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Magnetically recoverable nanostructured Pd complex of dendrimeric type ligand on the MCM-41: Preparation, characterization and catalytic activity in the Heck reaction

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Abstract: A palladium complex of a dendrimer type ligand of aminoethylacrylamide immobilized onto the mesoporous channels of MCM-41 with magnetic core was prepared and characterized using various techniques such as XRD, TEM, BET, FT-IR, TGA, and VSM. The prepared nanostructured material was found as a magnetically recoverable catalyst for Heck reaction of aryl halides and vinylic C–H. The catalyst is easily recoverable with an external magnet and is reusable with different leaching amounts depending to loading of Pd. A hot filtration test was also performed and gave evidence that Palladium in heterogeneous samples can dissolve and then redeposit on the surface of the support material.

Keywords: dendrimer ligand; palladium complex; MCM-41; Fe_3O_4 ; Heck reaction; reusable catalyst

1 Introduction

Palladium catalyzed Heck-type vinylation of aryl halides is one of the most important and versatile tool for carbon-carbon coupling reaction in the field of synthetic organic chemistry including natural products, pharmaceuticals, liquid crystals and heteroarenes (Gruber-Woelfler et al., 2012). Generally, Heck reaction is catalyzed by homogeneous palladium phosphine

complexes, while, these types of catalysts suffer from several disadvantages associated with the separation of the expensive palladium, reusability, instability at high temperature and toxicity of phosphine ligands (Liu et al., 2015). To overcome difficulties caused by homogeneous catalysts, in recent decades, heterogeneous catalysts have been developed. Among them, many heterogeneous catalysts containing Palladium have been designed and used in organic transformations (Tarahomi et al., 2019; Veisi et al., 2015a). Recently, many heterogeneous catalysts containing palladium which, Pd nanoparticles or complexes are involved as active catalyst sites have been used as catalyst in Heck reaction including polymer supported Pd complex (Schwarz et al., 2000), modified silica supported Pd complex (Clark et al., 2000), Pd anchored to layered double hydroxide (Choudary et al., 2002), Pd(II) salen complex covalently anchored to multi-walled carbon nanotubes (Movassagh et al., 2015), Pd(0)-complex supported on boehmite nanoparticles (Ghorbani-Choghamarani et al., 2016), Pd(0)-S-methylisothiurea grafted onto mesoporous MCM-41 (Noori et al., 2016), ferromagnetic nanoparticle-supported palladium complex (Bahrami et al., 2017), Pd salen complex@cpgo (Ghabdian et al., 2018), $\text{Fe}_2\text{O}_3@\text{SiO}_2-(\text{CH}_2)_3\text{-Pdtc-Pd}$ (Tashrifi et al., 2019) Pd nanoparticles inside the pores of Zif-8 (Azad et al., 2019), Pd–ninhydrin immobilized on magnetic nanoparticles (Hajjami and Shirvandi, 2020), $\text{Bnps}@\text{SiO}_2(\text{CH}_2)_3\text{NH-CC-Amp-Pd}$ (0) (Khodamorady and Bahrami, 2020), Palladium anchored on guanidine-terminated magnetic dendrimer (Niknam et al., 2020), Palladium complex supported on MCM-41 (Nikoorazm et al., 2020). Among them, silica support is highly regarded because of some advantages such as availability, excellent stability and ability of robust anchoring of organic moiety for providing catalyst site.

Mesoporous silica, is a very widely used support, due to bearing a very high surface area and uniform array

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of hexagonal channels (Abdollahi-Alibeik and Heidari-Torkabad, 2012; Abdollahi-Alibeik and Rezaeipoor-Anari, 2016; Hashemi-Uderji et al., 2018b). Moreover, silanol groups on the surface of MCM-41 are useful for immobilization of organic modifiers (Abdollahi-Alibeik and Pouriaeyevali, 2011). Linkage of modifier with the silanol groups onto the inner surface of hexagonal channels can provide active catalytic sites and therefore hexagonal channels of MCM-41 can act as nanoreactor. Recently, a wide variety of transition metal complexes have been anchored on the surface of MCM-41 and have been applied as catalysts in various organic transformations (Chang et al., 2013; Gao et al., 2015).

Dendrimers are particularly well-suited for hosting metal nanoparticles because the dendrimer templates are of fairly uniform composition and structure, and therefore they yield well-defined nanoparticle replicas (Crooks et al., 2001). Immobilizing of metal complex of dendrimeric ligands on the solid supports is of practical importance due to the ability of loading a large amounts of metal ions on the surface of the support, as well as their recoverability and reusability (Isfahani et al., 2013). Many dendrimer functionalized solid support have been used as heterogeneous catalysts in organic reactions such as SO_3H -dendrimer functionalized magnetic nanoparticles (Maleki et al., 2019), HPA-dendrimer functionalized magnetic nanoparticles (Jamshidi et al., 2018), magnetic multi-walled carbon nanotubes functionalized with polyamidoamine (PAMAM) dendrimers (Adibian et al., 2020), dendritic chiral auxiliaries on silica (Chung and Rhee, 2002; Gharibpour et al., 2017; Isfahani et al., 2013; Tarahomi et al., 2019). MCM-41-supported copper-complexed dendrimer (Gharibpour et al., 2017), Pd

nanoparticles on the ternary hybrid system of graphene oxide, Fe_3O_4 nanoparticles, and pamam dendrimer (Tarahomi et al., 2019), Ce(IV) immobilized on halloysite nanotube-functionalized dendrimer (Ataee-Kachouei et al., 2020).

