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Pd-functionalized MCM-41 nanoporous silica as an efficient and reusable catalyst for promoting organic reactions†

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Pd-functionalized MCM-41 nanoporous silica has been explored as an efficient and recyclable catalyst to effect Suzuki and Mizoroki–Heck cross-coupling reactions, under various conditions. In Suzuki–Miyaura reactions, various aryl halides were coupled with aryl boronic acids at 100 °C under solvent-free conditions using K_2CO_3 as base and the maximum Ar–Ar yield reached 95%. The MCM(Pd)-41 catalyst was also used for a good range of Heck reactions using different aryl halides with styrene or *n*-butyl acrylate esters at 130 °C under solvent-free conditions using *n*-Pr_3N as base that gave the maximum yields of 95% and 92%, respectively. High yield, low reaction times, non-toxicity and recyclability of the catalyst are the main merits of this protocol. The catalyst has been characterized by FT-IR, XRD, SEM, TEM, XPS, EDX, ICP-AES, TG and N_2 adsorption–desorption.

Introduction

Palladium-based catalysts as versatile catalysts in modern organic synthesis are widely employed in a significant number of synthetic transformations such as, hydrogenations, Heck, Suzuki, Stille and Sono-gashira cross coupling reactions.[1–7] The resulting products have found widespread applications in the synthesis of natural products, agrochemicals, pharmaceuticals, and advanced materials.[8–10]

In designing new catalysts, two important parameters, activity and recovery, in catalysis science have to be considered. Some of the catalysts such as, homogeneous catalysts are very active but their separation is not easy and they cannot be reused in subsequent reactions. So, some demands cannot be satisfied.

Heterogeneous catalysts are superior to conventional homogeneous catalysts because of easy recovering from the reaction mixture by simple filtration and reused after activation and they cause economical viability in the processes involved,[11–14] but have low activity. Their low activity is attributed to the low active sites availability that limits the use of such catalysts when in need of a perfect catalyst.[15]

A strategy for overcoming this problem could be fixing a homogeneous catalytic system into a heterogeneous system in which the active centers are supported on large surface area supports in order to achieve a high dispersion of the catalytic active sites.[16] Hence, mesoporous silica seems a promising candidate as a support for homogeneous catalysts.[17–19] At first, mesoporous silica synthesized by Mobil's researchers in 1992. The mesoporous molecular sieves such as MCM-41 with high surface areas, tunable pore size, controlled morphology, thermal stability and rich silanol groups in the inner walls has proven to be suitable to be used as a catalyst support and adsorbent.[20–24] The chemical surface modification of MCM-41 is essential because the mesoporous silica surface covered with silanol groups is not selective enough to incorporation of active metals such as Pd and its metallic complexes. Their surface modification with addition of organic groups by grafting organosiloxane precursors and ligands which lead to formation of electron-rich metal complexes can enhance their stability and selectivity.

In this work, we report the production of Pd catalyst based on Schiff-base functionalized mesoporous molecular sieve MCM-41, as an efficient and recyclable catalyst for C–C coupling reactions including the Heck and Suzuki coupling reactions. The reactions were performed under Solvent free condition with high efficiency and excellent yields.

Results and discussion

The preparation and characterization of Pd immobilized onto Schiff-base modified mesoporous silica surfaces (MCM(PA)-41) are studied, and their catalytic performances are investigated. These steps are illustrated in Fig. 1.

Fig. 2 shows the FTIR spectra of MCM(NH_2)-41 and MCM(Pd)-41. C–H and N–H vibration bands appeared in the region 3000–3418 cm^{-1} and 1450–1650 cm^{-1} in the IR spectrum of amine modified moiety, MCM(NH_2)-41. The reaction between amine group of 3-amino-propyltriethoxysilane (ATES) and

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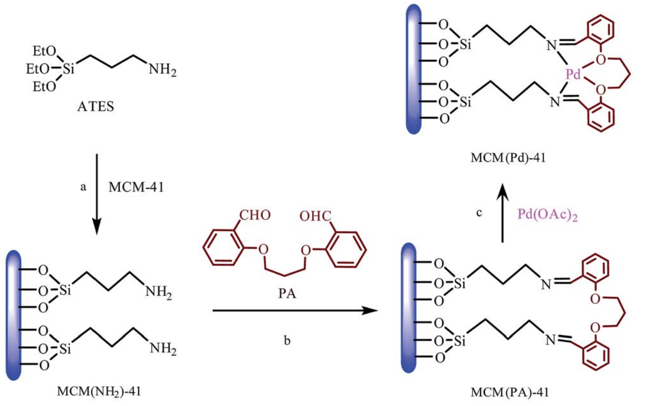


Fig. 1 Preparation of MCM(Pd)-41: (a) toluene/reflux, (b) CH_3OH/reflux and (c) CH_3OH/reflux/Ar.

