APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2007; **21**: 670–675

(www.interscience.wiley.com) DOI:10.1002/aoc.1244

Palladium chloride anchored on organic functionalized MCM-41 as a catalyst for the Heck reaction

Guo-zhi Fan[1]*, Si-qing Cheng[1], Ming-fang Zhu[2] and Xin-lei Gao[1]

[1]Department of Chemical and Environmental Engineering, Wuhan Polytechnic University, 430023 Wuhan, People's Republic of China
[2]College of Pharmacy, Guangdong Pharmaceutical University, 510006 Guangzhou, People's Republic of China

Received 24 January 2007; Revised 8 February 2007; Accepted 10 March 2007

Palladium chloride was grafted to amino-functionalized MCM-41 to prepare heterogeneous catalysts. XRD, N_2 adsorption–desorption isotherms, IR, ^{13}C and ^{29}Si cross-polarization magic-angle spinning NMR spectroscopy and XPS techniques were employed to characterize the catalytic materials. The heterogeneous palladium catalyst exhibited excellent catalytic activity for the Heck vinylation of iodobenzene with methyl acrylate, giving 92% yield of methyl cinnamate in the presence of *N*-methylpyrrolidone (NMP) and triethylamine (Et_3N). The stability of the heterogeneous catalyst was also studied in detail. The catalytic tests showed that the palladium leaching correlated to solvent, base and palladium loading. The heterogeneous catalyst exhibited excellent stability towards loss of activity and palladium leaching was not observed during six recycles in the presence of toluene and Na_2CO_3. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: MCM-41; Heck reaction; palladium complex; functionalized; heterogeneous catalyst

INTRODUCTION

The Heck reaction has received growing interest for carbon–carbon bond formation and widespread applications in the organic synthesis of various alkenes.[1–5] Palladium species have largely been used as catalysts for C–C bond forming reactions in allylic substitutions and Heck coupling of aryl halides with olefins.[6–10] Therefore, the recovery and reuse of the noble metal catalyst is highly important from an economic point of view. Accordingly, the search for recoverable supported catalysts has received much attention in recent years.[11–19]

Palladium catalysts supported on polymer,[18] activated carbon,[20] metal oxides[21] and zeolites[22] have been developed to overcome typical problems such as separation and recycling in homogeneous catalysis. However, traditional heterogeneous catalysts are rather limited in the nature of their active sites, and thus these systems do not achieve the excellent activities observed with homogeneous catalysts.[23] Since much is known about how organic moieties serve as catalysts in homogeneous reactions, the immobilization of these moieties onto solids to create organic–inorganic hybrid catalysts where the organic functionality is covalently attached to porous inorganic solids can be accomplished with some aspects of design. The goal is to utilize the organic moieties as the active sites and the solid to provide avenues for recovery and possibly recyclability of the organic active sites.[24,25] Periodic mesoporous silica materials with organic groups bridged in the framework have been considered as catalyst supports. The grafting of organic functional groups onto ordered, mesoporous materials has been accomplished, and catalysts prepared from these hybrid solids have been applied in many reactions such as oxidation and C–C coupling reactions.[26–35]

In this paper, 2-acetylpyridine was reacted first with γ-aminopropyltriethoxysilane to produce (1-methyl-2-pyridyl-methyl)[(triethoxylsilyl)propyl]amine **1**. Then $PdCl_2$ was anchored onto hybrid periodic mesoporous organosilica, which was prepared from MCM-41 modified by containing nitrogen ligand **1**. Different methods of characterization, including powder XRD, N_2 adsorption-desorption, IR, ^{13}C and ^{29}Si solid-state CP-MAS NMR spectroscopy were applied to obtain information about structural features. In addition, the catalytic performance of the resulting anchored palladium catalysts for the Heck vinylation of iodobenzene with methyl acrylate was also studied.

---

*Correspondence to: Guo-zhi Fan, Department of Chemical and Environmental Engineering, Wuhan Polytechnic University, 430023 Wuhan, People's Republic of China.
E-mail: fgzcch@163.com

EXPERIMENTAL

Materials

Iodobenzene and 2-acetylpyridine were sourced from Aldrich and used as received. γ-Aminopropyltriethoxysilane was provided by Wuhan University with a purity greater than 98%. Triethylamine (Et_3N), *N*-methylpyrrolidone (NMP), dimethylformamide (DMF), dioxane, acetonitrile, toluene and benzene were distilled prior to use. Other reagents were obtained from Shanghai Reagents Company (China) with analytical grade and used directly without further purification.

