MCM-41 Supported Aminopropylsiloxane Palladium Acetate Complex: A Highly Active and Stereoselective Catalyst for Heck Reaction

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A new MCM-41 supported aminopropylsiloxane palladium acetate was prepared and characterized. This catalyst is highly active and stereoselective for Heck reaction at 70℃.

Keywords   Heck reaction, heterogeneous, palladium catalyst, stereoselective synthesis

Introduction

The palladium catalyzed vinylation of aryl and vinyl halides has been extensively investigated by Heck and others[1-5] because of its wide application in organic synthesis. Several challenges, however, remain for chemical practitioners to grapple with when performing a palladium catalyzed process at scale. Firstly, the relatively high price of palladium complexes, albeit in catalytic amounts, contributes significantly to the overall cost of production. Spent palladium is usually recovered and sent to its manufacturer for salvage, and new catalyst needs to be purchased for each batch of reaction. Secondly, residual palladium in the product may have adverse impact on downstream chemistry and final product purity. To address these concerns, heterogeneous catalysts were applied, but the preparations of these catalysts were rather complicated and the reaction conditions were critical. For above-mentioned reasons, the existing catalysts have, as yet, been limited in industrial application.

Among the M41S family of mesoporous crystalline solids, MCM-41 is the most attractive mesoporous materials because of its characteristic structure of well-ordered hexagonal mesopores.[6] In recent years there have been several significant developments in the use of organically modified mesoporous MCM-41 molecular sieve as catalysts in a variety of organic syntheses. For example, several solid base catalysts using simple aminopropyl functionalised MCM-41 materials have been shown to be very effective in Knoevenagel reaction.[7] In this paper, we are to report the preparation and characterization of MCM-41 supported aminopropylsiloxane palladium acetate complex [abbreviated as MCM-NH$_2$ · Pd(OAc)$_2$] and its excellent catalytic properties in Heck reactions.

Results and discussion

The title catalyst could be easily prepared from MCM-41 supported aminopropylsiloxane [abbreviated as MCM-NH$_2$] and palladium acetate in acetone (Scheme 1).
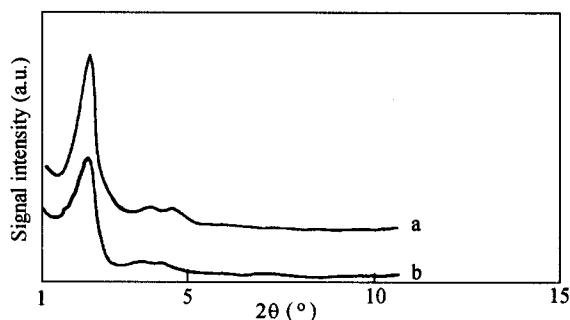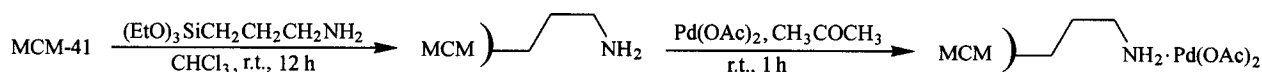
Typical X-ray diffraction pattern of MCM-NH$_2$ · Pd(OAc)$_2$ shown in Fig. 1 is comparable to that of pure silica MCM-41. The results show that the structure of MCM-41 molecular sieve has not been damaged in the preparation of solid catalysts. The major diffraction peaks of palladium acetate are not found in the XRD pattern of MCM-NH$_2$ · Pd(OAc)$_2$, indicating that the palladium acetate is highly dispersed.

Scheme 1

$$MCM\text{-}41 \xrightarrow[\text{CHCl}_3, \text{ r.t., 12 h}]{(EtO)_3SiCH_2CH_2CH_2NH_2} MCM\rangle\!\!-\!\!/\!\!\diagdown\!\!/\!\!\diagdown\!NH_2 \xrightarrow[\text{r.t., 1 h}]{Pd(OAc)_2, CH_3COCH_3} MCM\rangle\!\!-\!\!/\!\!\diagdown\!\!/\!\!\diagdown\!NH_2\cdot Pd(OAc)_2$$

