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RESEARCH ARTICLE

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Synthesis of MCM-41 supported amino-palladium complex and its catalytic performance for heck reaction

Abstract Using MCM-41 as the supporter, a series of MCM-41 supported amino-palladium complexes has been prepared and characterized by XRD (X-ray diffraction) and XPS (X-ray photoelectron spectroscopy), etc. The XRD and XPS results indicate that the Pd coordinates with the $-NH_2$ groups on the MCM-41 surface, and the structure of MCM-41 has been not damaged. Its catalytic performance for Heck arylation of alkene with aryl iodide shows that the catalysts have high activity and stereoselectivity in 70–90°C. The product of Heck reaction is in *E* form. And the effect of the preparation condition of catalyst on the catalytic performance was examined.

Keywords MCM-41, palladium complex, heterogeneous catalyst, Heck reaction

1 Introduction

Transition metal catalyzed C–C coupling between aryl halides and vinyl compound is an important method for the stereo-selective formation of a new C–C bond and has found widespread applications in organic synthesis [1]. Palladium was the most used transition metal catalyst for the Heck reaction. In general, the activity of the homogeneous palladium catalysts is sufficiently high, such as $Pd(OAc)_2$, but they suffer from the drawbacks of difficult separation, difficulty in recycling from the reaction system, as well as serious environmental pollution. Such drawbacks have limited its application. Therefore, the development of heterogeneous palladium catalyst to overcome the above drawbacks has important theoretical and practical significance, and this is also one of the main objectives of green chemistry.

Generally, solid materials such as polymer materials, carbon, amorphous SiO_2, zeolite, and molecular sieves are used to immobilize palladium catalysts [2–10]. Te Palladium complex has been incorporated into polymer materials such as polystyrene through the coordination connection of unsaturated phosphine or phenanthroline. Using SiO_2 as the supporter, palladium was attached to its surface mainly through the phosphine or sulfur ligand. Recently, the research of the heterogeneous palladium catalysts immobilized on the supporter has obtained considerable development. Using natural polymer chitosan as the supporter, chitosan palladium (0) complex catalyst was first obtained by a simple method. Trans-3-phenylacrylate has been synthesized by Liu *et al.* [11] in a high conversion rate and high-yield with the catalyst which can be used repeatedly. Polystyrene-supported cyclopalladated compound which can be multiply recycled has been synthesized by Luo *et al.* [12]. These catalysts show good activity in the reaction of methacrylate with aryl bromide or aryl iodide and yields are all over 90%. Triarylphosphine with single-tooth, high steric hindrance and high electron-donating ability is the most common used ligand in the palladium catalyzed coupling reaction. However, the use of triarylphosphine is unfavorable for industrialized manufactured processes. Recently, amine ligand has been a research focus [5]. In this paper, the palladium complexes were anchored onto the amino-functionalized mesoporous molecular sieve MCM-41, which was firstly synthesized via surface modification of MCM-41. The anchored-palladium complexes were obtained as shown in Eq. (1). Then, we examined different substitution groups for the Heck arylation of conjugate alkene with aryl iodide as shown in Eq. (2).

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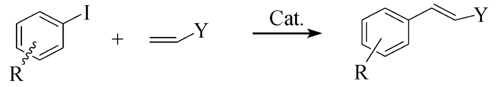
$$\text{MCM-X} + \begin{matrix}\text{PdCl}_2\\ \text{or}\\ \text{Pd(OAc)}_2\end{matrix} \xrightarrow[\text{t.t.,1 h}]{\text{acetone}} \begin{matrix}\text{MCM-X}\cdot\text{PdCl}_2\\ \text{or}\\ \text{MCM-X}\cdot\text{Pd(OAc)}_2\end{matrix} \qquad (1)$$



(2)

1 **2** **3**

1a: R=H **2a**: Y=COOH **3a–3c**: R=H,Y=COOH,COOMe,Ph
1b: R=COOH **2b**: Y=COOMe **3d–3f**: R=COOH,Y=COOH,COOMe,Ph
1c: R=OCH$_3$ **2c**: Y=Ph **3g–3i**: R=OCH$_3$,Y=COOH,COOMe,Ph

2 Experimental

2.1 Instrument and materials

XRD characterization was performed on a Rigaku D/max-IIIB X-ray powder diffraction instrument. The determination of specific surface area and pore size distribution were performed on an OMNISORP 100CX instrument. ICP analyses of Pd content in the complexes were obtained by a Leeman-Plasma Spec I instrument. IR spectra were obtained using a Nicolet-MAGNA 560 infrared Spectrometer with KBr pellet, and ^{1}H NMR spectra were recorded on a Bruker Arance 400 instrument with TMS as internal standard. All reagents were analytically pure.

