

Letter

MCM-41 supported aminopropylsiloxane palladium(0) complex: a highly active and stereoselective catalyst for Heck reaction

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Abstract

A new MCM-41 supported aminopropylsiloxane palladium(0) complex was prepared and characterized. The catalyst is highly active and stereoselective for Heck reaction at 70 °C. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Heck reaction; Heterogeneous; Palladium catalyst; Stereoselective synthesis

Palladium catalyzed carbon–carbon bond formation, the Heck reaction [1,2], represents one of the most versatile tools in modern synthetic chemistry and has great potential for industrial applications. Recent advances in homogeneous [3,4] and heterogeneous [5,6] Heck catalysis have attracted considerable attention. But it is difficult to separate and recycle the homogeneous palladium catalysts from reaction mixture, and the catalysts and ligands influence the purity of the products. In order to overcome these drawbacks, heterogeneous catalysts were applied, but the preparations of these catalysts were rather complicated and the reaction conditions were critical. For above-mentioned reason, the existing catalysts have, as yet, been limited in industrial application.

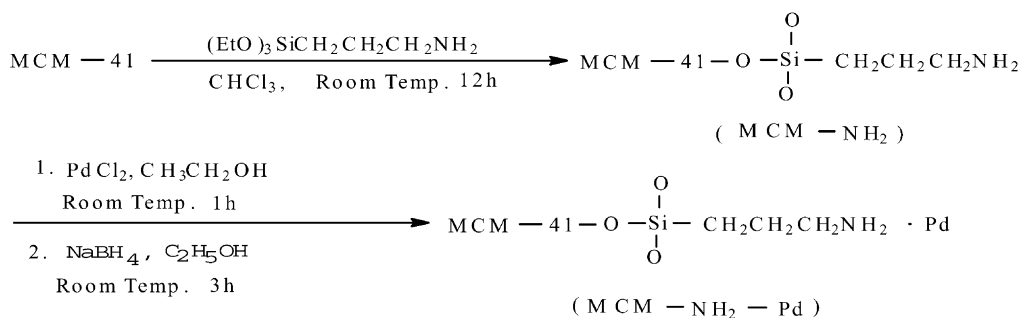
Current research focuses on the synthesis and application of modified mesoporous MCM-41 materials [7–11], which have an active species attached to the

framework via host–guest interactions, creating discrete and uniform catalyst sites on the inner walls of the porous systems. In this paper, we report the preparation and characterization of MCM-41 supported aminopropylsiloxane palladium(0) complex (MCM–NH₂·Pd(0)) and its excellent catalytic activity and stereoselectivity in Heck reactions.

This complex catalyst could be easily prepared from MCM-41 supported aminopropylsiloxane (MCM–NH₂) and palladium chloride in ethanol followed by reduction with NaBH₄ in ethanol (Scheme 1).

In a typical experiment, 3 g MCM-41 synthesized according to literature [7] was mixed with a chloroform solution of aminopropyltriethoxysilane (50 ml, 0.6 mol l⁻¹) and stirred at room temperature for 12 h, then the MCM–NH₂ (white solid) was filtered and washed with chloroform and dichloromethane, respectively. To a solution of PdCl₂ (0.1 g, 0.56 mmol) in ethanol (100 ml) was added MCM–NH₂ (3.5 g), the mixture was stirred at room temperature for 1 h. The brown solid was filtered, washed with ethanol,

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Scheme 1.

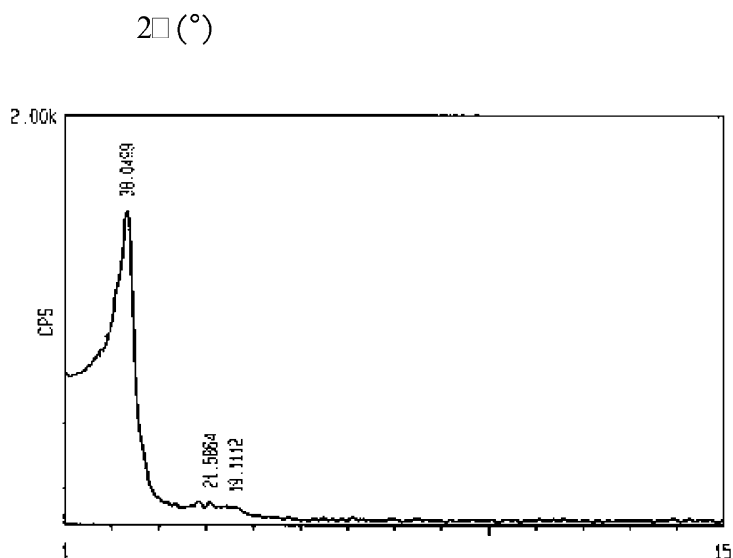
then mixed with NaBH_4 (20 mg) in ethanol (60 ml) and stirred at room temperature for 3 h. The resulting product was filtered, washed with EtOH and Et_2O , respectively, and dried under vacuum to give the grey palladium(0) complex. The palladium content was 1.67 wt.% and nitrogen content was 2.49 wt.%.

