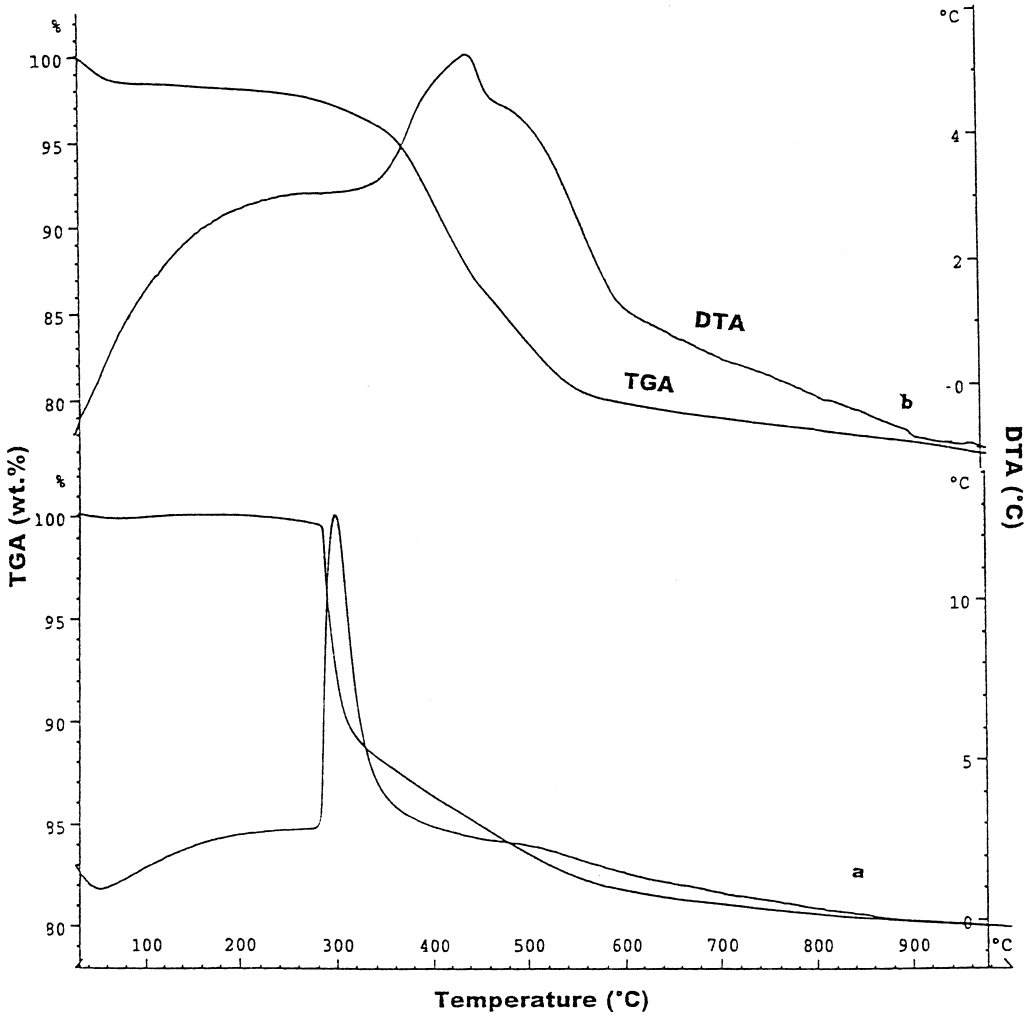


Figure 2. TGA-DTA of OH-MCM-41 and Pd-OMS; a: OH-MCM-41 and b: Pd-OMS.

