Dicyano-functionalized MCM-41 anchored-palladium complexes as recoverable catalysts for Heck reaction

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Abstract

Palladium(II,0) complexes were anchored on dicyano-functionalized MCM-41, producing new heterogeneous catalysts of the Heck reaction, which were synthesized via two-step surface modification of mesoporous molecular sieve MCM-41. The developed catalysts demonstrated easy separation after reaction, and reusability. BET, XRD, FT-IR, ICP-AES, H_2 chemisorption as well as XPS techniques were employed to characterize the catalytic materials.
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Keywords: Heck reaction; Dicyano-functionalized mesoporous materials; Reusability

1. Introduction

Palladium catalyzed Heck reaction is one of the most versatile tools in modern organic synthesis for the formation of a new C–C bond, and has a great potential for industrial application [1,2]. Although recent advances in heterogeneous and homogeneous catalysts of the Heck reaction have been achieved, these catalysts currently suffer from several drawbacks, such as low turnover numbers (TON) or limited lifetime [3]. In general, the activity of the homogeneous catalysts is sufficiently high, but they suffer from drawbacks of difficult catalyst-product separation and catalyst recycle. Such drawbacks can be obviated by hydrogenising the homogeneous catalysts on ligand-modified supports [4]. These catalysts named hybrid catalysts which generally consist of matrix, spacer and metal complex, can be easily reused like heterogeneous catalysts while acting as the homogeneous ones with high activity [5]. So, currently the development of the palladium complexes immobilized on supports via spacers as heterogeneous catalysts for the Heck reaction receives much attention [6,7].

The mesoporous molecular sieves such as MCM-41discovered by Mobil researchers in 1992 have large and uniform pore sizes, ultrahigh surface areas, big pore volume and rich silanol groups in the inner walls [8]. As demonstrated by much work reported, these properties make them great potential matrixes for immobilizing homogeneous catalysts because of the following reasons (i) easy modification with organic groups and metal complexes, (ii) readily creating discrete and uniform active sites, (iii) easy access for substrates involving bulky molecule [9,10]. Currently, much attention is devoted to the field without exception of Heck reaction catalysts [11,12].

In this paper, the palladium complexes were anchored onto the dicyano-functionalized mesoporous molecular sieve MCM-41, which was firstly synthesized via two-step surface modification of MCM-41. The resulting anchored-palladium complexes as new heterogeneous catalysts for the Heck reaction showed good activity and reusability.
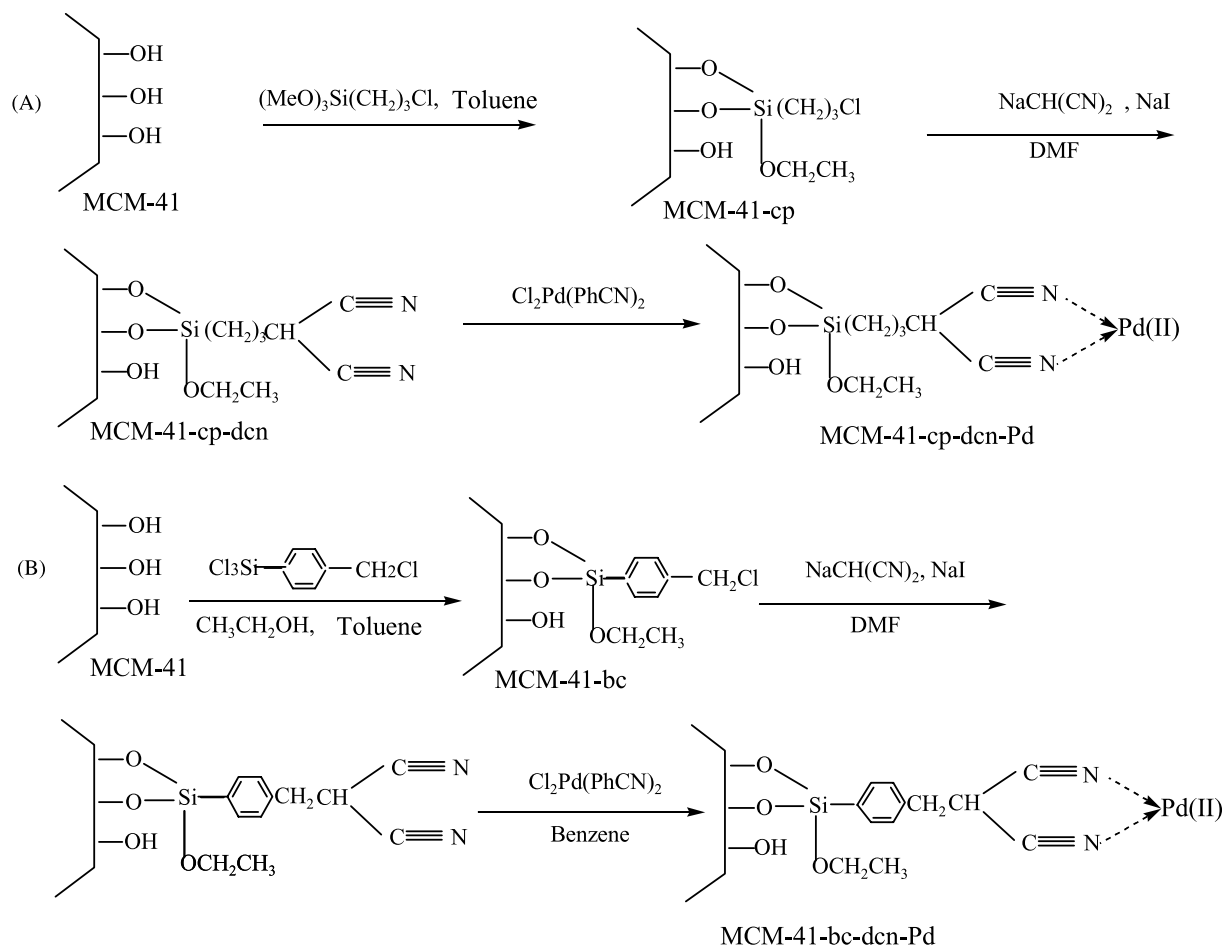
2. Experimental