2.2 Catalyst preparation

2.2.1 Synthesis of molecular sieve MCM-41

The molecular sieve MCM-41 was synthesized according to Ref. [14].

2.2.2 Organic functioning of molecular sieve MCM-41

Molecular sieve MCM-41 (1.0 g) was mixed with a chloroform solution of aminopropyltriethoxysilane (100 mL, 10 mmol) and the mixture was stirred at room temperature for 12 h. Then, the solid was filtered and washed with chloroform under vacuum to afford MCM-(CH$_2$)$_3$NH$_2$.

Aminopropyltriethoxysilane (10 mmol) was mixed with ethylenediamine (40 mmol) in chloroform (75 mL). The mixture was heated under reflux for 1 h and cooled to room temperature. Then, 1.0 g molecular sieve was added and the mixture was stirred at room temperature for 12 h. The solid was filtered and washed with chloroform under vacuum to afford MCM-(CH$_2$)$_3$NH(CH$_2$)$_2$NH$_2$.

The preparation of MCM-CH$_2$CH(OH)CH$_2$NH(CH$_2$)$_2$NH$_2$ was followed using epoxypropyltriethoxysilane as the substrate by a similar way as described above.

2.2.3 Preparation of supported palladium (II) catalysts

Functionalized molecular sieve MCM-41 (1.0 g) was mixed with PdCl$_2$[or Pd(OAc)$_2$] (0.04 g) in acetone (40 mL) and the mixture was stirred at room temperature for 1 h. The solid was filtered and washed with acetone under vacuum to afford MCM-41 supported palladium (II) catalyst. The palladium content of MCM-X·Pd (II) catalysts are summarized in Table 1.

Table 1 Pd content of MCM-X·Pd(II) catalysts

Catalyst	Pd content/%
MCM-(CH$_2$)$_3$NH$_2$·PdCl$_2$	1.67
MCM-(CH$_2$)$_3$NH(CH$_2$)$_2$NH$_2$·PdCl$_2$	1.86
MCM-CH$_2$CH(OH)CH$_2$NH(CH$_2$)$_2$NH$_2$·PdCl$_2$	1.77
MCM-(CH$_2$)$_3$NH$_2$·Pd(OAc)$_2$	1.70
MCM-(CH$_2$)$_3$NH(CH$_2$)$_2$NH$_2$·Pd(OAc)$_2$	1.94
MCM-CH$_2$CH(OH)CH$_2$NH(CH$_2$)$_2$NH$_2$·Pd(OAc)$_2$	1.81

2.2.4 Reduction of palladium complex catalysts

MCM-41 supported palladium (II) complex (0.5 g) was mixed with an absolute ethanol solution of KBH$_4$ (2–5 equiv.) and the mixture was stirred at room temperature for 1 h. Then, the solid was filtered, washed with absolute ethanol and dried under vacuum to afford MCM-41 supported palladium (0) catalyst.

2.3 A variety of Heck coupling reaction of aryl iodine with conjugate alkene

A mixture of substituted iodobenzene (10 mmol), conjugate alkene (15 mmol), appropriate alkali additives, solvent, and the MCM-X·Pd (II or 0) (contain Pd 0.03 mmol) was stirred in a N$_2$ atmosphere. After completion of the reaction, the MCM-X·Pd (II or 0) was separated from the mixture by filtration. The filtrate was poured into HCl solution for acidification. The solid precipitate was filtered, washed with H$_2$O and dried in air to give the crude product. The crude product was purified by recrystallization.

The characterization data of the product are shown in Table 2.