Although, these heterogeneous catalysts are easily recoverable by simple filtration, however, some nanoparticles may remain in the reaction media. To overcome this problem many magnetically recoverable catalysts have been improved (Abdollahi-Alibeik et al., 2015; Kazemi and Mohammadi, 2020). Due to coupling with organic ligands such as dendrimeric type support and inorganic compounds such as silica, Fe_3O_4 nanoparticles has been used as magnetic core in the preparation of magnetic separable catalysts such as Palladium immobilized on amidoxime-functionalized magnetic Fe_3O_4 nanoparticles (Veisi et al., 2015b), multifunctional magnetic core-shell dendritic mesoporous silica nano spheres (Sun et al., 2016), magnetic iron oxide/phenylsulfonic acid (Elhamifar et al., 2018), magnetic mesoporous MCM-41 supported boric acid (Ramazani et al., 2019), Fe_3O_4 -AMPD-Pd (Tamoradi et al., 2018), Fe_3O_4 @FSM-16- SO_3H (Hashemi-Uderji et al., 2018a) and pyridine-2-carboimine copper(I) complex immobilized on Fe_3O_4 @MCM-41 (Moaddeli and Abdollahi-Alibeik, 2018).

However, due to importance of recovery and reusability of solid catalysts, improvement of new magnetically recoverable catalytic system is also desirable.

In this research, our strategy is developing a heterogeneous catalyst by immobilizing a dendrimeric type ligand on the surface of MCM-41 (MMNP, Scheme 1) with various loading amounts of palladium and application of metal complex in Heck reaction in order

Scheme 1: Steps of preparing the MMNP catalyst.

to study of the catalytic activity and also leaching of Pd (Scheme 2).

2 Result and discussion

2.1 The catalyst characterization

MCM-41 with magnetic core (MNPs) was prepared according to the presented method in Scheme 1, and functionalization with dendrimer type ligand and then a complexation was carried out according to presented method in Scheme 1. To confirm successful functionalization of the synthesized MNPs@MCM-41, the MMNP catalyst was characterized using FT-IR spectroscopy in the range of 400–4000 cm^{-1} and the corresponding spectra are shown in Figure 1. MNPs@MCM-41 shows characteristic peaks at 806, 1082 and 1240 cm^{-1} linked to stretching bands of Si–O–Si and the peak at 461 cm^{-1} linked to bending Si–O–Si (Figure 1a). In this spectrum, the characteristic peaks around 585 and 630 cm^{-1} can be assigned to Fe–O bands. The presence of stretching and bending peaks of aliphatic C–H and N–H bonds (the peaks at 2940, 1495, and 1560 cm^{-1}) in the MNPs@MCM-41-NH₂ (Figure 1b) spectrum in comparison

to the MNPs@MCM-41 spectrum (Figure 1a) confirms successful modification of MNPs@MCM-41 surface by APTMS. The reaction between amino group of 3-amino-propyltrimethoxysilane (APTMS) and terminal alkene of ethyl acrylate has formed on the MNPs@MCM-41-NH₂. Formation of this bond was confirmed by FT-IR spectra of MNPs@MCM-41-NH₂ with a characteristic band at 1736 cm^{-1} (Figure 1c). After the formation of the amide group, carbonyl peak of this group is appeared at 1653 cm^{-1} in MNPs@MCM-41-NE₂-EDA spectrum (Figure 1d). This carbonyl peak is shifted to 1657 cm^{-1} in the spectrum of palladium complex (Figure 1e). This result confirms

Scheme 2: Heck reaction in the presence of the MMNP catalyst.

Scheme 3: Catalyst preparation.

Figure 1: FT-IR spectra of: (a) MNPs@MCM-41, (b) MNPs@MCM-41-NH₂, (c) MNPs@MCM-41-NE₂, (d) MNPs@MCM-41-NE₂-EDA, (e) MMNP.

formation of complex between Pd and amide ligand on the MCM-41.

The FT-IR spectra of reused catalyst after the first run to the third run were studied to investigate effect of possible leaching of Pd from ligand and also possible deformation of ligand (Figure 2). Results show that all of main peaks of the ligand remained unchanged. The carbonyl peak in 1657 cm^{-1} is unchanged in all three spectra. This result confirms that there is not significant leaching of Pd from the ligand.