Measurements

Powder X-ray (XRD) measurements were performed on a χ 'Pert PRO diffractometer with Cu K_α radiation at 40 kV and 40 mA in the range of $2\theta = 0{-}10°$. The scanning rate was 2 deg/min.

Nitrogen adsorption–desorption isotherms were measured at the liquid nitrogen temperature, using a Coulter Omnisorp 100 CX analyzer. Samples were degassed at 100 °C for 3 h before measurement. Specific surface areas were calculated using the BET model. The pore volumes were estimated at a relative pressure (P/P_0) of 0.98, assuming full surface saturation with nitrogen. The pore size distributions were evaluated from the desorption branches of the nitrogen isotherms using the BJH model.

Infrared spectroscopy (IR) was carried out on an Equinox 55 spectrometer in the range of 4000–500 cm^{-1}. The solid samples were ground with dried KBr powder, and compressed into a disk prior to analysis.

Solid-state ^{13}C (100.6 MHz) and ^{29}Si (79.5 MHz) cross-polarization magic-angle spinning nuclear resonance spectroscopy (CP-MAS NMR) were obtained on a Bruker Avance 400 MHz spectrometer. The number of scans was 1000, and the spin rate was 8 kHz. Tetraethoxysilane (TEOS) was used as reference.

X-ray photoelectron spectroscopy (XPS) was recorded on a Kratos XSAM800 spectrometer with Mg Kα radiation (1253.6 eV) operated at 12 kV and 10 mA without a monochromator. The pressure inside the analytical chamber was 2×10^{-7} Pa.

The Pd loading and leaching in the reaction solution were determined by atom absorption spectroscopy (AAS) with a Perkin-Elemer Analyst 300 using acetylene (C_2H_2) flame. The analysis of the reaction products was performed on a GC9800 gas chromatograph with HP-1 capillary column (30 m × 0.25 × 0.25 mm, cross-linked methylsiloxane) and flame ionic detector (FID).

Catalyst preparation

Mesoporous MCM-41 was prepared as Brunel *et al.* reported in the literature.[29] A typical procedure is as follows: 2.2 g (0.6 mmol) cetyltrimethylammonium bromide (CTAB) is added to a solution of 53.4 g of aqueous ammonia (26 wt%, 40 mmol NH_4OH), then stirred for 30 min in a closed polyethylene bottle; 10.4 g (10 mmol) TEOS is then slowly added to the base/surfactant solution while stirring. The resulting solution is stirred further for 2 h at room temperature before aging at 80 °C for 96 h. The white powder product is recovered by filtration and washing with distilled water thoroughly, drying at ambient temperature, and then calcination at 560 °C in air for 7 h.

In a typical experiment, 3 g MCM-41 (dried at 180 °C for 2 h) was added to 60 ml anhydrous toluene, and the solution was stirred for 30 min. An aliquot of 1.81 g (5.6 mmol) of (1-methyl-2-pyridylmethyl)[(triethoxylsilyl)propyl]amine **1**, which was synthesized according to the literatures,[36,37] was added to the suspension of MCM-41, followed by refluxation of the resulting solution for 20 h under N_2. The product was recovered by filtration, washed thoroughly with distilled water and ethanol, and dried at 60 °C under vacuum. We denoted this hybrid mesoporous material as PY-N-MCM-41 **2**.

The Pd $(PhCN)_2Cl_2$ complex was prepared according to the reported procedure.[38] An aliquot of 1.15 g (2 mmol) $Pd(PhCN)_2Cl_2$, 3 g hybrid mesoporous materials **2** and 120 ml CH_2Cl_2 were placed in a round-bottom flask. The mixture was stirred at room temperature for 24 h, filtered and washed. The product was Soxhlet-extracted with CH_2Cl_2 for 24 h to remove physically adsorbed $Pd(PhCN)_2Cl_2$, and dried at room temperature under vacuum to achieve the heterogeneous catalyst **3**. The Pd loading was determined by AAS.[37]

Catalytic reaction

In a typical experiment, a 100 ml round-bottom flask equipped with a reflux condenser and a stirring bar was charged with 0.216 g catalyst (containing 0.1 mmol Pd), 6.12 g (30 mmol) iodobenzene, 3.23 g (37.5 mmol) methyl acrylate, 3.79 g (37.5 mmol) Et_3N and 15 ml of freshly distilled NMP. The mixture was heated to 110 °C under argon until complete conversion of iodobenzene was monitored by GC. The reaction mixture was cooled to room temperature. The catalyst was separated from the reaction system by filtration and washed thoroughly with CH_2Cl_2, dried at 80 °C under vacuum, then reused in the next run without changing the reaction conditions. The reaction products were analyzed by GC analysis by adding isopropylbenzene as internal standard.