3 Results and discussion

3.1 Characterization of the MCM-41 supported amino-palladium (0, II) complexes

3.1.1 Determination of XRD

The XRD pattern of molecular sieve MCM-41 had diffraction peaks at (100), (110), (200), (210). The diffraction peak (100) was stronger than others, and the 2θ angle was about in the vicinity of 2.3°. The diffraction peak at (100) of the MCM-X·Pd (0, II) was decreased compared to that of MCM-41, but this typical diffraction

Table 2 ^{1}H NMR and IR spectral data of compounds **3a**–**3i**

Product	^{1}HNMR ($CDCl_3$ or DMSO-d_6 ,TMS)δ	IR (KBr), v /cm^{-1}
3a: *E*-PhCH = $CHCO_2H$	6.45 (d, *J* = 16.0 Hz, 1H, 3-CH), 7.26–7.58 (m, 5H, ArH), 7.83 (d, *J* = 16.0 Hz, 1H, 2-CH)	1682(w, ArC = O), 1630, 1578, 1495 (s, Ar), 875, 770, 711
3b: *E*-PhCH = $CHCO_2Me$	3.81(s, 3H, OCH_3), 6.43(d, *J* = 16.0 Hz, 1H, 3-CH), 7.26-7.54(m, 5H, ArH), 7.72(d, *J* = 16.0 Hz, 1H, 2-CH)	3073,3030(w, ArH), 2950 (w, CH3),1716(s, ArC = O), 1638, 1578, 1495 (s, ArH), 870, 773, 713
3c: *E*-PhCH = CHPh	7.11(s, 2H, CH = CH), 7.24–7.53(m, 10H, ArH)	3077,3058, 3020(w, ArH), 1597, 1577,1496(s, ArH), 765, 693
3d: *E*-4-CO_2HPhCH = $CHCO_2H$	6.64(d, *J* = 16.0 Hz, 1H, 3-CH), 7.67(d, *J* = 16.0 Hz, 1H, 2-CH), 7.81–7.97(m, 4H, ArH), 12.85(s, 2H, COOH)	1679(s, ArC = O), 1632, 1608, 1570,1509(s, ArH), 850, 777
3e: *E*-4-CO_2HPhCH = $CHCO_2Me$	3.75(s, 3H, OCH_3), 6.75(d, *J* = 16.0 Hz, 1H, 3-CH), 7.74(d, *J* = 16.0 Hz,1H, 2-CH), 7.84–7.97(d, 4H, ArH)	3070, 3030(s, ArH) 2960(s, CH_3), 1731(s, ArC = O), 1641, 1607, 1570 (S, ArH), 847, 774, 718
3f: *E*-4-CO_2HPhCH = CHPh	7.27–7.42(m, 5H, ArH), 7.62–7.64(d, 2H, CH = CH), 7.69–7.93(m, 4H, ArH)	3026(s, ArH), 1684(s, ArC = O), 1606, 1566, 1507, 1491(s, ArH), 876, 836, 774, 696
3g: *E*-4-MeOPhCH = $CHCO_2H$	3.86(s, 3H, CH_3), 6.36(d, *J* = 16.0 Hz, 1H, 3-CH), 6.96(d, *J* = 8.80 Hz, 2H, ArH), 7,57(d, *J* = 16.0 Hz, 1H, 2-CH), 7.65(d, *J* = 8.80 Hz, 2H, ArH)	2972, 2938(w, CH3), 1686(s, ArC = O), 1600, 1577(s, ArH), 827, 775
3h: *E*-4-MeOPhCH = $CHCO_2Me$	3.79(s, 3H, CH_3), 3.84(s, 3H), 6.29(d, *J* = 16.0 Hz, 1H, 3-CH), 6.89–7.49(m, 4H, ArH), 7.67(d, *J* = 16.0 Hz, 1H, 2-CH)	3032(w, ArH), 2964, 2950(w, CH_3), 1718(s,ArC = O), 1638, 1604, 1575, 1514(s,ArH), 839, 824
3i: *E*-4-MeOPhCH = CHPh	3.83(s, 3H, CH_3), 6.89(d, *J* = 2.04 Hz, 1H, 3-CH), 6.91(d, *J* = 2.04 Hz, 1H, 2-CH), 6.96–7.50(m, 9H, ArH)	3012(w, ArH), 2956(w, CH_3), 1697(w, ArC = O), 1600, 1511 (s, ArH), 820, 754

peak of MCM-41 was still remained. These results indicated that the crystal-phase structure of the MCM-41 was not damaged in the whole process of catalyst preparation. Major diffraction peaks of palladium crystal were not found in the XRD pattern of MCM-X·Pd (0, II), indicating that the palladium metal was highly dispersed.