2.1. Materials

3-(chloropropyl)triethoxysilane (95%, Aldrich), trichloro[4-(chloromethyl)phenyl]silane (98%, Aldrich), iodobenzene (98%, Aldrich), 4-iodoanisole (98%, Aldrich). $PdCl_2$,

Scheme 1.

Sodium borohydride, malononitrile, tetraethyl orthosilicate, cetyltrimethylammonium bromide, methyl acrylate, butyl acrylate, 1-bromo-4-nitrobenzene, dimethylformamide (DMF) and other reagents are commercially available in China.

2.2. Design of the catalystic materials

The proposed synthetic strategy was schematically presented in Scheme 1, and the symbols that designated various modified MCM-41, were included in it.

2.3. Preparation of catalytic materials

MCM-41 and MCM-41-cp were prepared according to the reported procedures [13,14]. MCM-41-bc was prepared as followed: 1.8 ML of trichloro[4-(chloromethyl)phenyl]silane reacted with 1.4 ML of anhydrous ethanol in 100 ML anhydrous toluene at N_2 atmosphere for 10 h, then 8.5 g of MCM-41 (dried at 200 °C under vacuum) and 0.9 ML of anhydrous pyridine were added to the mixture system. The reaction was preceded at 100 °C for 9 h. The resulting solid was obtained by filtration, extracted with

toluene and the mixture of dichloromethane and ethyl ether in soxhlet apparatus, and dried at 280 °C under vacuum for 8 h.

NaCH(CN)$_2$ was prepared via the reaction of malononitrile with NaOCH$_2$CH$_3$. The dicyano-functionalized MCM-41, i.e. MCM-41-cp-dcn or MCM-41-bc-dcn were prepared in the following manner: MCM-41-bc (or MCM-41-cp) was reacted with an excess of NaCH(CN)$_2$ and NaI (dried) in DMF (dimethylformamide) at 90 °C for 48 h. The solid was filtered out, extracted thoroughly with acetone, ethanol and methanol in sequence, and dried under vacuum.

The bis(benzonitrile)dichloropalladium complex was prepared according to the reported procedure [15]. The dicyano-functionalized MCM-41 was reacted with bis(benzonitrile)dichloro-palladium by ligand exchange in benzene, the solid separated from the mixture was washed thoroughly with benzene and ethanol, and dried in vacuum, resulting in the target catalysts MCM-41-cp-dcn-pd(II) or MCM-41-bc-dcn.-Pd(II). MCM-41-cp-dcn-pd(II) and MCM-41-bc-dcn.-Pd(II) were reduced by NaBH$_4$ in ethanol, leading to the catalysts MCM-41-cp-dcn-pd(0) and MCM-41-bc-dcn.-Pd(0), respectively.