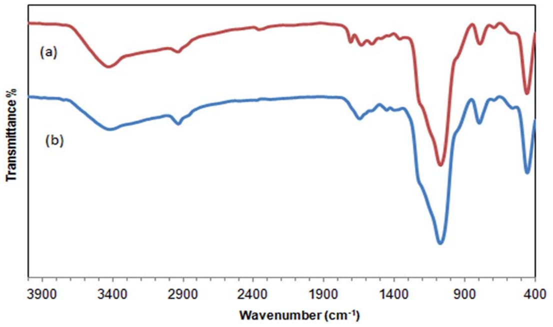


Fig. 2 FTIR spectra of (a) MCM(NH_2)-41 and (b) MCM(Pd)-41.

carbonyl group of 2,2′-(propane-1,3-diylbis(oxy))dibenzaldehyde (PA) formed a C═N bond. Formation of this bond was identified with FT-IR spectra with an absorption band at 1646 cm^{-1}.

Low-angle powder X-ray diffraction (XRD) patterns of pure MCM-41, MCM(PA)-41 and MCM(Pd)-41 are illustrated in Fig. 3. The patterns of MCM-41 showed four characteristic peaks that can be indexed on a hexagonal lattice of a typical mesoporous MCM-41 material as (100), (110), (200) and (210) planes.[25] However, decreased intensity and some broadened reflections are observed for the Schiff-base-modified mesoporous, indicating some structural disorder (Fig. 3b). This may indicate a reduction in arrangement of ordered two dimensional hexagonal mesoporous channels of silica as a result of functionalization. Also, the peak indicative of (100) diffraction shifted to the higher 2θ, indicating a decrease in basal spacing (d_{100}) owing to the increase of wall thickness of the pore channels. The MCM(Pd)-41 exhibited an even weaker and broader peak indicative of (100) diffraction, which demonstrated that the deposition of metallic Pd particles on the Schiff-base-modified mesoporous could further decrease the ordering degree of the mesoporous structure. The damage of the ordered mesoporous structure could be mainly attributed to the blockage of the pore channels by these Pd particles. This was confirmed by the TEM morphologies. As shown in the HR-TEM image in Fig. 4, the MCM(Pd)-41 still preserved the ordered hexagonal mesoporous structure. However, Pd particles deposited on the MCM(PA)-41 support in two ways. Most Pd particles of the Pd particles anchored on the outer surface of the support and a fraction of the Pd particles were distributed in the pore channels, which could account for the positive shift of the peak position observed in Fig. 3c, owing to the increase of the pore wall thickness. Also this was confirmed by (BET) and (BJH) analysis in Fig. 8a and b. However, it must be emphasized that HR-TEM in any case cannot provide unambiguous molecular level characterization of the active sites for two reasons. First, HR-

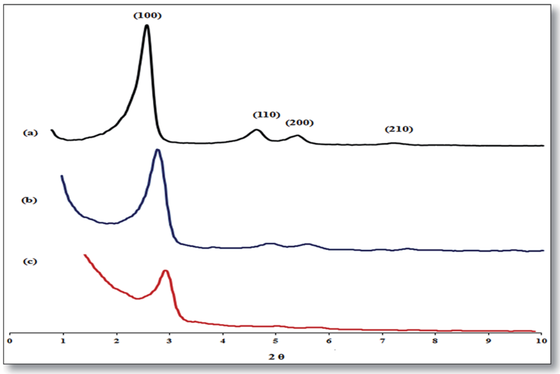


Fig. 3 XRD pattern of (a) MCM-41, (b) MCM(PA)-41 and (c) MCM(Pd)-41.