3.1.2 Determination of XPS

The XPS results of the amino-functionalized MCM-41 and amino-functionalized MCM-41 supported Pd(0, II) complex were listed in Table 3. The data show that the electron bonding energy of O_{1s} did not change much, indicating that oxygen did not participate in the coordination with palladium. But the electron bonding energy of N_{1s} significantly increased after loading Pd (0, II) on MCM-X, indicating that the N atom of the catalyst exists higher electropositivity due to the lone-pair electrons' transfer to palladium. The $Pd_{3d5/2}$ binding energy of the catalyst was higher than metal Pd or $PdCl_2$, indicating that the N atoms coordinate to Pd (0, II). MCM-$(CH_2)_3NH_2 \cdot Pd(OAc)_2$ and MCM-$(CH_2)_3NH_2 \cdot PdCl_2$ catalysts have two sets of $Pd_{3d5/2}$ data, respectively. One set is slightly lower than Pd (II) (337.45 eV) but higher than Pd (0) (334.89 eV). Another set value was higher than the bivalence palladium, indicating that there were two valences of palladium: zero-valent palladium and

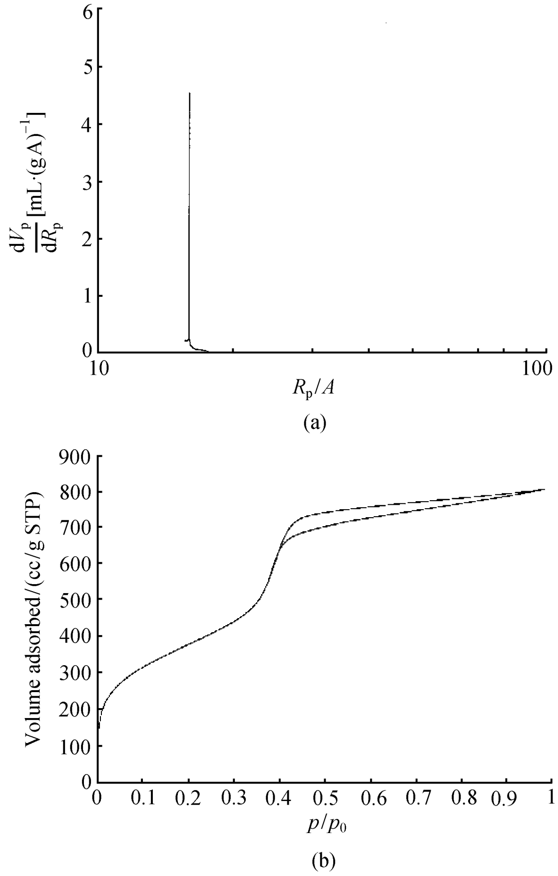
Table 3 Data of XPS for MCM-X and MCM-X·Pd (0, II)

Sample	XPS data /eV		
	$Pd_{3d5/2}$	N_{1s}	O_{1s}
Metal Pd	334.89		
$PdCl_2$	337.45		
$Pd(OAc)_2$	338.10		
MCM-$(CH_2)_3NH_2$		401.31	531.67
MCM-$(CH_2)_3NH_2 \cdot Pd(0)$	338.79	402.87	531.84
MCM-$(CH_2)_3NH_2 \cdot Pd(OAc)_2$	335.80, 338.18	402.50	532.02
MCM-$(CH_2)_3NH_2 \cdot PdCl_2$	336.35, 338.31	402.29	531.63
MCM-$(CH_2)_3NH(CH_2)_2NH_2$		399.04	531.61
MCM-$(CH_2)_3NH(CH_2)_2NH_2 \cdot PdCl_2$	337.94	400.81	531.89
MCM-$(CH_2)_3NH(CH_2)_2NH_2 \cdot Pd$	334.96, 338.40	400.95	531.84
MCM-$CH_2CH(OH)CH_2NH(CH_2)_2NH_2$		398.55	531.47
MCM-$CH_2CH(OH)CH_2NH(CH_2)_2NH_2 \cdot PdCl_2$	337.98	400.53	531.78
MCM-$CH_2CH(OH)CH_2NH(CH_2)_2NH_2 \cdot Pd$	334.74, 337.48	400.79	531.55