2.4. Characterization

The BET surface area and pore analysis were performed on ASAP2010 (micromeritics) by N_2 physical adsorption–desorption at 77.4 K. H_2 chemisorption was performed on Autochem 2910(micromeritics). X-ray powder diffraction was obtained on Damx-rA (Rigaka). RT-IR spectrum was recorded on TFS-25PC (Digilab Corporation). C, H and N elemental analysis were conducted on vario EL (Elementar). Metal content was determined with inductively coupled plasma atom emission Atomscan16 (ICP-AES, TJA Corporation). X-ray photoelectron spectra was recoded on XSAM800 (Kratos).The analyses of reaction products were performed on 9A gas chromatography with SE-30 stationary liquid (Shimadzu) and DRX-300 ^{1}H-NMR (Bruck).

2.5. General procedure for the heck reaction

In a typical experiment, catalyst containing 0.1 mmol Pd, 320 molar equivalent of iodobenzene with respect to Pd, 384 equivalent of methyl acrylate, 10 ML of triethylamine as base and 20 ML of anhydrous dimethylformamide as solvent, were placed in a 50 ML round bottom-flask equipped with a magnetic stirring bar and condenser. The system was flushed thoroughly with N_2 before reaction. The flask was heated and remained with oil bath at 70 °C, and the system was sealed to keep the air out during the reaction. Iodobenzene in reaction was monitored by TLC. After iodobenzene was completely converted ca. 3–4 h, and the reaction was allowed to cool to room temperature. The catalyst was separated from the reaction system by filtration and stored for reuse. The separated solution was washed with 1 mol/L of HCl solution resulting in precipitation. The precipitation was washed with brine and dried. Then the product was obtained, which was analyzed with gas chromatography and ^{1}H NMR. The Heck reactions for other substrates were performed in the similar procedures.

3. Results and discussion

3.1. Textural analysis and elemental analysis

N_2 sorption isotherm is an efficient way for providing information about the pore system of mesoporous materials. The isotherms in Figs. 1 and 3 have remarkable changes at each stage of modification as expected because the organic fragments or metal complexes entered the channels, but all the catalytic materials gave similar adsorption–desorption isotherms of type IV according to the IUPA nomenclature, indicating the mesoporous structure was remained. The BJH pore size distribution is based on the Kelvin equation and has been widely used in mesoporous materials. The pore volume and size reduced apparently at each step of modification (illustrated in Figs. 2 and 4), also indicating the organic groups or the metal were successfully introduced into
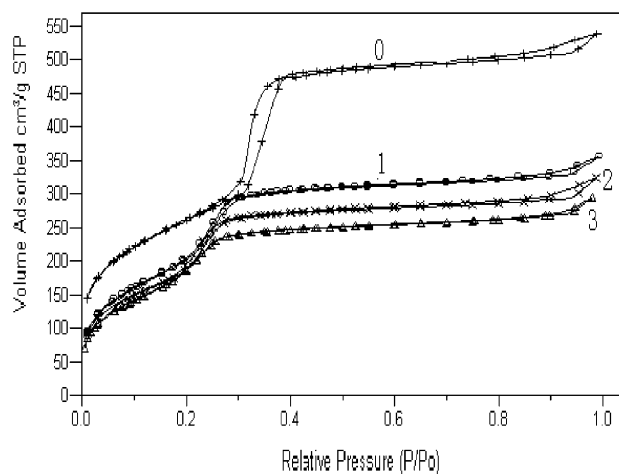

Fig. 1. Isotherms of catalytic materials. 0, MCM-41; 1, MCM-41-cp; 2, MCM-41-cp-dcn; 3, MCM-41-cp-dcn-pd (II).
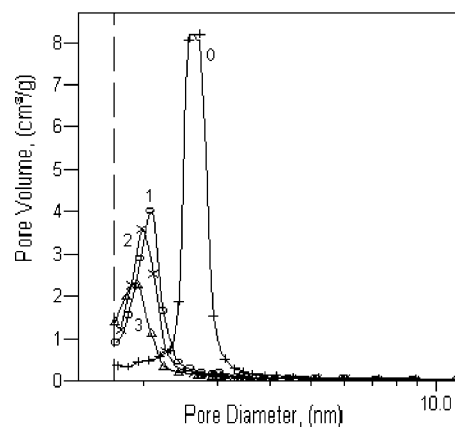