Low angle powder X-ray diffraction (XRD) patterns of all samples: pure MCM-41 (a), MNPs@MCM-41 (b) and MMNP (c) were displayed in Figure 3. The XRD analysis

Figure 2: FT-IR spectra of the recycled catalyst after: (a) first run, (b) second run, and (c) third run.

Figure 3: Low angle XRD pattern of: (a) MCM-41, (b) MNPs@MCM-41, and (c) MMNP.

of MCM-41 revealed three characteristic Bragg reflections peaks at low angle pattern ($2\theta = 2^\circ$ – 6°). The presence of these three Bragg reflexes can be indexed highly ordered pore system with a high porosity in a hexagonal mesoporous structure of MCM-41, corresponding to d_{100} , d_{110} , and d_{200} planes at $2\theta = 2.4^\circ$, 4.0° , and 4.6° , respectively (Figure 3a). On the other hand, an overall decreased intensity, some broadened reflections of d_{100} and a decrease in 2θ based on the Bragg's equation (an increase in the d-spacing) are observed at low angle XRD pattern of MNPs@MCM-41 (Figure 3b) compared to pure MCM-41, which are due to the decrease in ordered structure degree of hexagonal mesostructures after incorporation of magnetic iron oxide into the MCM-41 framework. At low angle XRD pattern of MMNP (Figure 3c) compared to Fe_3O_4 @MCM-41, the organometallic functionalization of palladium complex dendrimer reduces the intensity of d_{100} , increases the d-spacing and shifts it to the higher angle ($2\theta = 1.84^\circ$), corresponded to blockage of the mesoporous channels by palladium complex dendrimer. These changes often observed in mesoporous silica materials.

High-angle powder X-ray diffraction (XRD) patterns of all samples: MNPs (a), pure MCM-41 (b), MNPs@MCM-41 (c) and MMNP (d) were illustrated in Figure 4. There are reflection peaks at $2\theta = 30^\circ$, 36° , 43° , 57° , 63° , and 74° in the XRD patterns of MMNP (Figure 4d), which is observed at pure Fe_3O_4 (Figure 4a) and MNPs@MCM-41 (Figure 4c), indexed to the pure stoichiometric Fe_3O_4 structure. The low molar ratio of MNPs in the support ($\text{Si/Fe} = 119/1$) caused low intensity MNPs peaks at XRD patterns. The broad peak at the range of $2\theta = 14^\circ$ – 31° is indicated to the amorphous silica network.

The transmission electron microscopy (TEM) image of MMNP was shown in Figure 5. TEM image of MMNP shows that the ordered hexagonal mesoporous structure of MCM-41 channels is remained unchanged

Figure 4: High angle XRD pattern of: (a) MNPs, (b) MCM-41, (c) MNPs@MCM-41, and (d) MMNP.

after organometallic functionalization on the MMNP (Figures 5a,b). The MNPs anchored onto the MCM-41 can be detected in Fig 5c.

The superparamagnetic behavior of FMNC was confirmed by magnetization curves of MNPs@MCM-41 and MMNP (Figure 6). The magnetic hysteresis loops were accomplished by an applied magnetic field at room temperature (300 K). There was no apparent hysteresis

Figure 5: TEM image of MMNP: (a) mesoporous channels of MCM-41, (b) MNPs anchored onto MCM-41 and (c) A 28-nm magnetic core.

Figure 6: Magnetization curves of: (a) MNPs@MCM-41 and (b) MMNP.

detected, zero coercivity and remanence on the loop of magnetization, suggesting that both of MNPs@MCM-41 and MMNP exhibited a superparamagnetic feature. The magnetic saturation values of MNPs@MCM-41 and MMNP were 4.05 emu/g and 2.50 emu/g (Figures 6a,b), respectively. There was some decrease in saturation magnetization value after surface modification of MNPs@MCM-41 (MMNP, Figure 6b), in comparison with MNPs@MCM-41 (Figure 6a), which confirms modified organic matter on the MNPs@MCM-41 surface and relative low mass ratio of MNPs in the MMNP sample. The isolation of the MMNP was achieved using an external permanent magnet beside the reactor wall, making the resumption of the MMNP very straightforward, which is necessary for magnetic separation (Figure 7).

The mesoporous structure of MNPs@MCM-41 was confirmed by nitrogen adsorption-desorption isotherms. In this isotherms a sharp inflection at $p/p^\circ = 0.2-0.4$ is related to the nitrogen capillary condensation in the uniform mesopores, which confirms the mesoporous structure of synthesized MNPs@MCM-41. A sharper hysteresis was observed at higher p/p° ($p/p^\circ > 0.8$) related to the nitrogen condensation within the formed voids by nanoparticles (Figure 8a). Figure 8b shows the nitrogen adsorption-desorption isotherms of the MMNP catalyst that a mesoporous inflection was not observed at the medium p/p° partial pressure region ($p/p^\circ = 0.2-0.4$). This means that organic matters occupied the inner voids of the MMNP@MCM-41. According to the obtained results from N_2 sorption, the surface area (S_{BET}), pore volume (V_{pore}), and pore diameter (D_{pore}) of MMNP@MCM-41 are 783.24 m²/g, 1.00 cm³/g, and 7.4 nm, respectively. There is some decrease amount of S_{BET} and V_p in Table 2 which identified cavities filling by organic matter.