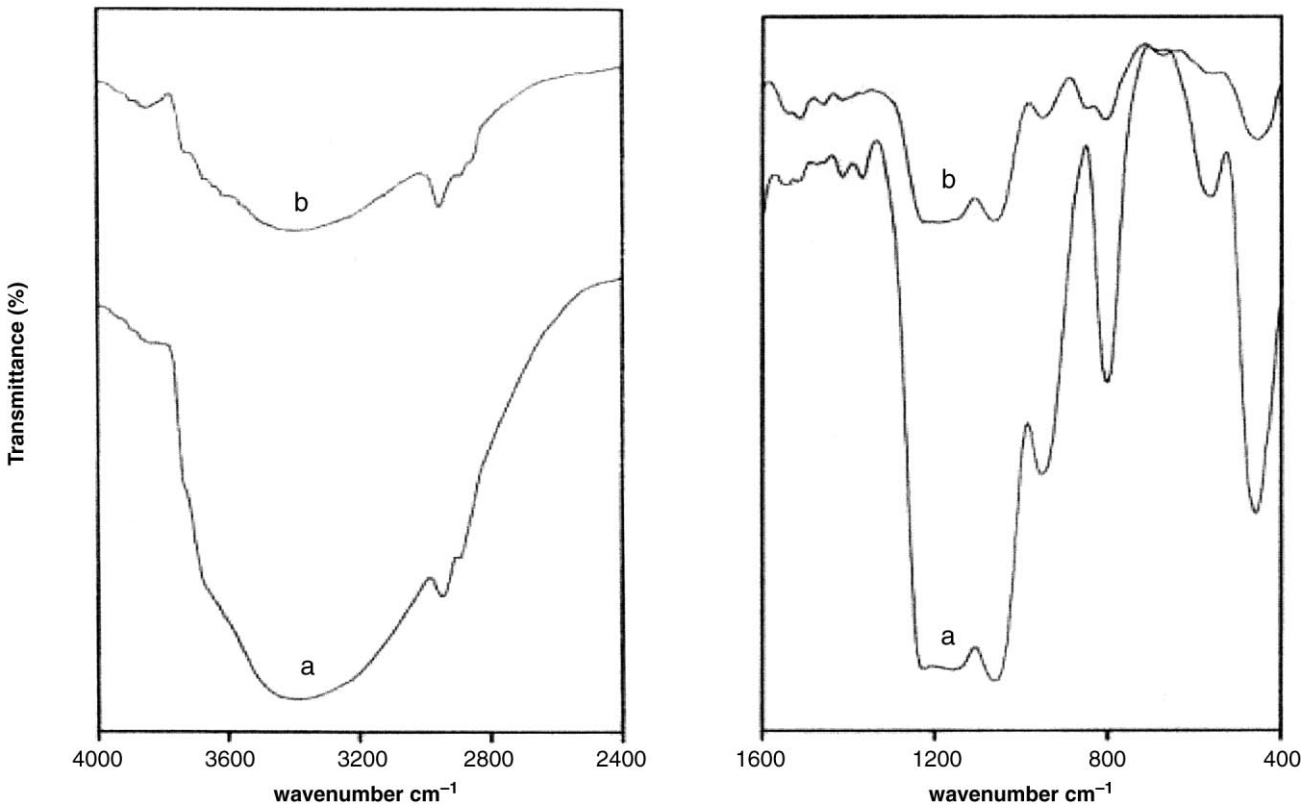


Figure 3. FTIR spectrum of OH-MCM-41 and Pd-OMS; a: OH-MCM-41 and b: Pd-OMS.

with aqueous methanol at reflux condition for 2 h to convert all the –Cl groups into OH groups (scheme 1(b)).

Palladation was carried out over OH-MCM-41 with the weakest palladation reagent, Li_2PdCl_4 and base NaOAc, in methanol under reflux conditions for two days (scheme 1(c)). After palladation, the gray colored material, which is denoted here as Pd-OMS, was washed thoroughly with water and methanol to remove all the unreacted palladium salt and the inorganic base. The catalytic properties of the palladated catalyst (Pd-OMS) were tested in the Heck reaction of nonactivated haloaromatic, namely, bromobenzene, with styrene (scheme 2).

3. Results and discussions

The catalyst, Pd-OMS, retains its hexagonally packed porous structure as shown in X-ray diffraction (Rigaku Miniflex diffractometer with Cu K_α radiation, $\lambda = 1.5406$ Å) pattern (figure 1). Although the diffraction pattern of Pd-OMS and OH-MCM-41 are almost identical, the d-value of Pd-OMS was decreased owing to radiation diffusion caused by the metallated palladium inside the pore. The XRD pattern of palladium metal has major diffraction peaks at $2\theta = 40.0°(111)$ and 46.5°(200), which are found in the case of Pd-OMS confirming the presence of Pd.

ICP analysis of Pd-OMS sample shows palladium metal content on the catalyst is 1.68 wt%. The BET (NOVA 1200 (Quanta chrome) at 77 K) surface area of the sample Pd-OMS is 887 $m^2\,g^{-1}$, while the corresponding starting material has 598 $m^2\,g^{-1}$. The increase in surface area is attributed to the metal content and the cyclization of the propyl group inside the pores of MCM-41. The BJH (Braunauer–Joyner–Halenda) pore size distribution of Pd-OMS illustrates a narrow peak centered at 28.8 Å for the pore diameter, which is, as expected, slightly higher than that of OH-MCM-41 starting material (28.4 Å), and the pore volume increased from 0.43 to 0.63 cc g^{-1} owing to the palladation and cyclization of the propyl group inside the pores of MCM-41.