bivalence palladium. There were also two sets of $Pd_{3d5/2}$ data in MCM-$(CH_2)_3NH(CH_2)_2NH_2 \cdot Pd(0)$ and MCM-$CH_2CH(OH)CH_2NH(CH_2)_2NH_2 \cdot Pd(0)$. One was close to the value of the zero-valent palladium, and the another one was higher than the bivalence palladium due to the coordination of two N atoms in the ethylenediamine modified MCM-41 supporter. The two N atoms in the ligand and the $PdCl_2$ could form a stable five-membered ring structure, resulting in a strong coordination bond.

3.1.3 Determination of BET surface area, pore volume, and pore size distribution

Table 4 shows the BET surface area and pore structure data of the amino-functionalized MCM-41 and the functionalized MCM-41supported Pd (0, Ⅱ) catalysts. The data shows that, the surface area and pore volume of molecular sieve MCM-41 were relative large (1277.1 $m^2 \cdot g^{-1}$ and 0.905 $mL \cdot g^{-1}$, respectively), and the average pore diameter was 2.83 nm. The pore size distribution and N_2 adsorption-desorption isotherms were shown in Fig. 1. The surface area, pore volume and mean pore size of the molecular sieve MCM-41 reduced after it was functionalized and loaded with palladium salts. It can be seen from the pore size and distribution, and the curve of N_2 adsorption-desorption isotherms of the sample in Fig. 2, that the pore size distribution range of the molecular sieve MCM-41 was narrower before loading the palladium complex, indicating that the molecular sieve MCM-41 of the sample has a very regular channel structure. The pore size distribution range was wider after loading the palladium complex, but its pore size and distribution, and the curve of N_2 adsorption-desorption isotherms were relatively similar to those of the original MCM-41, indicating that the structure of MCM-41 has been not damaged.



(a)

(b)

Fig. 1 Pore size distribution (a) and N_2 adsorption-desorption isotherm (b) of MCM-41

Table 4 Pore structure data of MCM-41 and MCM-X·Pd (II)

Sample	$S/(m^2 \cdot g^{-1})$	$V/(mL \cdot g^{-1})$	D/nm
MCM-41	1277.1	0.905	2.83
MCM-$(CH_2)_3NH_2 \cdot PdCl_2$	533.7	0.169	1.27
MCM-$(CH_2)_3NH(CH_2)_2 NH_2 \cdot Pd(OAc)_2$	661.8	0.180	1.09
MCM-$CH_2CH(OH)CH_2NH (CH_2)_2NH_2 \cdot Pd(OAc)_2$	629.3	0.2568	1.63

3.2 Study of catalytic performance of MCM-41 supported amino-palladium (0, II) complexes

3.2.1 The effect of the reducer's properties and reduction conditions on the catalytic performance

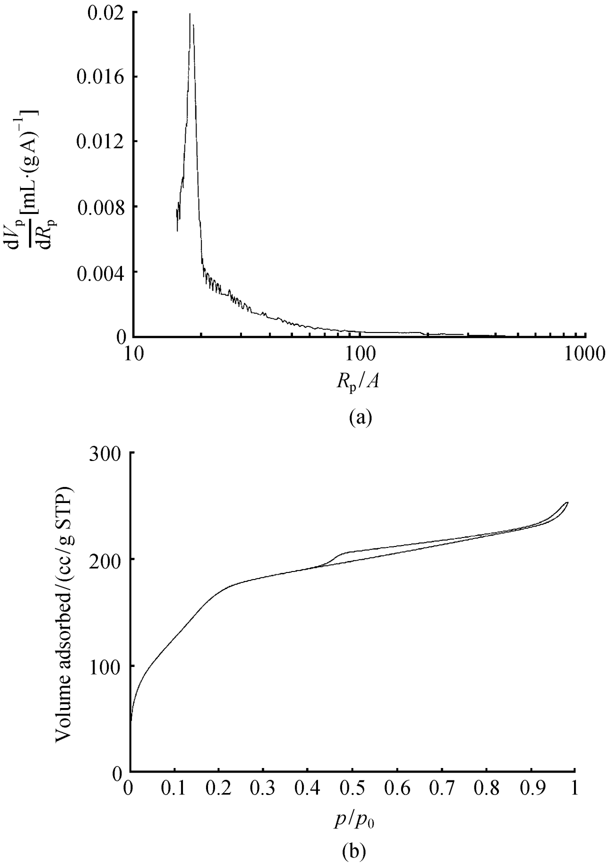
With MCM-$(CH_2)_3NH_2 \cdot PdCl_2$ as the catalyst, we studied the effect of reduction condition on the performance of the catalyst for the Heck coupling reaction of iodobenzene with acrylic acid. The results are summarized in Table 5, it was found that the activity of the catalyst treated by KBH_4/C_2H_5OH solution was the best, and the activity obtained by $NaBH_4$ was the secondary. However, it was less active than that from the original process after being reduced by H_2 at room temperature, and was much less active at 100°C.