Fig. 2. Isotherms of catalytic materials. 0, MCM-41; 1, MCM-41-cp; 2, MCM-41-cp-dcn; 3, MCM-41-cp-dcn-pd (II).
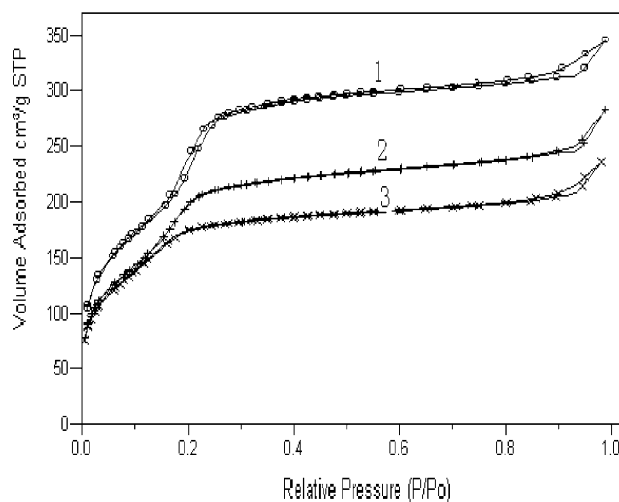

Fig. 3. Pore distribution of catalytic materials. 1, MCM-41-bc; 2, MCM-41-bc-dcn; 3, MCM-41-bc-dcn-Pd (II).
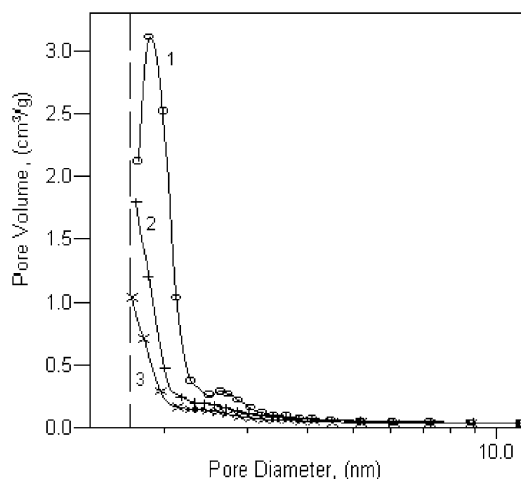
Fig. 4. Pore distribution of catalytic materials. 1, MCM-41-bc; 2, MCM-41-bc-dcn; 3, MCM-41-bc-dcn-Pd (II).

the inner channels, but the pore still remained a narrow distribution for each modified material. The pore distribution of MCM-41-bc-dcn (II) and MCM-41-bc-dcn-pd(II) was not completely given because the BJH method is unsuitable to pore size less than 1.7 nm, However, we could conclude the maximum pore distribution of them centered about 1.7 nm from Fig. 4. The results in detail were summarized in Table 1.

Table 1 also listed the results of C and N elemental analysis and palladium content. The increase of C or N content after thorough treatment shows the organic fragments were successfully introduced. The N content of MCM-41-bc-dcn is much higher than that of MCM-41-cp-dcn, which is attributed that chloromethyl group in MCM-41-bc has a high activity towards the nuleophilic displacement, leading to the chloromethyl groups nearly complete transformation to the di-cyano group based on the elemental content calculation. The presences of IR peak at 2207 and 2184 cm^{-1} for MCM-41-cp-dcn and 2200 and 2172 cm^{-1} for MCM-41-bc-dcn also confirmed the success of introducing the dicyano groups. The major stretching band of NaCH(CN)$_2$ centers about 2150 cm^{-1}, which did not present in MCM-41-cp-dcn and MCM-41-bc-dcn, and

it is proved that the N fragments was not physically adsorbed NaCH(CN)$_2$ after thorough extraction. The dicyano-functionalized MCM-41 had much higher Pd loading than the unmodified MCM-41 in the same condition. This indicates the dicyano group as bidentate ligand in the channel remarkably enhanced the performance of immobilizing the Pd complex.