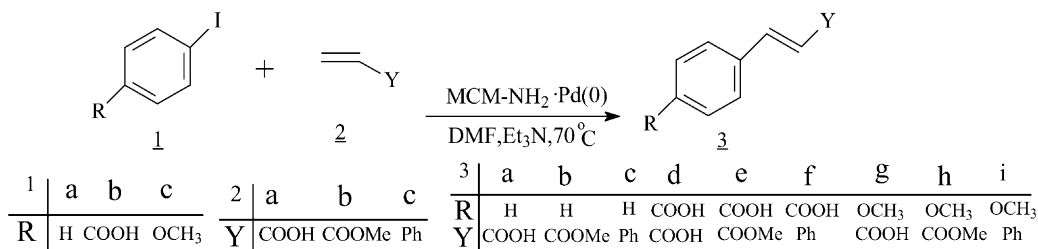
Typical X-ray diffraction (XRD) pattern of $\text{MCM-NH}_2\cdot\text{Pd}(0)$ shown in Fig. 1 is comparable to the diffraction pattern of pure silica MCM-41 [7]. The result shows that the structure of MCM-41 has been not damaged in the preparation of solid catalysts. The XRD pattern of palladium metal has major diffraction peaks at $2\theta = 40.1(111)$ and $46.7(200)$, which are

not found in the XRD pattern of $\text{MCM-NH}_2\cdot\text{Pd}(0)$, indicating that the palladium metal is highly dispersed.

The result of XPS measurement shows that the binding energies of N 1s and Pd $3d_{5/2}$ for $\text{MCM-NH}_2\cdot\text{Pd}(0)$ are 402.9 and 344.26 eV, respectively, which are higher than those of N 1s for MCM-NH_2 (401.3 eV) and Pd $3d_{5/2}$ for Pd particle (335.5 eV) due to the lone-pair electrons' transfer to palladium. It proves that nitrogen atoms coordinate to palladium.

In a typical reaction, a mixture of acrylic acid (2a, 1.1 g, 15 mmol), iodobenzene (1a, 2.05 g, 10 mmol), Et_3N (3.6 g, 35 mmol) 6 ml DMF and the $\text{MCM-NH}_2\cdot\text{Pd}(0)$ complex (0.2 g, 0.0312 mmol) was stirred

Fig. 1. XRD pattern of $\text{MCM-NH}_2\cdot\text{Pd}(0)$.



Scheme 2.

under N₂ in an oil bath at 70 °C for 2.0 h. Then the MCM–NH₂·Pd(0) complex was separated from the mixture by filtration. The filtrate was poured into 2% HCl solution. The white solid precipitate was filtered, washed with H₂O and dried in air to give trans-cinnamic acid. The reaction progress was monitored by TLC and all reactions were complete in for 2–5 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 Table 1.

The catalyst can be easily recovered by filtration. Two recycles were carried out for the arylation of acrylic acid (2a) with iodobenzene (1a), and it was found that the yield of trans-cinnamic acid (3a) decreased only by 1–3% in each recycle. The second recycle also resulted in 90% yield. As for the arylation reaction of acrylic acid with iodobenzene, the TOF

(mol product per mol Pd per h) of 156 and TON (mol turnover number) of 301 at 70 °C are larger than those of 67 and 230 at 100 °C in the corresponding Heck reaction reported by Cai [12]. Even after the catalyst had been exposed in air for 50 days, its activity did not decrease remarkably.

The arylation of conjugated alkenes was no effective using bromobenzene or chlorobenzene as arylating agent in the present studies. Similar results have been also observed by Cai and Choudary [12,13].

In summary, a new catalyst for Heck reaction—MCM-41 supported MCM–NH₂·Pd(0) complex has been synthesized, the preparation of which is rather simple and convenient. This complex not only has high activity and stereoselectivity for Heck reaction at 70 °C, but also offers practical advantages such as easy handling, separation from the product and reuse.

Table 1
Heck arylation of conjugated alkenes catalyzed by MCM–NH₂·Pd(0)^a

Aryl iodide	Alkene	Product	Yield (%) ^b	TOF ^c
1a	2a	3a	94	156
1a	2b	3b	90	115
1a	2c	3c	95	112
1b	2a	3d	98	81
1b	2b	3e	84	90
1b	2c	3f	93	60
1c	2a	3g	92	98
1c	2b	3h	91	97
1c	2c	3i	89	71

^a All products were characterized by IR and ¹H NMR; all reaction are carried out at 70 °C; 0.2 g catalyst is used.

^b Isolated yield.

^c TOF: mol product per mol Pd per h.

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