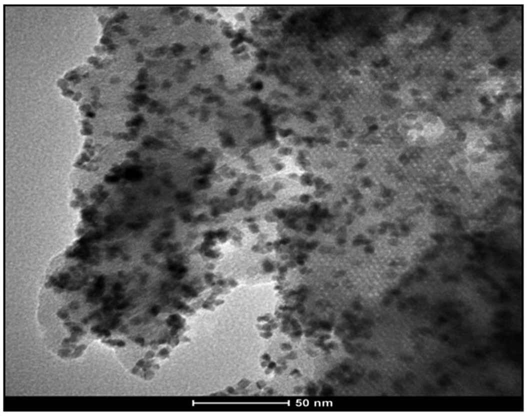


Fig. 4 The HR-TEM images of MCM(Pd)-41.

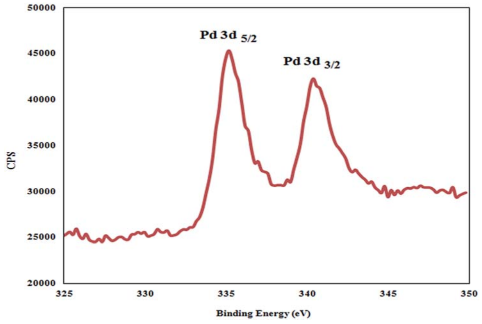


Fig. 5 XPS spectra of MCM(Pd)-41.

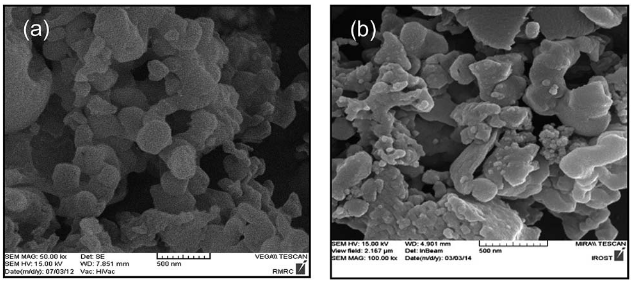


Fig. 6 The SEM micrographs of (a) MCM-41 and (b) MCM(Pd)-41.

TEM is known to modify small metal clusters on supports during the imaging process.[26] Secondly, the size of a tethered mononuclear complex is expected to be beyond the reliable resolution limit of HR-TEM.

X-ray photoelectron spectroscopy (XPS) helped determine the oxidation state of the Pd surface in the catalyst (Fig. 5). The binding energy curve showed a double peak at 335.35 ($3d_{5/2}$) and 340.55 eV ($3d_{3/2}$) that related to Pd (0).

The SEM micrographs of MCM-41 and MCM(Pd)-41 are shown in Fig. 6a and b, respectively. SEM micrographs show both materials have similar texture and there is no significant difference and also indicated that Pd is well dispersed in MCM(C=N)-41 and can be used as a heterogeneous catalyst.

Thermogravimetric analysis of the MCM(Pd)-41 catalyst was performed using the powder sample under nitrogen atmosphere. TG curve as shown in Fig. 7 indicates that upon heating, MCM(Pd)-41 showed a weight loss of about 3.47 wt% between room temperature to 160 °C, which are related to removal of adsorbed water and solvent molecules. Upon further heating, the TG curve shows a mass loss, about 21%, in the temperature range from 180 to 640 °C, which may be due to decomposition of the organically modified framework. The loss centered at higher temperature should be attributed to desorption of several organic species. A third slight mass loss in TG curve of about 0.94%, is also found in the temperature range from 680 to 800 °C, which corresponds to the water loss caused the weight loss also, as a result of the condensation of the silanol groups.

Nitrogen adsorption and desorption isotherms and BJH pore size distribution of MCM-41, MCM(PA)-41 and MCM(Pd)-41 catalyst are presented in Fig. 8a and b. The results obtained for analysis of textural characteristics (BET surface area, average pore size and pore volume) of the samples are given in Table 1.

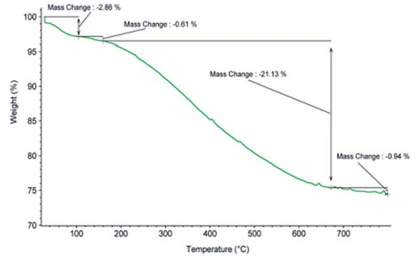


Fig. 7 Thermogravimetric analysis of the MCM(Pd)-41.