RESULTS AND DISCUSSION

Characterization

The powder XRD patterns of MCM-41, PY-N-MCM-41 **2** and heterogeneous catalyst **3** are shown in Fig. 1. Three peaks are observed in the XRD pattern of MCM-41. They can be indexed as the (100), (110) and (200) reflections of the hexagonal symmetry lattice of MCM-41 materials,[39] respectively. Compared with MCM-41, the (100), (110) and (200) reflections of **2** and **3** remain with decreased intensity,

DOI: 10.1002/aoc

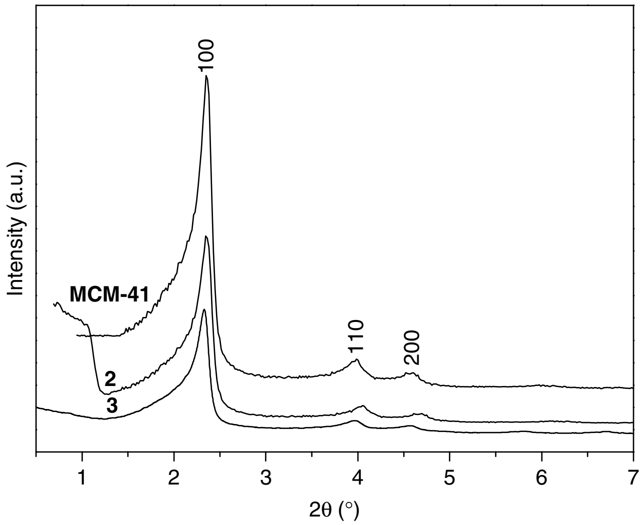

Figure 1. XRD patterns of MCM-41, PY-N-MCM-41 **2** and heterogeneous catalyst **3**.

indicating that the hybrid support and catalyst possess highly ordered structure after modification. The intensity reduction of reflections may be mainly due to contrast matching between the silicate framework and organic moieties which are located inside the framework of MCM-41.[40,41]

N_2 adsorption–desorption isotherms of MCM-41 and heterogeneous catalyst **3** are given in Fig. 2. The two samples exhibit type IV isotherms (defined by IUPAC) with small hysteresis, which is characteristic for the mesoporous materials. A sharp increase in the adsorption of N_2 between the relative pressures of 0.3 and 0.4 can be assigned to capillary condensation.[40] From Fig. 2, it can be also seen that lower pore volumes and size distributions are obtained in the heterogeneous catalyst. It was reported that organic groups in a grafted mesoporous sample are mainly located on internal surfaces close to the pore windows.[42] The decrease in the pore volumes and size is also possible proof that the organic groups and metal complex are successfully introduced into the framework.[30,43]

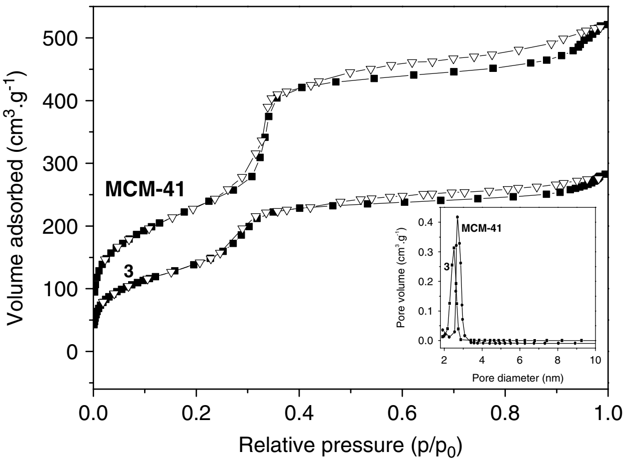

Figure 2. Nitrogen adsorption–desorption isotherms and pore size distributions (inset) of MCM-41 and heterogeneous catalyst **3**.