The thermal stability of the MMNP was studied by thermogravimetric analysis (TGA). TGA measurement was conducted by the heating of 47 mg MMNP sample in

Figure 7: Isolation of MMNP by employing an external field.

the range of 25–800°C (Figure 9). TGA curve presents two exothermic peaks in the range of 25–280°C and 280–700°C. The exothermic peak at 25–280°C contains 7.4% weight loss which corresponded to the removal of physically adsorbed moisture and other solvents. The second exothermic peak at 280–700°C contains 17% weight loss can be assigned to the decomposition of organometallic dendrimer on the surface of MMNP@MCM-41. According to the TGA curve, organometallic dendrimer on the MMNP@MCM-41 surface can be thermally stable up to 280°C.

2.2 Catalytic activity

The catalytic performance of MMNP catalyst was investigated in the reaction of *p*-bromonitrobenzene and ethyl acrylate as a model reaction. The results summarized in Tables 3 and 4. The reaction was carried out under the

optimum conditions using various Pd loading, catalyst amount, solvents, bases, temperatures and the reacting components ratios.

The effect of the palladium loading on the catalytic activity of MMNP was studied by using the catalyst with different loading amounts of Pd with mass ratios of ligand: PdCl₂ = 100:5, 100:10, 100:15 and 100:20 in the Heck model reaction for three runs (Table 3). As shown in Table 3, MMNP with loading mass ratio of ligand: PdCl₂ = 100:10 had the best catalytic behavior rather than other loading mass ratios in terms of reaction time and palladium loss percent after third runs. In the loading mass ratio of ligand: PdCl₂ = 100:5, the reaction was not complete at all, so the palladium amount in this loading was not enough for this reaction (Table 3, entry 1). In 100:10 loading, the reaction time is 1.5 times in the second cycle, also palladium loss percent after second cycle is about 9.4%, which is negligible compared to the fresh catalyst (Table 3, entry 2). While for the 100:15 and 100:20 loading, the reaction times are 8.4 and 14 times respectively in the second cycle, and palladium loss percent after second cycle is about 9.1 and 7.6%, respectively, compared to the fresh catalyst (Table 3, entries 3 and 4). The reaction times at 100:15 and 100:20 fresh catalysts were better than 100:10, but the reaction times after second cycle for 100:15 and 100:20 were worse than 100:10, while the palladium loss for 100:15 and 100:20 after second cycle were less than 100:10. These results suggest that a part of palladium chloride used in the construction of 100:15 and 100:20, formed complexes at MMNP catalyst and

Figure 8: N₂ adsorption-desorption isotherms of: (a) MNPs@MCM-41 and (b) MMNP.

Figure 9: Thermogravimetric analysis of: (a) MMNP and (b) magnification of MMNP thermogravimetric analysis.

Table 1: d-spacing calculation of MCM-41, MNPs@MCM-41 and MMNP.

Entry	Sample	2θ (°)	d-spacing (nm)*
1	MCM-41	2.4	3.8
2	MNPs@MCM-41	1.72	5.1
3	MMNP	1.84	4.8

$$* d_{100} = n\lambda / 2\sin \theta, (n = 1, \text{Fix } \lambda (\text{Cu } K\alpha) = 1.54 \text{ \AA}).$$

Table 2: Textural properties of MNPs@MCM-41 and MMNP samples.

Entry	Sample	d _p BJH ^a (nm)	S _{BET} ^b (m ² /g)	V _p ^c (cm ³ /g)
1	MNPs@MCM-41	1.97	783.2	1.00
2	MMNP	2.06	175.7	0.49

^a Pore diameter according to the maximum of the BJH desorption pore size distribution.

^b BET Surface Area.

^c Single point adsorption total pore volume.

Table 3: Screening of various catalyst loading in the Heck reaction.^a

Entry	Ligand:PdCl ₂ mass ratio (mg)	Reaction cycle	Pd mol% before reaction	Pd mol% after reaction	Time (min)	Yield (%) ^b
1	100:5	Fresh	0.1	0.06	Over night	24
		1	0.06	0.03	Over night	24
		2	0.03	0.02	Over night	20
2	100:10	Fresh	0.85	0.82	60	95
		1	0.82	0.79	75	95
		2	0.79	0.77	90	91
3	100:15	Fresh	0.88	0.84	25	95
		1	0.84	0.81	90	97
		2	0.81	0.80	210	91
4	100:20	Fresh	0.92	0.90	10	95
		1	0.90	0.88	100	94
		2	0.88	0.85	140	90

^a The reaction was carried out with aryl halide (1 mmol), olefine (2.5 mmol), TEA (3 mmol), DMF (1 mL), and MMNP (20 mg) as catalyst at 130°C under an air atmosphere.