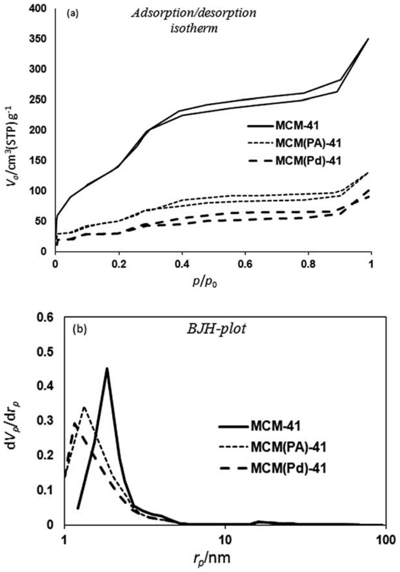


Fig. 8 (a) N_2 adsorption–desorption isotherms of MCM-41, MCM(PA)-41, MCM(Pd)-41. (b) The BJH pore size distribution calculated from the desorption branch of the isotherms of MCM-41, MCM(PA)-41, MCM(Pd)-41.

As shown in this Table, the Schiff-base-modification caused the decrease in the S_{BET}, V_P and d_P, possibly due to the coverage of the pore wall of the MCM-41 by the Schiff-base-groups, which caused an increase in the wall thickness. The Pd-modification further decreased the S_{BET}, V_P and d_P, which could be easily understood by considering the coverage of the Pd particles on the outer surface, which may result in the blockage of the pore channels, and the occupation of Pd particles in the pore channels, which may increase the pore wall thickness.

Inductively coupled plasma optical emission spectroscopy (ICP/OES) analysis of the catalyst showed that the Pd content was about 4.3 wt% Pd in the systems.

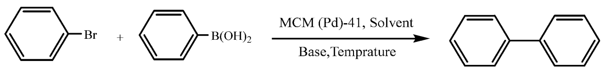
Suzuki cross-coupling reaction by MCM-(Pd)-41

In order to investigate the catalytic performance of MCM(Pd)-41 and the effect of media upon the reaction, we preliminary examined the model coupling reaction of bromobenzene with phenylboronic acid as test compounds. The effects of solvents, bases, reaction temperature and conditions on the yield were studied using non-solvent condition and various solvents such as DMSO, DMF, toluene and EtOH (Table 2). Comparison of the results clearly shows that the reaction in solvent-free conditions proceeded much better than in solvents with an excellent yield

Table 1 Textural properties of MCM-41 and MCM-41@Pd samples

No.	Sample	BET surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	Pore diameter (nm)
1	MCM-41	953.29	0.84	2.7
2	MCM(PA)-41	370	0.29	1.5
3	MCM(Pd)-41	227.32	0.23	1.3

Table 2 Optimization studies for reaction of bromobenzene and phenylboronic acid in the Suzuki reaction[a]



Entry	Base	Catalyst (g)	Solvent	T (°C)	Time	Yield[b] (%)
1	—	0.01	None	100	12 h	—
2	K_2CO_3	0.01	None	80	1 h	85
3	K_2CO_3	0.005	None	100	1 h	82
4	K_2CO_3	0.01	None	100	45 min	90
6	K_2CO_3	0.01	DMF	130	6 h	78
7	K_2CO_3	0.01	DMSO	130	6 h	73
8	K_2CO_3	0.01	Toluene	Reflux	6 h	55
9	K_2CO_3	0.01	EtOH	Reflux	6 h	60
10	KOAc	0.01	None	100	1 h	80
11	NaOH	0.01	None	100	1 h	84
12	DABCO	0.01	None	100	1 h	55
13	n-Pr_3N	0.01	None	100	1 h	40

[a] Reaction conditions: 1 mmol of bromobenzene, 1.5 mmol of phenylboronic acid, base (2 mmol), catalyst. [b] Isolated yield.

and shorter reaction time. Also, various bases were examined and it was found that the catalyst was very active and selective for the reaction in the presence of K_2CO_3.

As seen in this table, it was noticed that, the reaction worked out best at 100 °C under solvent-free conditions using a (0.01 g) catalyst using K_2CO_3 as base (90%, entry 4). This achievement encouraged us to extend the scope of the reaction to a variety of aryl halides and aryl boronic acids under the optimized conditions in the Suzuki reaction (Table 3).