The incorporation of the organic moieties into mesoporous materials can be further confirmed by IR. The IR spectra of MCM-41, PY-N-MCM-41 **2** and catalyst **3** are presented in Fig. 3. All characteristic peaks exist but give the vibrations of organic moieties in the spectra of PY-N-MCM-41 **2** and catalyst **3** compared with MCM-41. The peaks of the organic groups are relatively weak because of their low content in functionalized hybrid materials. The vibrations at about 2969 cm^{-1} are assigned to the asymmetric stretching vibration of $-CH_3$ unit. The vibrations at about 2926 and 2854 cm^{-1} are due to the asymmetric and symmetric stretching vibrations of $-CH_2$ units, respectively.

The ^{13}C CP-MAS NMR spectrum of PY-N-MCM-41 is shown in Fig. 4. The sharp peak at 10.1 ppm is ascribed to the carbon atom bonded to silicon. The signal at 22.0 ppm corresponds to the methyl carbon and the inner carbon atom of the propyl group.[44] The peak at 42.8 ppm can be attributed to carbon atoms attached to the nitrogen atom. The existence of carbon atoms of the pyridine ring is identified by the peaks in the range of 123.5–149.9 ppm.

Three peaks are observed in the ^{29}Si CP-MAS NMR spectrum of PY-N-MCM-41 (Fig. 5). The peaks at −66.5, −100.5 and −109.6 ppm can be attributed to the $SiC(OSi)_3$ (T^3), $Si(OH)(OSi)_3$ (Q^3) and $Si(OSi)_4$ (Q^4) silicon species,[30,45] respectively. The existence of T^3 confirms that MCM-41 has been modified by organic moieties.[44] The appearance of the Q^3 signal indicates the presence of some residual noncondensed OH groups attached to the silicon atom.[46,47] ^{13}C and ^{29}Si CP-MAS NMR spectra provide direct evidence

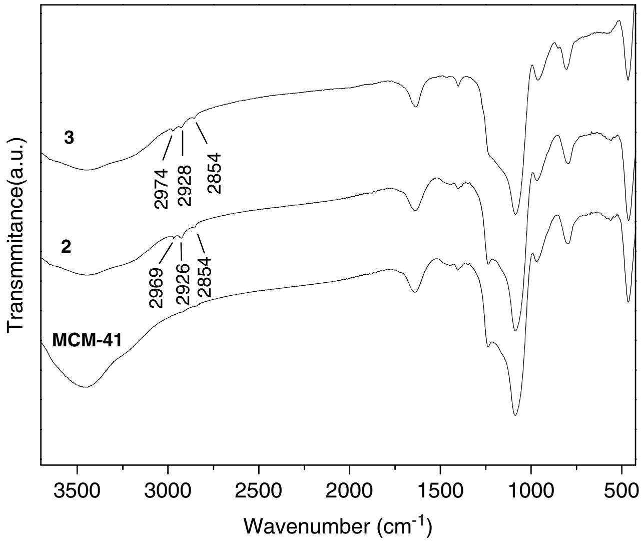

Figure 3. IR spectra of MCM-41, PY-N-MCM-41 **2** and heterogeneous catalyst **3**.

DOI: 10.1002/aoc

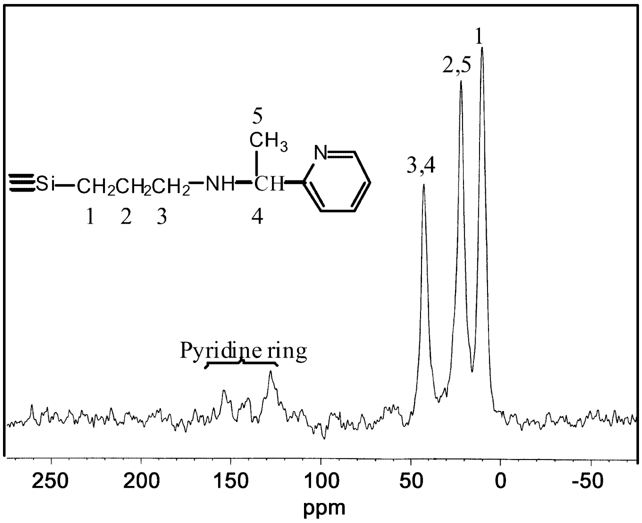

Figure 4. ^{13}C CP-MAS NMR spectrum of PY-N-MCM-41.