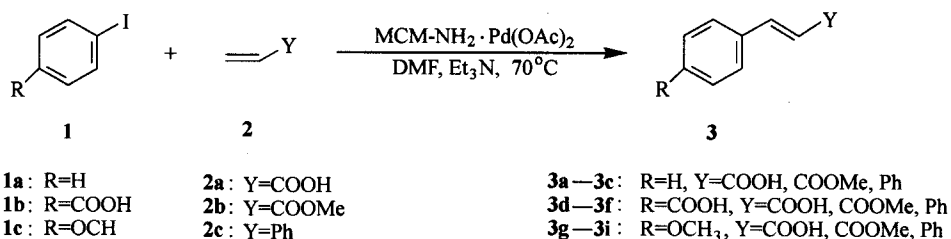**Fig. 1** XRD patterns of MCM-NH$_2$·Pd(OAc)$_2$ and MCM-41.
(a) MCM-41; (b) MCM-NH$_2$·Pd(OAc)$_2$.

The results of XPS measurement show that the N_{1s} electron binding energy of MCM-NH$_2$ · Pd (OAc)$_2$ (402.5 eV) is higher than that of MCM-NH$_2$ (401.3 eV) due to the lone-pair electrons' transfer to palladi-

tum, indicating that the direct covalent binding to silica surfaces has been achieved by coordinative binding of the metal Pd center to supported amino group.

The results of BET surface area and pore size measurement show that the surface area and average pore radius of MCM-41 were 924.51 m^2/g and 3.9 nm, respectively, and those of MCM-NH$_2$·Pd(OAc)$_2$ were 649.9 m^2/g and 1.2 nm, respectively.

In the presence of this catalyst, the arylation reactions of aryl iodides with styrene or acrylic acid or methyl acrylate were curried out at 70℃. The reactions were monitored by TLC and all reactions were complete in 1.8—4.0 h to give the corresponding *trans*-products in high yields. The *trans*-selectivity was near quantitative and no *cis*-product was observed (Scheme 2). The results are summarized in Tables 1 and Table 2.

Scheme 2

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	2c : Y=Ph	3g—3i : R=OCH$_3$, Y=COOH, COOMe, Ph

The catalyst can be easily recovered by filtration. The activity of recovered catalyst has been tested for the arylation of acrylic acid (2a) with iodobenzene (1a) for two recycles and the Pd content of the catalyst was also measured using ICP instrument. The results are shown in Table 3. It shows that the Pd content and the activity of the catalyst decreased very slightly after two recycles of Heck reaction.

As for the arylation of acrylic acid with iodobenzene, the molar turn over number (TON) of 167 at 70℃ is much larger than that of 67 at 100℃ in the corresponding Heck reaction reported by CAI Ming-Zhong .[8] Even after the catalyst had been exposed in air for 50 days, its activity has not decreased remarkably. However, the catalyst was not effective in the arylation of conjugated alkenes using bromobenzene or chlorobenzene as

Table 1 Heck arylation of conjugated alkenes catalyzed by MCM-NH$_2$·Pd(OAc)$_2$

Aryl iodide	Alkene	Product	Yield (%)[a]	TOF[b]
1a	2a	3a	93	167
1a	2b	3b	90	114
1a	2c	3c	80	84
1b	2a	3d	91	82
1b	2b	3e	93	84
1b	2c	3f	98	78
1c	2a	3g	91	96
1c	2b	3h	94	99
1c	2c	3i	88	79

[a] Isolated yield. [b] TOF: molar turn over number, mol product per mol Pd per h.   Reaction conditions: All reactions were carried out at 70℃; catalyst (0.2 g), aryl iodide (10 mol), 15 mL styrene or acrylic acid or methyl acrylate, DMF (6 mL) and Et$_3$N (7 mL) were used; reaction time was 1.8—4.0 h.