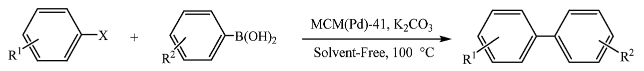
The ability to recover and reuse is another aspect that was investigated for this catalyst. The reaction of phenylboronic acid and bromobenzene as the model was chosen. After separating the catalyst from the reaction, it was washed, dried and then directly carried forward to the next reaction. As shown in Table 4, it was noticed that the recovered catalyst was recycling in subsequent runs without observation significant decrease in activity even after tenth run.

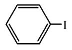
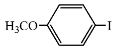
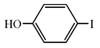
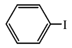
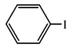
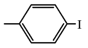
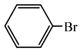
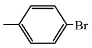
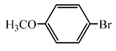
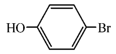
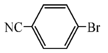
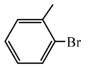
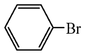
Mizoroki–Heck cross-coupling reaction catalyzed by MCM-(Pd)-41

The MCM(Pd)-41 catalyst were also used for a good rang of Heck reactions where the reaction of bromobenzene with styrene was used as the model reaction. Various solvent, base, temperature and catalyst loading were investigated in mentioned reactions. The obtained optimized reaction conditions are presented in Table 5.

As seen in Table 5, the reaction worked out best at 130 °C under solvent-free conditions using a (0.005 g) catalyst using n-Pr_3N as base (92%, entry 4). The reaction was then investigated with different aryl halides with styrene and n-butyl acrylate esters at the determined optimized conditions and the results are summarized in Table 6.

Table 3 Suzuki reaction of aryl boronic acids with aryl halides[a]



Try	Ar^1X	Boronic acid	Time (h)	Yield[b] (%)
1		$PhB(OH)_2$	20 min	92
2		$PhB(OH)_2$	30 min	90
3		$PhB(OH)_2$	4 min	85
4		$PhB(OH)_2$	30 min	90
5		$4\text{-}NO_2C_6H_4B(OH)_2$	15 min	95
6		2-Naphthyl$B(OH)_2$	1 h	90
7		2-Naphthyl$B(OH)_2$	1 h	80
8		$PhB(OH)_2$	45 min	90
9		$PhB(OH)_2$	1 h	86
10		$PhB(OH)_2$	1 h	87
11		$PhB(OH)_2$	1 h	90
12		$PhB(OH)_2$	40 min	91
13		$PhB(OH)_2$	2 h	85
14		$4\text{-}NO_2C_6H_4B(OH)_2$	40 min	92

[a] Reaction condition: MCM(Pd)-41 (0.01 g), aryl halide (1 mmol), aryl boronic acid (1.5 mmol) and K_2CO_3 (2 mmol) under solvent free conditions. [b] Isolated yield.

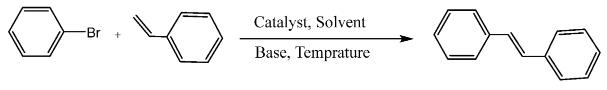
Experimental

Chemicals used in this work were purchased from Fluka, Lancaster, Aldrich and Merk chemical companies and used without further purification. 1H NMR spectra were measured for samples using a BRUKER DRX-300 AVANCE instrument at 300.13 and 75.47 MHz respectively, using Me_4Si as internal

Table 4 Recycling of the Pd-functionalized MCM-41 nanoporous silica as the catalyst in Suzuki reaction of bromobenzene with phenylboronic acid

	Cycle									
	1	2	3	4	5	6	7	8	9	10
Yield (%)	90	90	88	87	85	83	81	80	80	78

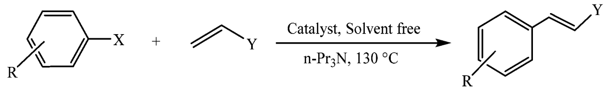
Table 5 Optimization studies for reaction of bromobenzene with styrene in the Heck reaction[a]

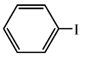
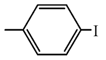
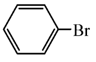
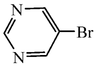
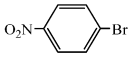
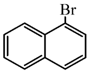
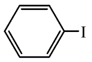
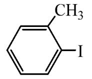
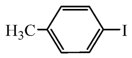
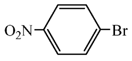
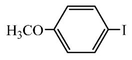
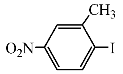
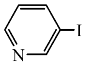
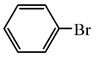
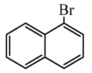
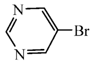