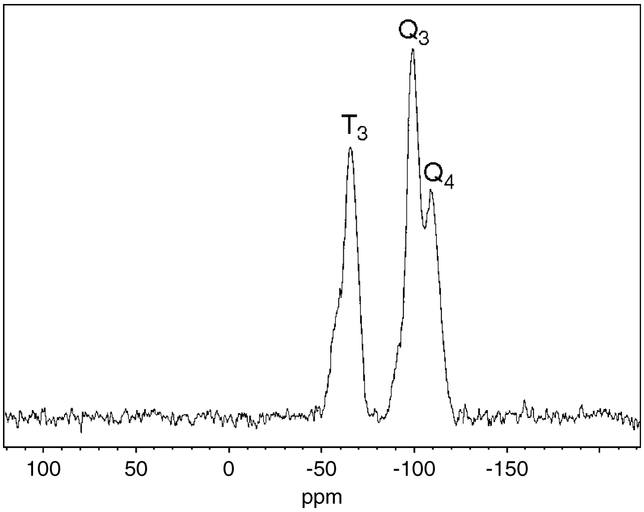

Figure 5. ^{29}Si CP-MAS NMR spectrum of PY-N-MCM-41.

for the presence of organic moieties as part of the hybrid mesoporous materials.

Figure 6 presents the XPS of PY-N-MCM-41 **2** and catalyst **3**. The N atoms in the hybrid support donate electrons to Pd(II). As a result, the electron cloud around Pd(II) increases and the peak of Pd $3d_{5/2}$ at 336.5 eV in catalyst **3** is lower than that of $PdCl_2$ at 337.9 eV.[43] The peak of N 1s in catalyst **3** at 400.1 eV is higher than that of support at 399.4 eV. These changes in binding energies reveal that there is an electronic interaction between Pd(II) and N, indicating the formation of heterogeneous catalyst **3**.

Catalytic properties

The main aim of the present investigation is to solve the problems of homogeneous catalyst such as separation and regeneration, so controlling and minimizing the Pd amount in the solution at the end of the reaction is one of the most important issues. However, the heterogenized palladium complex will be insignificant if the catalytic activity is too low. Accordingly, the effects of various reaction parameters on the yield of methyl cinnamate and Pd leaching were studied here. Several solvents and bases for the Heck reaction of iodobenzene with methyl acrylate in the presence of heterogeneous Pd(II) catalyst were examined. The results in Table 1 suggest that both catalytic activity and Pd leaching correlated to the solvent and base. The heterogeneous catalyst exhibited excellent catalytic performance in NMP-Et_3N system, giving 92% yield of methyl cinnamate.

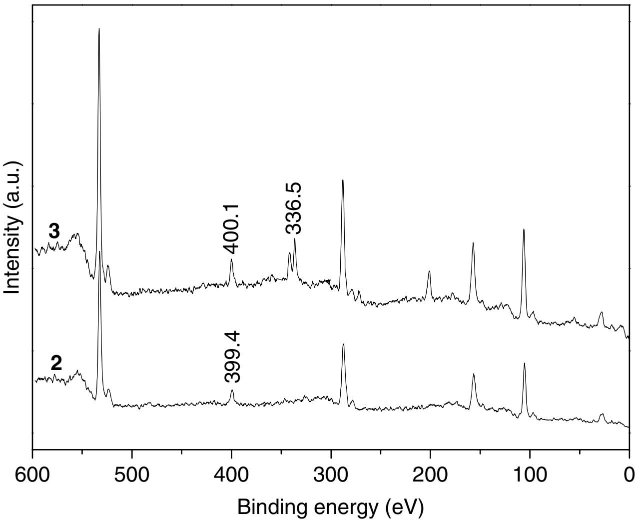

Figure 6. XPS spectra of PY-N-MCM-41 **2** and heterogeneous catalyst **3**.

Et_3N may be a potential ligand for Pd(II), which leads to more Pd species to enter the solution. Thus, higher Pd loss ranging from 4.7 to 5.3wt% was observed when Et_3N was employed as base. Although the Pd loss remained almost constant with different solvents in the presence of Et_3N, significant differences in Pd leaching were observed when $NaHCO_3$ or Na_2CO_3 were employed, indicating the choice of the solvent also affected Pd leaching. The results in Table 1 show that the Pd loss was close in NMP and DMF, but higher than that in other solvents. This may be caused by the coordination of solvent containing nitrogen with Pd complex, which led to higher Pd loss. In addition, higher yield was obtained in NMP and DMF, indicating that the Pd species in the solution may be the actual active sites in the Heck vinylation of iodobenzene with methyl acrylate.[23] The results of Pd leaching also indicate that Et_3N may play a more important role than solvent in Pd leaching, so insignificant differences were observed in different solvents in the presence of Et_3N.