Table 5 Effect of reduction conditions on catalytic performance[a]

Treatment condition	React. time/h	Yield/%	TOF[b]
No treatment	3.5	80	76
H_2/r.t., 1 h	3.5	70	66
H_2/100°C, 1 h	4	66	55
$CH_3OH/H_2O(1:1)$, 1 h, r.t.	3	80	89
$N_2H_4 \cdot H_2O/C_2H_5OH$, 1 h, r.t.	3	86	95
KBH_4/C_2H_5OH, 1 h, r.t	2	94	156
$NaBH_4/C_2H_5OH$, 1 h, r.t.	2	90	149

[a] Reaction temperature 70°C, DMF as the solvent, Et_3N as the alkaline reagent

[b] Mol product per mol Pd per hour, similar to the following.



(a)

(b)

Fig. 2 Pore size distribution (a) and N_2 adsorption-desorption isotherm (b) of MCM-$(CH_2)_3NH(CH_2)_2NH_2 \cdot Pd(OAc)_2$

3.2.2 Comparison of palladium catalyst performance before and after reduction

Each kind of complexing $PdCl_2$ catalyst was reduced by KBH_4/C_2H_5OH and then Pd(II) was transformed to Pd(0). Table 6 shows the catalytic activity for the Heck coupling reaction of iodobenzene with acrylic acid, which was catalyzed by the supported palladium catalyst. It indicates that the performance was conspicuously improved after reduction. The activity was not high before reduction, because there were two Cl^- around Pd^{2+} making difficulties to form the spatial coordination.

3.2.3 The effect of coordinating group in palladium salt on catalytic activity

We have studied the influence of the original coordinate groups in palladium salt to catalytic activity. Palladium salt with different coordinating group[$PdCl_2$, $Pd(OAc)_2$] reacted with MCM-X at the same condition to give the catalyst. The catalytic performance of the Heck coupling reaction of iodobenzene with acrylic acid, were shown in Table 6. It can be seen that the coordinating groups in palladium salt make sense in the catalytic activity of the catalyst. The order of catalytic activity before reduction is $Pd(OAc)_2 > PdCl_2$.

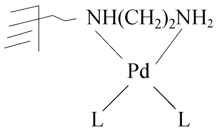
Table 6 Catalytic performance of the catalysts before and after reduction [a]

No.	Catalyst	React. time/h	Yield/%	TOF
1	MCM-$(CH_2)_3NH_2 \cdot PdCl_2$	3.5	80	76
2	MCM-$(CH_2)_3NH_2 \cdot Pd(0)$	2.0	94	156
3	MCM-$(CH_2)_3NH_2 \cdot Pd(OAc)_2$	1.8	93	167
4	MCM-$(CH_2)_3NH(CH_2)_2NH_2 \cdot PdCl_2$	16.5	40	8
5	MCM-$(CH_2)_3NH(CH_2)_2NH_2 \cdot Pd(0)$	6.0	93	52
6	MCM-$(CH_2)_3NH(CH_2)_2NH_2 \cdot Pd(OAc)_2$	3.5	90	86
7	MCM-$CH_2CH(OH)CH_2NH(CH_2)_2NH_2 \cdot PdCl_2$	24.0	15	2
8	MCM-$CH_2CH(OH)CH_2NH(CH_2)_2NH_2 \cdot Pd(0)$	6.5	92	47
9	MCM-$CH_2CH(OH)CH_2NH(CH_2)_2NH_2 \cdot Pd(OAc)_2$	2.5	95	126