Entry	Base	Catalyst (g)	Solvent	T (°C)	Time (h)	Yield[b] (%)
1	—	0.005	None	130	24 h	—
2	n-Pr$_3$N	0.005	None	120	1 h	84
3	n-Pr$_3$N	0.002	None	130	0.5	82
4	n-Pr$_3$N	0.005	None	130	0.5	92
5	n-Pr$_3$N	0.008	None	130	0.5	93
6	n-Pr$_3$N	0.005	DMF	130	5 h	82
7	n-Pr$_3$N	0.005	DMSO	130	5 h	78
8	n-Pr$_3$N	0.005	Toluene	Reflux	12 h	Trace
9	n-Pr$_3$N	0.005	H_2O	Reflux	12 h	20
10	n-Pr$_3$N	0.005	EtOH	Reflux	12 h	Trace
11	KOAc	0.005	None	130	3 h	75
12	NaOH	0.005	None	130	3 h	61
13	DABCO	0.005	None	130	3 h	88
14	Et$_3$N	0.005	None	130	3 h	45

[a] Reaction conditions: 1 mmol of bromobenzene, 1.5 mmol of styrene, base (2 mmol) and catalyst. [b] Isolated yield.

Table 6 Heck reaction of aryl halides with n-butyl acrylate or styrene[a]



Entry	ArX	Y	Time (h)	Yield[b] (%)
1		Ph	20 min	95
2		Ph	3 h	84
3		Ph	30 min	92
4		Ph	4 h	80
5		Ph	4 h	91
6		Ph	10 h	84
7		–CO$_2$Bu-n	30 min	92
8		–CO$_2$Bu-n	4 h	87
9		–CO$_2$Bu-n	4 h	90
10		–CO$_2$Bu-n	1 h	88
11		–CO$_2$Bu-n	4 h	82
12		–CO$_2$Bu-n	1 h	87
13		–CO$_2$Bu-n	1 h	88
14		–CO$_2$Bu-n	1.5 h	91
15		–CO$_2$Bu-n	12 h	6
16		–CO$_2$Bu-n	6	82

[a] Reaction condition MCM(Pd)-41 (0.005 g), aryl halide (1 mmol), n-butyl acrylate (1.5 mmol) or styrene (1.5 mmol) and n-Pr$_3$N (2 mmol) under solvent free conditions. [b] Isolated yield.

standard. Melting points were measured on a SMPI apparatus. The products were characterized by X-ray powder diffraction (XRD) on Holland Philips X-pert diffractometer (Cu Kα = 1.5418 Å). The FT-IR spectra were recorded on a Thermo Scientific NICOLET IR100 FT-IR Spectrometer. The pellets made with KBr and the catalysts were prepared before the analyses. Inductively coupled plasma (ICP) data are provided by Varian vista-PRO. The textural surface properties of the samples were determined by physical adsorption–desorption of N_2 at −196 °C using a BELSORP-mini II (Bel Japan). Before the measurements, the samples were degassed at 150 °C for 1 h. The specific surface area and the pore size distribution were calculated by the Brunauer–Emmett–Teller (BET) and Brunauer–Joyner–Hallenda (BJH) methods, respectively. The field emission scanning electron microscopy (FESEM) analysis was carried out using a Philips XL-300. TEM images were taken using a Hitachi H 7600 TEM. The corresponding energy-dispersive X-ray (EDAX) spectrum was obtained on a Holland Philips XL30 microscope instrument. Thermogravimetric analysis (TG) was performed using PL-STA 1500 apparatus with the rate of 10 °C min^{-1} under flowing compressed N_2. X-ray photoelectron spectroscopy (XPS) was carried out by Dual anode (Mg and Al K alpha) achromatic X-ray source.

Preparation of MCM(Pd)-41 catalyst

Preparation of MCM-41 and inclusion of amine groups into MCM-41. Mesoporous MCM-41 silica was prepared by the method as described elsewhere.[27] MCM-41 (1.0 g) and 3-aminopropyltriethoxysilane (ATES) (1.0 mL) in dry toluene (20 mL) were taken in a 50 mL round bottom flask and was stirred at reflux for 12 h under Ar atmosphere. The white solid was removed from the solvent by filtration, washed with toluene and chloroform, and dried at room temperature (MCM(NH$_2$)-41).