^b Isolated yield.

the excess palladium chloride have been settled on the catalyst surface. So the Heck reaction in the presence of 100:15 and 100:20 was done with palladium-complex and free palladium particles at fresh catalyst and after the first run, free palladium particles deactivated and still existed on the catalyst surface so it seems less palladium loss in the loading mass ratios of ligand: PdCl₂ = 100:15 and 100:20 rather than 100:10 (Table 3, entries 2-4).

After selecting the best loading of palladium chloride on dendrimer ligand (ligand: PdCl₂ = 100:10), the reaction was carried out under the optimum conditions using various catalyst amount, solvents, bases, temperatures, and the reacting components ratios using model reaction (*p*-bromonitrobenzene with ethyl acrylate as the model reaction). The solvents had significant effects on the MMNP catalytic activity. Among the different polar and nonpolar solvents (H₂O, CH₃CN, CH₃CN:H₂O, DMF, DMF:H₂O, and toluene) or solvent-free condition; the polar solvent such as dimethylformamide (DMF) gave higher yield than nonpolar solvent such as toluene (Table 4, entries 2-9) and solvent-free condition was not appropriate (Table 4, entry 1). Amount of DMF also affected on the product yield. As shown in Table 4 (entries 8 and 26-29), with decreasing DMF amount from 4 mL to 0.5 mL, it was observed that the suitable amount of DMF is 1 mL. The bases (such as TEA, Na₃PO₄, K₃PO₄, and K₂CO₃) used in the Heck reaction had great influences on the MMNP catalytic activity. As shown in Table 4 (entries 8 and 10-13) the organic base

(TEA) gave a better result than inorganic bases (Na₃PO₄, K₃PO₄ and K₂CO₃), whereas, there is no reaction progress in the absence of base. Interesting results were obtained by changing in the amount of base. The use of lower or more than 3 mL TEA, caused weakening in the MMNP catalytic activity (Table 4, entries 8 and 14-18). When the Heck reaction was accomplished at different temperatures in the presence of MMNP, it was found that temperature at 130°C is the best. The Heck reaction in the absence of the catalyst was not carried out at all. Notwithstanding, the amounts of 10 and 20 mg of MMNP showed good results for the Heck reaction and 40 mg of the catalyst had negative effect on the Heck reaction. At first it seemed that 2 mg is the optimal amount of the catalyst, but was not enough for other derivatives, so finally; 10 mg MMNP (0.42 mol% palladium) was selected as the optimal amount of the catalyst (Table 4, entries 8 and 22-25). The ethylacrylate usage in amount of 2, 2.5 and 3 mmol (as an olefin) was studied in Heck reaction and as shown in Table 4 (entries 24, 30, and 31) the amount of 1:2.5 mmol of aryl halide:olefin was the best reacting component ratio. More interestingly, reaction atmosphere changing from inert to air had better effect on MMNP catalytic activity (Table 4, entry 24 and 32).

To investigate the application of MMNP as catalyst in Heck reaction, a variety of olefins were coupled with different aryl halides in the presence of 10 mg MMNP (0.42 mol% palladium) using TEA as a base in DMF.

Table 4: Screening of various parameters for the Heck reaction.