[a] Reaction temperature 70°C, DMF as the solvent, Et_3N as the alkaline reagent

3.2.4 The effect of single atomic ligand and chelating ligand on the catalytic performance

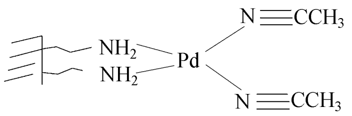
When the carrier has the same coordinating N atom and active centers' metal atom, the number of the N atoms as well as the substituted group have significant effect on catalytic performance. From Table 6, we knew that the activity of the catalyst with a single N atom ligand was higher than that of the catalyst with the chelating ligand, although the catalyst contained the same amount of palladium salt. It was known that moderate binding force between N and Pd was suited for the Heck coupling reaction. In the case of chelating ligand, the two N atoms in the ligand and the active center palladium could form a ring chelating structure:



This five-membered ring structure was stable. Therefore, the binding force between N and Pd of the catalyst 4,6,7 and 9 was stronger than 3 in the Table 6, which goes against the process of Pd^{2+} reducing to Pd(0) and to make the catalyst less active.

3.2.5 The effect of solvent and alkali reagent on catalytic performance

We have studied the effect of solvent and alkali reagent and their amount on the reaction. The Heck coupling reaction of iodobenzene with acrylic acid was catalyzed by MCM-$(CH_2)_3NH_2 \cdot Pd(0)$ in different solvent (6 mL), and the results are shown in Table 7. It can be seen that the influence of solvent to the Heck coupling reaction is based on the solvent polarity effect. With the enhancement of the solvent polarity, the substrate was easier to diffuse to the active center. Thus, the catalytic activity was improved. However, with the stronger polar solvent CH_3CN, it did not follow the law because CN of the CH_3CN can strongly coordinate with the active center Pd atom via triple bond:



Therefore, there was no more spatial coordination possible and it was not easy to form Ar-Pd-I complex on the active center. These decreased the catalytic activity.

In the Heck coupling reaction circulation between the substituted iodobenzene and conjugated alkene, the active center Pd(0) mainly restores through the process: H-Pd-I→ Pd(0)+ HI. So alkali reagent should be used to promptly eliminate HI in the reaction system. With different alkali reagents, we studied the Heck coupling reaction of iodobenzene with acrylic acid, catalyzed by MCM-$(CH_2)_3NH_2 \cdot Pd(0)$. The results are summarized in Table 8. It can be seen that the alkali reagent such as Et_3N or Bu_3N promoted the reaction by weak coordination with the active center. And it was proper to use the reagent like Et_3N, the amount of which was 5 times (mole ratio) more than that of the corresponding substrate.

Table 7 Effect of solvent on catalytic performance [a]

Solvent	1,4-$(Me)_2Ph$	CH_3CN	$(CH_3)_4NOH$	DMF
React. time/h	12.0	8.0	6.0	2.0
Yield/%	50	27	55	94
TOF	14	11	31	156

[a] Reaction temperature 70°C, DMF as the solvent.

Table 8 Effect of base on catalytic performance [a]

Base	$NaHCO_3$	Et_3N (25 mmol)	Et_3N (50 mmol)	Et_3N (75 mmol)	Bu_3N (50 mmol)
React. time/h	8.0	6.0	2.0	2.0	2.0
Yield/%	30	70	94	92	93
TOF	13	39	156	153	155

[a] Reaction temperature 70°C, DMF as the solvent

3.2.6 The effect of reaction temperature on catalytic performance

The reaction temperature at which supported palladium compounds catalyze Heck reaction is about 100°C, some even up to 160°C [15]. The high temperature of Heck reaction limited its application. Taking MCM-$(CH_2)_3NH_2 \cdot Pd(0)$ as the example, the catalytic activity in the reaction of iodobenzene with acrylic acid was investigated at different temperatures. The results are summarized in Table 9. A suitable temperature for high yield of cinnamic acid was 70–100°C. The yield of products decreased quickly at higher temperature (> 90°C).