The recycle performance of the supported catalyst was examined in the Heck reaction of iodobenzene with methyl acrylate in NMP–Et_3N and toluene–Na_2CO_3 systems. From

DOI: 10.1002/aoc

Table 1. Effect of solvent and base on the Heck vinylation of iodobenzene with methyl acrylate[a]

Solvent	Base	Temperature (°C)	Time (h)	Yield (%)[b]	Pd loss (wt%)[c]
NMP	Et_3N	110	5	92	5.1
DMF	Et_3N	110	5	86	5.3
Dioxane	Et_3N	110	7	79	5.0
Toluene	Et_3N	110	6	72	4.8
Acetonitrile	Et_3N	82	18	71	4.7
Benzene	Et_3N	80	23	65	4.9
NMP	$NaHCO_3$	110	7	80	1.9
DMF	$NaHCO_3$	110	8	74	1.8
Toluene	$NaHCO_3$	110	8	57	1.1
NMP	Na_2CO_3	110	7	75	2.1
DMF	Na_2CO_3	110	8	73	1.9
Toluene	Na_2CO_3	110	8	56	0.9

[a] Reaction conditions: Pd(II) 0.1 mmol; iodobenzene 37.5 mmol; methyl acrylate 37.5 mmol; base 37.5 mmol; Pd loading 4.9wt%.
[b] Determined by GC.
[c] Pd in the reaction solution/total amount of Pd introduced.

Table 2. Recycle performance for the heterogeneous Pd(II) catalyst[a]

	Yield (%)[b]		Pd loss (wt%)[c]	
Run	Condition 1[d]	Condition 2[e]	Condition 1[d]	Condition 2[e]
1	92	56	5.1	0.9
2	88	56	4.8	1.2
3	82	54	4.3	0.8
4	80	52	3.9	1.0
5	78	54	3.5	0.9
6	77	53	3.0	1.2

[a] Reaction conditions: Pd(II) 0.1 mmol; iodobenzene 37.5 mmol; methyl acrylate 37.5 mmol; base 37.5 mmol; reaction temperature 110 °C; Pd loading 4.9wt%.
[b] Determined by GC.
[c] Pd in the reaction solution/total amount of Pd introduced.
[d] NMP and Et_3N were employed.
[e] Toluene and Na_2CO_3 were employed.

Table 2, it can be seen that both the catalytic activity and Pd leaching remained almost constant during six reaction cycles in the toluene–Na_2CO_3 system. The yield of methyl cinnamate changed in the small range of 52–56%, and the overall Pd loss was only 6.0wt%. Compared with the toluene–Na_2CO_3 system, higher Pd leaching was observed in the NMP–Et_3N system; this obvious decrease in Pd content during the reaction led to a significant decrease in catalytic performance, and the yield of product decreased from 92 to 77% after six recycles. The catalytic activity comparison in NMP–Et_3N and toluene–Na_2CO_3 systems revealed that the decrease in catalytic performance may be due to the loss of the active Pd species. As shown in Table 1, Pd(II) complex anchored on organic functionalized MCM-41 revealed excellent stability if appropriate reaction conditions were chosen.

Heterogenized catalysts with different Pd loadings were prepared to investigate the effect on the structure, yield and Pd leaching. Table 3 clearly shows that as the Pd loading varied from 4.9 to 11.4wt%, the yield correspondingly changed within a small range of 88–92%. Therefore it can be reasonably concluded that the Pd loading showed negligible effects on the catalytic activity. However, the Pd loss increased with increasing Pd loading. This is attributed to the number of catalytic active sites that increased with increasing Pd loading, which facilitated for easier aggregation of Pd. Accordingly, higher Pd loss was observed when more active Pd species entered into the reaction solution.

The XRD patterns of the heterogeneous catalyst with 4.9 and 11.4wt% Pd loading are presented in Fig. 7. As shown in Fig. 7, the ordered mesoporous structure was maintained perfectly in the heterogeneous catalyst with low Pd content. However, only a wide and weak (110) reflection is present, and the higher reflections almost disappear in the pattern of catalyst with 11.4wt% Pd loading. This may be attributed to

Table 3. Effect of Pd loading on the Heck reaction[a]

Pd loading (wt%)	4.9	6.5	8.3	9.8	11.4
Yield (%)[b]	92	90	92	92	88
Pd loss (wt%)[c]	5.1	7.3	8.1	8.8	11.5

[a] Reaction conditions: Pd(II) 0.1 mmol; iodobenzene 37.5 mmol; methyl acrylate 37.5 mmol; base 37.5 mmol; reaction temperature 110 °C; NMP and Et_3N were employed.
[b] Determined by GC.
[c] Pd in the reaction solution/total amount of Pd introduced.