Entry	MMNP (mg:mol% Pd)	Solvent (mL)	Ethylacrylate (mmol)	Base (mmol)	Temp (°C)	Time (h)	Yield (%)
1	20:0.85	—	2.5	TEA (3.0)	70	6	0 ^a
2	20:0.85	H ₂ O (1) ^b	2.5	TEA (3.0)	Reflux	24	5 ^a
3	20:0.85	Toluene (1)	2.5	TEA (3.0)	Reflux	4	30 ^a
4	20:0.85	CH ₃ CN (1)	2.5	TEA (3.0)	Reflux	24	30 ^a
5	20:0.85	CH ₃ CN:H ₂ O (2:1)	2.5	TEA (3.0)	90	7:30	45 ^a
6	20:0.85	CH ₃ CN:H ₂ O (1:1)	2.5	TEA (3.0)	90	6:30	50 ^a
7	20:0.85	CH ₃ CN:H ₂ O (1:2)	2.5	TEA (3.0)	90	6:30	50 ^a
8	20:0.85	DMF (1)	2.5	TEA (3.0)	130	1	95 ^b
9	20:0.85	DMF:H ₂ O (1:1)	2.5	TEA (3.0)	90	24	20 ^a
10	20:0.85	DMF (1)	2.5	—	130	24	0 ^a
11	20:0.85	DMF (1)	2.5	Na ₃ PO ₄ (3.0)	130	24	97 ^c
12	20:0.85	DMF (1)	2.5	K ₃ PO ₃ (3.0)	130	24	77 ^c
13	20:0.85	DMF (1)	2.5	K ₂ CO ₃ (3.0)	130	24	67 ^c
14	20:0.85	DMF (1)	2.5	TEA (2.0)	130	2	97 ^c
15	20:0.85	DMF (1)	2.5	TEA (2.5)	130	1	81 ^c
16	20:0.85	DMF (1)	2.5	TEA (2.8)	130	1:30	95 ^c
17	20:0.85	DMF (1)	2.5	TEA (3.5)	130	2	93 ^c
18	20:0.85	DMF (1)	2.5	TEA (4.0)	130	2	10 ^a
19	20:0.85	DMF (1)	2.5	TEA (3.0)	110	24	93 ^c
20	20:0.85	DMF (1)	2.5	TEA (3.0)	120	3	87 ^c
21	20:0.85	DMF (1)	2.5	TEA (3.0)	140	1	90 ^c
22	—	DMF (1)	2.5	TEA (3.0)	130	5	0 ^a
23	2:0.085	DMF (1)	2.5	TEA (3.0)	130	3	97 ^c
24	10:0.42	DMF (1)	2.5	TEA (3.0)	130	2:15	95 ^c
25	40:1.7	DMF (1)	2.5	TEA (3.0)	130	1	90 ^c
26	10:0.42	DMF (4)	2.5	TEA (3.0)	130	5	90 ^c
27	10:0.42	DMF (3)	2.5	TEA (3.0)	130	3:30	93 ^c
28	10:0.42	DMF (1.5)	2.5	TEA (3.0)	130	2:30	95 ^c
29	10:0.42	DMF (0.5)	2.5	TEA (3.0)	130	1	87 ^c
30	10:0.42	DMF (1)	2.0	TEA (3.0)	130	2:50	93 ^c
31	10:0.42	DMF (1)	3.0	TEA (3.0)	130	2:30	95 ^c
32	10:0.42	DMF (1)	2.5	TEA (3.0)	130	3	40 ^d

^a Reaction progress with TLC (*n*-hexan:ethylacetate 80:20 as eluent) under air atmosphere.^b Reaction was carried out in the presence of 10 mol% SDS.^c Isolated yield, under air atmosphere.^d Reaction progress with TLC (*n*-hexan:ethylacetate 80:20 as eluent) under argon atmosphere.

These results are illustrated in Table 5. Aryl bromide with electron-donating groups has excellent yield compared with aryl bromide with electron-withdrawing groups and their activity were NO₂ > CHO > H > CH₃ > OCH₃ (Table 5, entries 1, 4 and 8-10). Halobenzene activities were I > Br > Cl

(Table 5, entries 6, 8 and 11). The order of activity for olefins is ethyl acrylate > acrylonitrile > styrene (Table 5, entries 1-7). The scope of the procedure was also investigated using aliphatic halides as starting material. Results show that alkyl halides react with olefins as well as aryl halides

Table 5: The Heck reaction of various alkyl and aryl halides and olefins in the presence of MMNP as a catalyst.

Entry	Aryl halide (1)	Olefine (2)	Product (3) ^a	Time (h:min)	Yield (%) ^b
1				2:15	95
2				24	98
3				2:15	91
4				1	90
5				3:15	91
6				0:30	98

Continued

Table 5: continued

Entry	Aryl halide (1)	Olefine (2)	Product (3) ^a	Time (h:min)	Yield (%) ^b
7				1	98
8				12	90
9				24	60
10				36	65
11				15	No reaction
12				3:30	90
13				4:45	95
14				4	90
15				6:30	90

Continued

Table 5: continued

Entry	Aryl halide (1)	Olefine (2)	Product (3) ^a	Time (h:min)	Yield (%) ^b
16				7	93

^a The reaction was carried out with aryl halide (1 mmol), olefine (2.5 mmol), TEA (3 mmol), DMF (1 mL) and MMNP (10 mg, 0.42 mol% palladium) as catalyst at 130°C under an air atmosphere.

^b Isolated yield.

and high yields of products have been achieved (Table 5, entries, 12-16).

The reuse of the MMNP catalyst was investigated in the Heck coupling reaction of *p*-bromonitrobenzene with ethyl acrylate as a model reaction. After completion of the reaction (monitored by TLC; eluent: EtOAc:*n*-hexane, 20:80) MMNP catalyst could be easily separated from reaction mixture using an external permanent magnet, washed with warm ethanol (3 × 3 mL) and dried at 100°C for 1 h, then reused in the model reaction at the same reaction condition. The results of reusability study are demonstrated in Table 6. As shown in Table 6 (entries 1-3), it was found that there is a low increase in the reaction time and low decrease in the product yield. These results suggest that the palladium leaching of MMNP catalyst can be ignored. To confirm this issue, the Pd loading of the recovered catalyst after second cycle was determined using atomic absorption spectroscopy and 0.38 mol% palladium was detected (Table 6, entry 3). Thus, 9.5% of Pd leaching (Table 6, the difference between entries 1 and 3) is a reason for ignored deactivation of the catalyst after the second cycle. It is noticeable that after each run, the catalyst easily and completely was separated by external magnet and there were no problems due to the reduction of magnetic properties.