From the small angle X-ray diffraction comparison of the unmodified MCM-41 with the developed catalysts shown in Fig. 5, the (1 0 0) reflection of the parent material MCM-41 with decreased intensity was remained after functionalization, while the (1 1 0) and (2 0 0) reflections became weak and diffuse, which could be due to contrast matching between the silica walls and the content of the channels after functionalization. These results indicated that the basic structure of the parent material MCM-41 was not damaged in the whole process of catalyst preparation, which is also confirmed by the isotherms and the pore distribution above. The cases of MCM-41-cp-dcn-pd (0) and MCM-41-bc-dcn-pd (0) catalysts were similar to their corresponding Pd (II) catalysts.

3.2. XPS and H$_2$ chemisorption analysis

The results of XPS and Pd dispersion measurements were listed in Table 2. 338.5 eV for MCM-41-cp-dcn-Pd(II) and 338.3 eV for MCM-41-bc-dcn-Pd(II) ware assigned to Pd(II). The binding energies of them were higher than PdCl$_2$, indicating that there was an electronic interaction between Pd (II) and the cyano groups. After reduction, the binding energy of them changed to 335.1 and 335.4 eV, respectively. However, Pd in MCM-41-Cl$_2$Pd(C$_6$H$_5$CN)$_2$ before reduction changed to Pd(0) according to the electron binding energy, which may be due to photo-reduction [16]. Metal Pd supported on the dicyano-functionalized MCM-41 had a higher dispersion than that on the unmodified MCM-41 and Nb-MCM-41 by impregnation [12], which may be explained that interaction of the dicyano groups with Pd (II) effectively hindered substantial Pd cluster formation during reduction process to some extent.

Table 1
Textural parameters and elemental content of the catalytic materials

Materials	Surface area[a] (m^2/g)	Pore volume[b] (cm^3/g)	Diameter[c] (nm)	C (wt.%)	N (wt.%)	Pd (wt.%)
MCM-41	903.9	0.83	2.7			
MCM-41-cp	700.9	0.55	2.2	5.94		
MCM-41-cp-dcn	641.6	0.50	2.1	7.10	0.90	
MCM-41-cp-dcn-Pd	576.6	0.45	2.0			3.56
MCM-41-bc	710.0	0.53	2.0	9.03		
MCM-41-bc-dcn	562.7	0.44	1.7	12.27	2.31	
MCM-41-bc-dcn-Pd	476.5	0.37	<1.7			7.91
MCM-41-Cl$_2$Pd(C$_7$H$_5$N)$_2$						0.62

[a] BET surface area.
[b] Single point total pore volume.
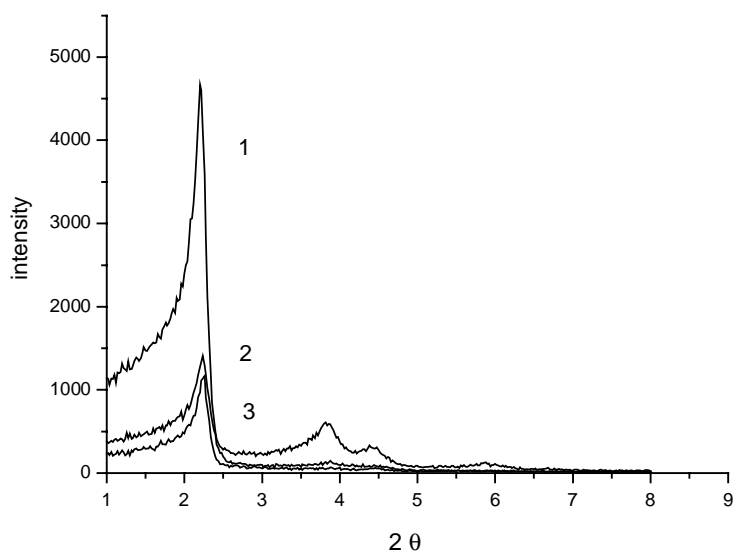[c] Pore diameter according to the maximum of the BJH pore size distribution.

Fig. 5. XRD patterns of catalytic materials. 1, MCM-41; 2, MCM-41-cp-dcn-Pd(II); 3, MCM-41-bc-dcn-Pd (II).