The TGA–DTA analysis (Mettler Toledo 851^e) of the sample confirms that Pd-OMS sample has higher thermal stability than the OH-MCM-41 (figure 2). The OH-MCM-41 shows a strong exothermic peak at 300 °C and a weak exothermic peak at 500 °C that corresponds to the loosely bonded propyl groups, whereas the palladated material Pd-OMS shows two exothermic peaks at 440 and 520 °C, clearly indicating that the propyl groups are in a different environment compared to that of the starting material. The Pd-OMS sample has a very slight weight loss below 400 °C, which indicates that the propyl group is in cyclic form, and requires higher energy to break and also shows the hydrophobic nature of the material as no physisorbed water is observed.

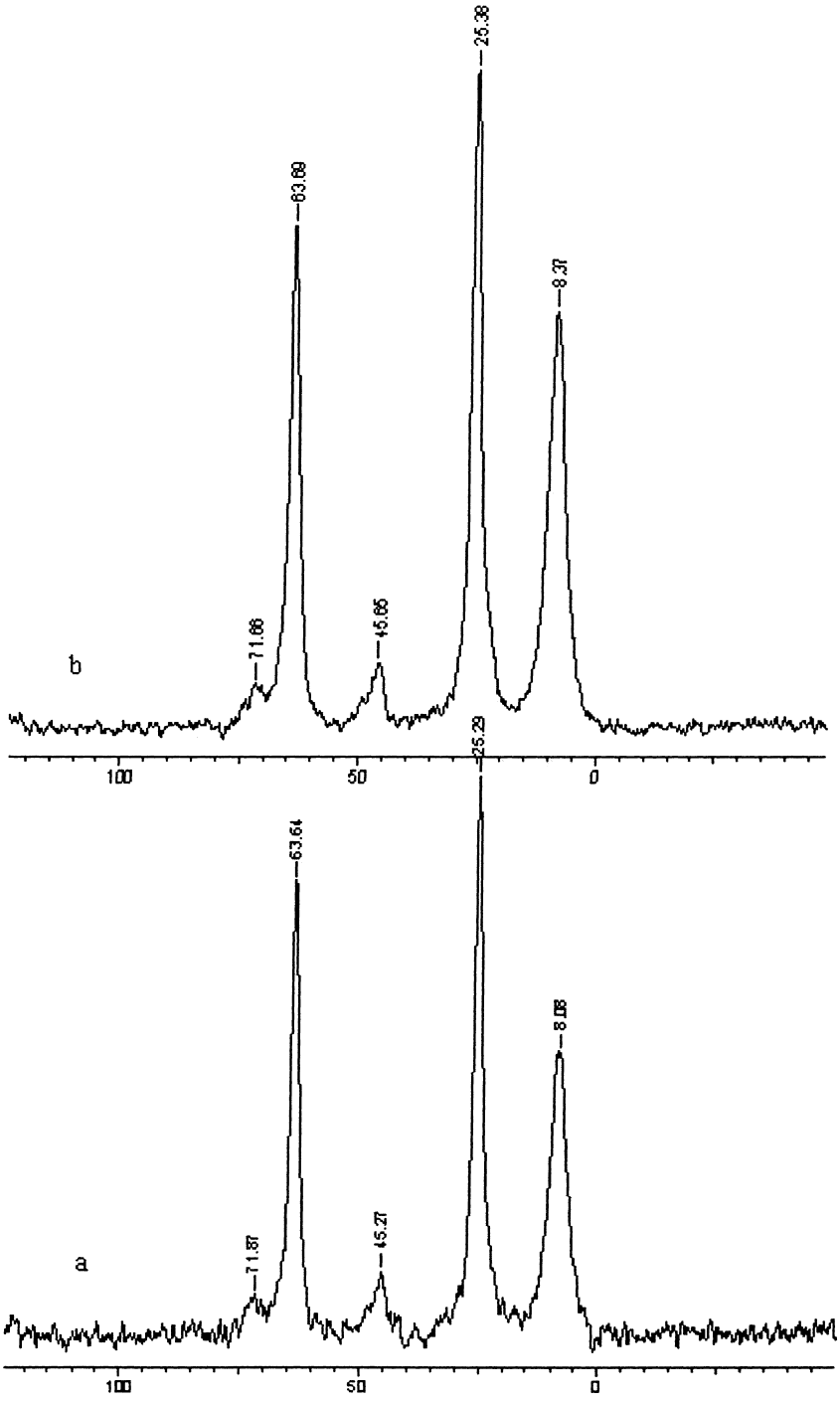


Figure 4. ^{13}C-CP MAS NMR spectra of OH-MCM-41 and Pd-OMS; a: OH-MCM-41 and b: Pd-OMS.