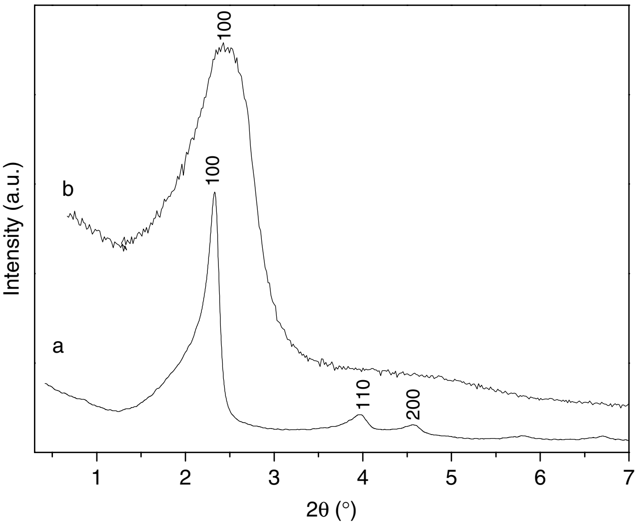

Figure 7. XRD patterns of heterogeneous catalysts (a: Pd loading = 4.9wt%; b: Pd loading = 11.4wt%).

some extent to structural collapse in the ordered hexagonal phase. The amounts of both organic groups and Pd complex must be increased to gain higher Pd loading catalyst. As more ordered SiO_2 is replaced, the ordered structure of the supported catalyst is further destroyed at higher Pd content.

CONCLUSIONS

$PdCl_2$ was successfully grafted to organic–inorganic hybrid mesoporous PY-N-MCM-41 modified by (1-methyl-2-pyridylmethyl)[(triethoxylsilyl)propyl]amine. The heterogeneous palladium catalyst exhibited excellent catalytic performance and stability for the Heck vinylation of iodobenzene with methyl acrylate. The yield of methyl cinnamate and Pd leaching in the reaction solution was obviously affected by reaction conditions such as solvent, base and Pd loading, giving 92% yield in the presence of NMP and Et_3N. The heterogeneous catalyst was recycled six times in a toluene–Na_2CO_3 system without significant loss of activity and palladium leaching.