The general methods for the leaching study is hot filtration test or split test. Especially in the case of the Heck reaction, how the reaction starts with a solid catalyst has received a great deal of attention. In principle, the two discussed possibilities were that either the reaction is catalyzed by a heterogeneous surface mechanism or that dissolved palladium, which is generated by metal leaching (Bucsi et al., 2017).

To improve the understanding of the dynamic leaching process under Heck reaction conditions, Köhler et al. (2002) reported that a large amount of Pd was dissolved into the solvent during the Heck coupling of chloroarenes and then the Pd species were redeposited on the surface of the support material. After further investigation, it was demonstrated that palladium is dissolved simultaneously

with the start of the reaction, the highest reaction rate matches the highest palladium concentration in solution, and palladium is redeposited on the support again after the reaction is completed (Gnad et al., 2020; Heidenreich et al., 2002; Zhao et al., 2002). It has been confirmed that solid palladium catalysts act as reservoirs for active Pd species in solution and the dissolved Pd species tend to readsorb onto the support after the reaction has been completed.

In the present study, in order to investigate whether the MMNP catalyzed Heck reaction takes place based on the heterogeneous surface or due to Palladium leaching from MMNP, we accomplished hot filtration test to differentiate between heterogeneous and homogeneous activity based on the comparison of observed results before and after MMNP catalyst separation using an external permanent magnet in the reaction temperature. The reaction was interrupted at 30 min and then the filtrate was collected from the hot reaction mixture. The reaction was then conducted for another 105 min using the filtrate in the absence of the solid catalyst. Results show that after removal of the solid catalyst, the reaction mixture retained its activity and after 135 min, the reaction was split at a conversion of 30%. This may be related to the presence of active dissolved Pd.

It may be established that the results of the hot filtration test were in accordance with those of the recycling experiments (Table 1). The atomic absorption spectroscopy data for palladium amount in MMNP after the general Heck reaction (Table 6, entry 1) shows that the palladium leached is about 2.4% that is negligible. As shown in Table 1, compare of the Pd loading on the fresh catalyst and reused catalyst after run 1 and also run 2, show that there is not considerable leaching. This result and also result of hot filtration confirms that Palladium in heterogeneous samples can dissolve and then redeposit on the surface of the support material.

We recommend that the MMNP catalyst is superior in terms of palladium consumption amount compared to some other catalysts that had been used in the Heck

reaction. A comparative study of the MMNP catalytic activity with other reported heterogeneous palladium base in Heck reaction is reported in Table 7. The results show that our work in terms of reaction time, yield and the palladium consumption amount is superior to the other catalysts. Furthermore, other advantages of our method are lack of usage of an inert atmosphere and moderate reaction temperature, with respect to the others. However, it should be emphasized that the results reported in Table 7 were obtained under very different reaction conditions and therefore the results could not be compared correctly.

3 Conclusion

Finally, we have introduced a new magnetically recyclable catalyst with magnetite core and dendrimeric palladium complex on the MCM-41 ($\text{Fe}_3\text{O}_4\text{@MCM-41-NE}_2\text{-EDA-Pd}$ (MMNP), $\text{Si:Fe}_3\text{O}_4 = 40:1$, loading mass ratio of ligand: $\text{PdCl}_2 = 100:10$). The catalyst is efficient in the Heck reaction at 130°C in DMF as solvent. The catalyst leaching was studied

for various loading of ligand: PdCl_2 and results showed less leaching for 100:10 ratio and also mild decrease in activity for this sample. High products yields, simple workup and easy recovery of the catalyst are some advantages of this catalyst.

Experimental

Material and methods

All chemicals were commercial and used as revived. Progress of the reactions were determined by thin layer chromatography and all yields refer to isolated products. NMR spectra for ^1H and ^{13}C were recorded on a Bruker DRX-400 AVANCE (400 MHz for ^1H and 100 MHz for ^{13}C) spectrometer in CDCl_3 . The melting point of solid products were determined by Buchi melting point model B-540. Infrared spectra of all products and the catalyst were recorded on a Bruker FT-IR Equinox 55 spectrophotometer in KBr disks. Thermogravimetric analysis (TGA) was performed using a thermal gravimetric analysis

Table 6: Recovery and reuse of MMNP for the Heck reaction.

Entry	Catalyst	Pd mol% before reaction	Pd mol% after reaction	Time (h)	Yield (%) ^a
1	Fresh	0.42	0.41	2:15	95
2	Cycle 1	0.41	0.39	3:00	95
3	Cycle 2	0.39	0.38	3:40	91

^a Isolated yield.