Table 9 Effect of reaction temperature on catalytic performance [a]

React. temp./ °C	60	70	80	90	100
React. time/min	300	120	120	100	80
Yield/%	88	94	94	89	83
TOF	58	156	156	177	165

[a] DMF as the solvent, Et_3N as the alkaline reagent

3.2.7 Test of catalyst stability

We paid attention to the stability of the catalyst complex. In this experiment, the catalytic activity could basically be restored after multiple recycles of Heck reaction and simple regeneration process. The performance of various catalysts in the Heck coupling reaction of iodobenzene with acrylic acid is shown in Table 10. It was found that the catalytic activity of the complex loaded with $PdCl_2$ significantly decreased after two recycles of Heck reaction.

Table 10 Stability of the catalysts [a]

Catalyst	Fresh			First circle			Second circle		
	Time/h	Yield/%	TOF	Time/h	Yield/%	TOF	Time/h	Yield/%	TOF
MCM-$(CH_2)_3NH_2 \cdot PdCl_2$	3.5	80	76	4.5	70	52			
MCM-$(CH_2)_3NH_2 \cdot Pd(0)$	2.0	94	156	2.0	90	149	2.0	90	149
MCM-$(CH_2)_3NH_2 \cdot Pd(OAc)_2$	1.8	93	167	1.8	88	160	2.0	88	150
MCM-$(CH_2)_3NH_2 \cdot Pd(0)$	2.0	90	134	2.0	87	130			
MCM-$(CH_2)_3NH(CH_2)_2NH_2 \cdot Pd(OAc)_2$	3.5	90	86	4.0	85	71	4.5	85	63
MCM-$CH_2CH(OH)CH_2NH(CH_2)_2NH_2 \cdot Pd(OAc)_2$	2.5	95	126	3.0	90	100	3.25	90	92

[a] Reaction temperature 70°C, DMF as the solvent, Et_3N as the alkaline reagent

Table 11 Catalytic performance of MCM-X·Pd(0, II) ^{a}

Aryl iodide	Alkene	Product	A			B			C			D		
			Time/h	Yield/%	TOF	Time/h	Yield/%	TOF	Time/h	Yield/%	TOF	Time/h	Yield/%	TOF
1a	2a	3a	2.0	94	156	1.8	93	167	3.5	90	86	2.5	95	126
1a	2b	3b	2.5	90	115	2.5	90	114	5.0	85	57	4.0	87	72
1a	2c	3c	2.75	95	112	3.0	80	84	9.5	80	28	7.0	82	39
1b	2a	3d	4.0	98	81	3.5	91	82	5.0	85	57	4.5	90	67
1b	2b	3e	3.0	84	90	3.5	93	84	5.0	86	57	4.5	86	64
1b	2c	3f	5.0	93	60	4.0	98	78	6.5	86	44	6.5	87	45
1c	2a	3g	3.0	92	98	3.0	91	96	4.5	92	68	4.0	93	77
1c	2b	3h	3.0	91	97	3.0	94	99	5.0	90	60	4.0	92	76
1c	2c	3i	4.0	89	71	3.5	88	79	7.0	90	43	6.5	90	46

^{a}A: MCM-$(CH_2)_3NH_2$·Pd(0), B: MCM-$(CH_2)_3NH_2$·$Pd(OAc)_2$
C: MCM-$(CH_2)_3NH(CH_2)_2NH_2$·$Pd(OAc)_2$, D: MCM-$CH_2CH(OH)CH_2NH(CH_2)_2NH_2$·$Pd(OAc)_2$

But the stability would be improved through reduction of Pd(II) to Pd(0) before the use. In the first recycle, the yield of cinnamic acid decreased only 2%–4%. And its performance was basically stable during the third to the sixth recycle. The complexes loaded with $Pd(OAC)_2$ kept good stability after multiple recycles of Heck reaction, and the changing tendency of their activity was similar to that of the complexes loaded with Pd(0).

3.2.8 The performance of the catalysts in Heck coupling reaction of a variety of aryl iodide with conjugate alkene

We studied the MCM-X·Pd (0, II) complex activity in the Heck coupling reaction using a variety of aryl iodide with acrylic acid, the methyl acrylate, and the styrene. In the presence of MCM-X·Pd (0, II) catalysts, DMF and Et_3N, the Heck coupling reaction was carried out at 70°C successfully. The results are summarized in Table 11. All reactions took place almost completely within 9.5 h to give the corresponding products in high yields (80%–98%). Generally speaking, the TOF value decreases with the increment of the reactant molecular volume, but the product yield is little affected.

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