Figure 3 shows the FTIR spectroscopy of the starting material OH-MCM-41 and Pd-OMS. OH-MCM-41 containing the propyl alcohol group has a strong band in the region between 1300 and 800 cm^{-1}, which are usually designated as the C–O stretching band and intense O–H stretching adsorption in the region of 3600 to 2500 cm^{-1}. The two bands at 1368 and 1416 cm^{-1} in OH-MCM-41 due to the in-plane bending of the O–H couples with C–H wagging vibrations were seen to be very weak in Pd-OMS. After the palladation, it was found that the intensity of the O–H stretching vibration decreased. The C–H stretching bands also shifted from 2887 2941 cm^{-1} to 2894 2951 cm^{-1}, respectively, and one more extra band at 2851 was also seen in Pd-OMS. These data provide the direct evidence of the cyclopalladation of the propyl alcohol group, which is anchored on the walls of MCM-41 in the presence of palladation reagents.

In order to confirm the cyclic palladation with aliphatic carbon and oxygen of OH group,

125.757 MHz solid state ^{13}C CP/MAS spectra of OH-MCM-41 and Pd-OMS have been recorded on a Bruker DRX-500 NMR spectrometer spun at 10 and 8 KHz, respectively, and are shown in figure 4. The three main peaks of OH-MCM-41 observed at (δ) 8.08, 25.2 and 63.64 ppm have been shifted to 8.37, 25.38 and 63.69 ppm, respectively, in Pd-OMS. The shift of the methylene carbon next to the silyl silicon is sufficiently higher, 0.29 ppm, compared to that of the middle carbon and carbon atom neighbored to the alcohol group, 0.09, and 0.05, respectively, in Pd-OMS. The shift of the signal of methylene carbon next to silyl silicon to a higher value confirms that the carbon exhibited a different environment after palladation while the other two carbons did not show much difference.

Pd-OMS catalyzes the Heck reaction, the C–C coupling reaction of aryl halides (scheme 2). The catalytic activity of the material was investigated using nonactivated aryl halide, bromobenzene and styrene as the vinylic substrate (table 1). The conversion and TON (turn over number, *i.e.*, moles of bromobenzene converted per mole of Pd) for the *trans*-stilbene, with respect to reaction time, amount of catalyst and reaction temperature, increases and shows that Pd-OMS catalyst has an excellent activity (table 1). The catalyst was recycled three times. A marginal decrease in activity in case of the first recycle was observed. Further, the second recycle gave lower activity than the first recycle but similar conversion level and product yield were obtained with the increase in reaction time. This can be explained by the fact that organic residue (inside the pores) blocks the active sites and hence the active sites may not be available for the reaction.

Table 1
Heck alkenylation of bromobenzene with styrene over Pd-OMS catalyst[a]

Amount of catalyst (Pd, mol %)	T (°C)	Time (h)	Conversion (wt%)[b]	Sel. to *trans*-stilbene (%)	TON[c]
0.125	160	10	26.6	100	212
0.1[d]	170	48	39.0	99	200
0.188	160	5	68.0	100	360
0.24	160	5	90.3	100	376
0.24[*]	150	5	70.0	100	291
0.24[**]	150	5	63.8	100	265
0.24[***]	150	5	19.7	100	82
0.24[***]	150	15	66.5	100	276
0.24	140	10	21.0	100	87

[a]All reactions are carried out in air. 1.2 equivalent of base K_2CO_3 with respect to bromobenzene; *N*-methyl 2-pyrrolidone (NMP) as solvent.
[b]Conversion of bromobenzene is determined by gas chromatography.
[c]Ton = mol of bromobenzene converted/mol Pd.
[d] From reference 6.
[*]Fresh; [**]first recycle; [***]second recycle.

4. Conclusion

In summary, the new aliphatic C-metallated Pd-OMS catalyst is prepared with the weakest palladation reagents, Li_2PdCl_4, and has been used in carbon–carbon coupling reactions. Remarkable activity, appreciable recyclability and exceptional thermal stability of the desired material provide a place for a new generation of heterogeneous catalysts for Heck catalysis.

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