REFERENCES

1. Papp A, Galbács G, Molnár Á. *Tetrahedron Lett.* 2005; **46**: 7725.
2. Zhao F, Shirai M, Ikushima Y, Arai M. *J. Mol. Catal. A: Chem.* 2002; **180**: 211.
3. Pröckl SS, Kleist W, Köhler K. *Tetrahedron.* 2005; **61**: 9855.
4. Sun Y, Thiel WR. *Inorgan. Chim. Acta* 2006; **359**: 4807.
5. Pryjomska-Ray I, Trzeciak AM. Ziólkowski JJ. *J. Mol. Catal. A: Chem.* 2006; **257**: 3.
6. Alonso F, Beletskaya IP, Yus M. *Tetrahedron* 2005; **61**: 11771.
7. Fairlamb IJS. *Tetrahedron.* 2005; **61**: 9647.
8. Gniewek A, Trzeciak AM, Ziolkowski JJ, Kepinski L, Wrzyszcz J, Tylus W. *J. Catal.* 2005; **229**: 332.
9. Sud A, Deshpande RM, Chaudhari RV. *Catal. Commun.* 2007; **8**: 183.
10. Caporusso AM, Innocenti P, Aronicaa LA, Vitulli G, Gallina R, Biffis A, Zecc M, Corainc B. *J. Catal.* 2005; **234**: 1.
11. Chen F, Toh K, Shen S, Gan GJ. *Catal. Commun.* 2007; **8**: 405.
12. Altava B, Burguete MI, García-Verdugo E, Karbass N, Luis SV, Puzary A, Sans V. *Tetrahedron Lett.* 2006; **47**: 2311.
13. Zhou J, Zhoua R, Moa L, Zhao S, Zheng X. *J. Mol. Catal. A: Chem.* 2002; **178**: 289.
14. Pryjomska-Ray I, Trzeciak AM, Ziólkowski JJ. *Tetrahedron Lett.* 2004; **45**: 8239.
15. Pryjomska-Ray I, Trzeciak AM. Ziólkowski JJ. *J. Mol.Catal. A: Chem.* 2006; **248**: 26.
16. Tsai FY, Wu CL, Mou CY, Chao MC, Lin HP, Liu ST. *Tetrahedron Lett.* 2004; **45**: 7503.
17. Bennur TH, Ramani A, Bal R, Chanda BM, Sivasanker S. *Catal. Commun.* 2002; **3**: 493.
18. Zhao F, Shirai M, Arai M. *J. Mol. Catal. A: Chem.* 2000; **154**: 39.
19. Lin K, Song M, Cai D, Hao X, Wu Y. *Tetrahedron Lett.* 2003; **44**: 3955.
20. Hagiwara H, Shimizu Y. Hoshi T, Suzuki T, Ando M, Ohkubo K, Yokoyama C. *Tetrahedron Lett.* 2001; **42**: 4349.
21. Biffis A. Zecca M, Basato M. *Eur. J. Inorg. Chem.* 2001; 1131.
22. Djakovitch L, Köhler K. *J. Am. Chem. Soc.* 2001; **123**: 5990.
23. Heidenreich RG, Krauter JGE, Pietsch J, Köhler K. *J. Mol. Catal. A: Chem.* 2002; **182–183**: 499.
24. Lu Z, Lindner E, Mayer HA. *Chem. Rev.* 2002; **102**: 3543.
25. Moreau JJE, Chi Man MW. *Coord. Chem. Rev.* 1998; **178–180**: 1073.
26. Corma A, Kumar D. *Stud. Surf. Sci. Catal.* 1998; **117**: 201.
27. Wong ST, Lin HP, Mou CY. *Appl. Catal. A: Chem.* 2000; **198**: 103.
28. Mukherjee P, Laha S, Mandal D, Kumar R. *Stud. Surf. Sci. Catal.* 2000; **129**: 283.
29. Brunel D. *Microporous Mesoporous Mater.* 1999; **27**: 329.
30. Seo JYK, Park SB, Park DH. *J. Solid State Chem.* 2006; **179**: 1285.
30. Yoshitake H, Yokoi T, Tatsumi T. *Chem. Mater.* 2002; **14**: 4603.
32. Lee CH, Lin TS, Mou CY. *J. Phys. Chem. B.* 2003; **107**: 2543.
33. Xu Q, Li L, Liu X, Xu R. *Chem. Mater.* 2002; **14**: 549.
34. Mukhopadhyay K, Sarkar BR, Chaudhari RV. *J. Am. Chem. Soc.* 2002; **124**: 9692.
35. Baleizão C, Corma A, Garía H, Leyva A. *J. Org. Chem.* 2004; **69**: 439.
36. Lagasi M, Moggi P. *J. Mol. Catal. A: Chem.* 2002; **182–183**: 61.
37. Fan G, Li T, Li G. *Appl. Organometal. Chem.* 2006; **20**: 656.
38. Lahaye J, Lagarde R. *J. Catal.* 1970; **60**: 270.
39. Beck JS, Vartuli C, Roth WJ, Leonowicz ME, Kresge CT, Schmitt KD, Chu CTW, Olson DH, Sheppard EW, McCullen SB, Higgins JB, Schlenker JL. *J. Am. Chem. Soc.* 1992; **114**: 10834.
40. Jia M, Seifert A, Thiel WR. *Chem. Mater.* 2003; **15**: 2174.
41. Hammond W, Prouzet E, Mahanti SD, Pinnavaia TJ. *Microporous Mesoporous Mater.* 1999; **27**: 19.
42. Stein A, Lim MH. *Chem. Mater.* 1999; **11**: 3285.
43. Yang H, Zhang G, Hong X, Zhan Y. *J. Mol. Catal. A: Chem.* 2004; **210**: 143.
44. Jiang D, Yang Q, Wang H, Chen H, Zhu G, Yang J, Li C. *J. Catal.* 2006; **239**: 65.
45. Feng X, Fryxell GE, Wang LQ, Kim AY, Liu J, Kemmner KM. *Science* 1997; **276**: 23.
46. Corriu RJP, Lectercq D. *Angew Chem. Int. Edn Engl.* 1996; **35**: 1420.
47. Jiang D, Yang Q, Yang J, Zhang L, Zhu G, Li C. *Chem. Mater.* 2005; **17**: 6154.