Table 2 Data of compounds 3a—3i synthesized

Product	IR (KBr) ν (cm^{-1})	^{1}H NMR (CDCl$_3$ or DMSO-d_6, TMS) δ
3a	1682 (w, ArC = O), 1630, 1578, 1495 (s, Ar), 875, 770, 711	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)
3b	3073, 3030 (w, ArH), 2950 (w, CH$_3$), 1716 (s, ArC = O), 1638, 1578, 1495 (s, ArH), 870, 773, 713	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)
3c	3077, 3058, 3020 (w, ArH), 1597, 1577, 1496 (s, ArH), 765, 693	7.11 (s, 2H, CH = CH), 7.24—7.53 (m, 10H, ArH)
3d	1679 (s, ArC = O), 1632, 1608, 1570, 1509 (s, ArH), 850, 777	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)
3e	3070, 3030 (s, ArH), 2960(s, CH$_3$), 1731 (s, ArC = O), 1641, 1607, 1570 (s, ArH), 847, 774, 718	3.11 (s, H, COOH), 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 (m, 4H, ArH)
3f	3026 (s, ArH), 1684 (s, ArC = O), 1606, 1566, 1507, 1491 (s, ArH), 876, 836, 774, 696	7.27—7.42 (m, 5H, ArH), 7.62—7.64 (m, 2H, CH = CH), 7.69—7.93 (m, 4H, ArH)
3g	2972, 2938 (w, CH$_3$), 1686 (s, ArC = O), 1600, 1577 (s, ArH), 827, 775	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),
3h	3032 (w, ArH), 2964, 2950 (w, CH$_3$), 1718 (s, ArC = O), 1638, 1604, 1575, 1514 (s, ArH), 839, 824	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),
3i	3012 (w, ArH), 2956 (w, CH$_3$), 1697 (w, ArC = O), 1600, 1511 (s, ArH), 820, 754	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)

Table 3 Results of Pd content of the catalyst and catalytic activity for two recycles

Heck reaction	w(Pd) content (%)	Yield (%)	TOF
Fresh catalyst	1.70	93	167
First recycle	1.68	88	160
Second recycle	1.61	88	150

Reaction conditions: All reactions were carried out at 70℃; catalyst (0.2 g), iodobenzene (10 mol), acrylic acid (15 mL), DMF (6 mL) and Et$_3$N (7 mL) were used.

arylating agent in the present studies.

In conclusion, we have synthesized a new catalyst for Heck reaction—MCM-41 supported aminopropyl-siloxane palladium acetate complex. The complex not only has high activity and stereoselectivity in Heck reaction at 70℃, but also offers practical advantages such as easy handling, separation from the product and reuse.

Experimental

General

IR spectra were obtained using a Nicolet-MAGNA 560 spectrometer. ^{1}H NMR spectra were recorded on a Bruker Arance 400 instrument with TMS as an internal standard in CDCl$_3$ or DMSO-d_6 as solvent. Microanalysis of N content was obtained using a Carlo-Erba-1110 elemental analyzer. ICP analyses of Pd content were obtained on a Leeman-Plasma Spec I instrument. The catalyst charaterization was performed by nitrogen desorption/desorption on an OMNISORP 100X instrument for BET surface area and pore size measurement, by XRD on a Rigaku D/max- IIIB X-ray diffractometer for crystalline identification, and by XPS with a VG-ESCALAB MKII system for the binding energy of N_{1s}.

Preparation of MCM-41 *materials*

MCM-41 was synthesized according to literature.[6]

Amino group functionization of MCM-41

MCM-41 (3 g) was mixed with a chloroform solution of aminopropyltriethoxysilane (50 mL, 0.6 mol/L) and stirred at room temperature for 12 h, then, the solid was filtered and washed with chloroform and dichloromethane.

Preparation of MCM-NH$_2$·Pd(OAc)$_2$ *complex*

To a solution of Pd(OAc)$_2$ (0.1 g, 0.444 mmol) in acetone (100 mL) was added MCM-NH$_2$ (2.7 g). The mixture was stirred at room temperature for 1 h. The yellow solid was filtered, washed with acetone, and then dried under vacuum to give the complex [MCM-NH$_2$·Pd-(OAc)$_2$]. w(Pd) content was 1.70% and w(N) content was 2.49%.

Typical procedure of trans-cinnamic acid (**3a**)

A mixture of acrylic acid (**2a**, 1.1 g, 15 mmol), iodobenzene (**1a**, 2.05 g, 10 mmol), Et$_3$N (3.6 g, 35 mmol), 6 mL DMF and the MCM-NH$_2$·Pd(OAc)$_2$ complex (0.2 g, 0.0317 mmol) was stirred under N$_2$ at 70 ℃ for 1.8 h. Then the MCM-NH$_2$·Pd(OAc)$_2$ complex was separated from the mixture by filtration. The filtrate was poured into 2% HCl solution. The white solid precipitate was filtered, washed with H$_2$O and dried in air to give trans-cinnamic acid (1.38 g, m.p. 130—131 ℃).

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