Table 2
Electron binding energy[a] and metal dispersion[b]

Catalysts	Pd 3d$_{5/2}$ (eV)	N 1s (eV)	Metal surface area (m^2/g)	Metal dispersion (%)
MCM-41-cp-dcn		399.2		
MCM-41-bc-dcn		399.3		
PdCl$_2$	337.9			
MCM-41-Cl$_2$Pd(C$_6$H$_5$CN)$_2$	335.5	398.0	3[c]	0.7
MCM-41-cp-dcn-Pd(II)	338.5	399.6		
MCM-41-cp-dcn-Pd(0)	335.1	399.5	60	15
MCM-41-bc-dcn-Pd(II)	338.3	399.4		
MCM-41-bc-dcn-Pd(0)	335.4	399.2	82	18

[a] C 1s: 248.4 eV as standard. m
[b] Based on the stiochiometric ratio of Pd:H is 1:1.
[c] After reduction with NaBH$_4$.

3.3. Catalytic performances

The reusing performances of developed catalysts towards vinylylation of iodobenzene were summarized in Table 3. The developed catalysts based on the dicyano-functionalized MCM-41 had high activity, which remained almost constant through four recycles, considering all the reactions were finished in ca. 3–4 h with exception of MCM-41-Cl$_2$Pd (C$_6$H$_5$CN)$_2$, Pd leaching of the dicyano-functionalized supported catalysts was very little after four recycles, while the yield had a gradual decrease when MCM-41-Cl$_2$Pd(C$_6$H$_5$CN)$_2$ was used as a catalyst and Pd leaching was up to 30.1% after four recycles. The comparison indicates that introduction of the dicyano groups via a spacer not only enhanced the catalytic activity, but also effectively hindered Pd leaching. This result is very impressive when compared with the heterogeneous catalysts Pd on silica [17]. In addition, the developed catalysts
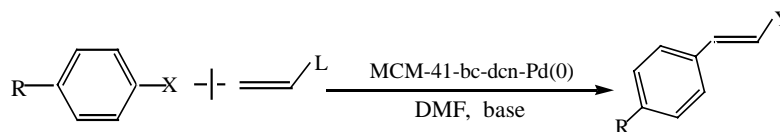
Table 3
Recycle performances of the developed catalysts[a]

Catalysts	First run yield[b] (%)	Second run yield[b] (%)	Third run yield[b] (%)	Fourth run yield[b] (%)	Pd loss (%)
MCM-41-cp-dcn-Pd(II)	88.7	89.7	91.7	89.5	1.0
MCM-41-cp-dcn-Pd(0)	91.1	89.6	92.2	90.8	0.8
MCM-41-bc-dcn-Pd(II)	89.7	91.9	90.6	91.8	0.3
MCM-41-bc-dcn-Pd(0)	91.9	94.5	91.8	90.9	0.5
MCM-41-Cl2Pd(C6H5CN)2[c]	87.7	88.1	85.6	78.7	30.1

[a] The Heck reaction with iodobenzene and methyl acrylate as substrates.
[b] Isolated yield.
[c] Molar ratio of Pd, iodobenzene and methyl acrylate was 1:640:768, reacted at 70 °C for 8 h.

Scheme 2.

Table 4
The Heck reaction of various substrates with MCM-41-bc-dcn-Pd(0) as catalyst[a]

Vinyl substrates	Aryl halide substrates	Temperature (°C), Reaction time (h)	Trans products isolated yield (%)
Methyl acrylate	IC_6H_5	70, 4	91.9
	$4\text{-}IC_6H_4OCH_3$	70, 5	89.3
Butyl acrylate styrene	$4\text{-}BrC_6H_4NO_2$	120, 4.5	89.0[b]
	IC_6H_5	70, 8	88.7
	$4\text{-}IC_6H_4OCH_3$	70, 8	89.3
	$4\text{-}BrC_6H_4NO_2$	120, 7	87.0[b]

[a] Molar ratio of Pd:aryl halide:vinyl substrate was 1:320:384 with triethylamine as base.
[b] Separation according to the reported way [12].

showed easy separation by a simple filtration and readily handling.

The general equation of the Heck reaction was presented as Scheme 2.

Take the developed catalyst MCM-41-bc-dcn-Pd (0) for example, as shown in Table 4. The developed catalyst demonstrated a good catalytic activity towards vinlylation of iodobenzen and actived bromobenzene.

4. Conclusions

The palladium complexes were successfully anchored on diyano-functionalized MCM-41 through different spacers, which were synthesized via two-step surface modification. The dicyano functionalized MCM-41 anchored Pd complexes as the Heck reaction heterogeneous catalysts showed easy recovery, high activity and reusability with minimal metal loss after four recycles.

Acknowledgements

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