(a) Preparation of 2,2′-(propane-1,3-diylbis(oxy))-dibenzaldehyde (PA). 1,3-Dibromo propane (0.1 mol) and NaOH (0.2 mol) were mixed and heated under reflux in 500 mL ethanol at 100 °C.

Salicylaldehyde (0.2 mol) in 30 mL ethanol was added and heated under reflux for 4 days. After the cooling, the resulting yellow crystals were filtered, washed and recrystallized.[28]

(b) Preparation of MCM-supported 2,2′-(propane-1,3-diylbis(oxy))-dibenzaldehyde (MCM(PA)-41). MCM(NH_2)-41 (1.0 g) was suspended in 15 mL of dry methanol and a solution of 0.1 g 2,2′-(propane-1,3-diylbis(oxy))dibenzaldehyde in 5 mL dry methanol was added. Then was refluxed for 24 h under Ar atmosphere. The solid was filtered, washed (3 × 10 mL) with methanol and then dried under vacuum.

(c) Preparation of palladium catalyst. MCM(PA)-41 (1.0) g was suspended in 15 mL of dry methanol and $Pd(OAc)_2$ (0.1 g) in dry methanol (5 mL) was added and the mixture was refluxed for 24 h under Ar atmosphere. The solid was filtered, washed (3 × 10 mL) with methanol and then dried under vacuum.

Application of catalyst for Suzuki reaction

A mixture of aryl halide (1.0 mmol), aryl boronic acid (1.5 mmol), K_2CO_3 (2.0 mmol), and MCM(Pd)-41 (0.01 g) are placed in a mortar. The reaction mixture was then heated at 100 °C for an appropriate time (Table 3) until the completion of the reaction was achieved as monitored by TLC. EtOAc (10 mL) was added to the mixture, stirred for 5 min and filtered to separate the catalyst. Then, water (3 × 15 mL) was added to the ethylacetate phase and decanted. The organic layer was dried over anhydrous Na_2SO_4. After evaporation of the solvent, the resulted crude products were purified by column chromatography (hexane/ethylacetate) giving the pure products in excellent yields.

Application of catalyst for Mizoroki–Heck reaction

A mixture aryl halide (1.0 mmol), *n*-butyl acrylate (1.5 mmol) or styrene (1.5 mmol), n-Pr_3N (2.0 mmol) and MCM(Pd)-41 (0.005 g) are placed in a mortar. The reaction mixture was then heated at 130 °C for an appropriate time (Table 6) until the completion of the reaction was achieved as monitored by TLC. EtOAc (10 mL) was added to the mixture, stirred for 5 min and filtered to separate the catalyst. Then, water (3 × 15 mL) was added to the ethylacetate phase and decanted. The organic layer was dried over anhydrous Na_2SO_4. After evaporation of the solvent, the resulted crude products were purified by column chromatography (hexane/ethylacetate) giving the pure products in excellent yields.

Conclusion

In conclusion, we have developed a novel approach for the preparation of supported Pd organometallic catalyst by using the Schiff-base functionalized MCM-41 as the support. MCM(Pd)-41 catalyst exhibited high activity and selectivity, as well as strong durability in Suzuki and Mizoroki–Heck cross-coupling reactions under solvent-free conditions, without using any Ar or N_2 flow. We have successfully applied 2,2′-(propane-1,3-diylbis(oxy))dibenzaldehyde as a cheap and easily prepared ligand for preparation of Schiff-base functionalized MCM-41. Also, various bases were examined in Suzuki and Mizoroki–Heck cross-coupling reactions, and it was found that the catalyst was very active and selective for the reactions in the presence of K_2CO_3 and n-Pr_3N, respectively. Moreover, the easy extractive recovery of the final product, and the solid residue can be reused for several times, can be considered as strong practical advantages of this method. This methodology could provide a facile, efficient, and environmentally friendly process for the Suzuki and Mizoroki–Heck cross-coupling reactions because of its wide applicability to various substrates, the use of less toxic reagents, and mild reaction conditions. High surface area and recyclability of the Pd-functionalized MCM-41 mesoporous silica, solvent-free conditions, high yields products, low catalyst loadings, stability toward air and short reaction times in many cases are comparable with other heterogeneous C–C coupling reactions.

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