Table 7: The comparative study of MMNP catalytic activity with other catalyst in Heck reaction.

Entry	Catalyst	Pd mol%	Temp ($^\circ\text{C}$)	Solvent	Time (h)	Yield (%) ^a	Reference
1	MMNP	0.42	130	DMF	2:15	95	This work
2	$\text{Pd-DABCO-}\gamma\text{-Fe}_2\text{O}_3$	1	100	Solvent-free	3	84	(Sobhani and Pakdin-Parizi, 2014)
3	$\text{HMMS-NH}_2\text{-Pd}$	4	130	NMP	8	>99	(Wang et al., 2014)
4	MNP@NHC-Pd	0.56	140	DMF	22	72	(Wilczewska and Misztalewska, 2014)
5	Si-PNHC-Pd	0.5	120	NMP	5	90	(Tamami et al., 2013)

^a Isolated yield.

instrument (STA 504 thermo-gravimetric analyzer) in the temperature range of 50–800°C (10°C/min). Transmittance electron microscopy (TEM) analysis was performed on a Zeiss-EM10C – 80 KV was used to obtain TEM images. XRD patterns were recorded by a Bruker D8 ADVANCE X-ray diffractometer using nickel filtered Cu K α radiation (λ = 1.5406 Å). The magnetic measurement of samples was carried out in a vibrating sample magnetometer VSM-4 inh, Daghigh Meghnatis Kashan Co at room temperature. Pd loading and leaching tests were carried out with an Atomic Absorption Spectroscopy (AAS) Analyticjena spectrometer model novAA 300. The pore analysis and BET surface area were performed on a micromeritics model ASAP2020 by N $_2$ physical adsorption–desorption at 77.4 K. Samples were degassed at 120°C under flowing nitrogen for 2 h. The pore size distribution was calculated by the Barret-Joyner-Halenda (BJH) method. The specific surface area (S_{BET}) was calculated from the adsorption data using the BET equation.

Preparation of palladium complex catalyst

Preparation of Fe $_3$ O $_4$ (MNPs)

The Fe $_3$ O $_4$ magnetic nanoparticles (MNPs) was readily prepared by co-precipitation of ferrous and ferric ions in a basic solution. Generally, FeCl $_2$ ·4H $_2$ O (1.52 g, 8 mmol) and FeCl $_3$ ·6H $_2$ O (4.24 g, 16 mmol) were dissolved in deionized water (100 mL) under vigorous stirring using a mechanical stirrer at 60°C for about 30 min. Then the pH was changed to basic by slow addition of ammonia solution (30 mL, 25%) and the mixture became black immediately. The stirring was continued for about 30 min and the black precipitate (MNPs) was collected using a permanent magnet at the bottom of the flask and washed with deionized water (3 × 30 mL). The synthesized MNPs was dried at 80°C in an oven for 3 h.

Hydrothermal preparation of MNP@MCM-41

Synthesis of magnetic MCM-41 was carried out via the hydrothermal method using Fe $_3$ O $_4$ (MNPs) as a magnetic nanoparticle agent, cetyltrimethylammonium bromide (CTAB) as the template, tetraethylorthosilicate (TEOS) as the silica source and ammonia as the pH control agent with the gel composition of Fe $_3$ O $_4$:H $_2$ O:CTAB:SiO $_2$:NH $_4$ OH = 0.025:480:0.127:1:1.26. At first, MNPs (0.132 g, 0.568 mmol) was dispersed in deionized water (200 mL) using ultrasound, followed by the slow addition of CTAB (1.04 g, 2.67 mmol) to the obtained suspension with stirring and the temperature was adjusted to 70°C. Tetraethyl orthosilicate

(5 mL, 22.6 mmol) was added dropwise to this suspension and then allowed to cool to ambient temperature. The micellar template was generated by hydrolysis of the precursor compound using aqueous ammonia to adjust the pH of the suspension up to 10 under vigorous stirring. The gel was transferred to a Teflon lined stainless steel autoclave and heated for 18 h at 120°C for hydrothermal treatment. The gel was collected by centrifugation and washed with deionized water (2 × 100 mL) and ethanol (2 × 100 mL). After filtration and washing, the MNP@MCM-41 was dried in an oven at 120°C for 2 h and the template was removed by calcination at 450°C for 6 h.

Preparation of palladium complex of dendrimer type ligand on magnetic MCM-41 (MMNP)

Post-synthesis organic modification of magnetic mesoporous materials was carried out by stirring a mixture of MNPs@MCM-41 (1 g) and 3-aminopropyltrimethoxysilane (APTMS) (1.075 g, 6 mmol) in CHCl $_3$ (10 mL) under reflux condition and inert gas for about 4 h. The resulting product (MNPs@MCM-41-NH $_2$, Scheme 3-II) was filtered, washed with CHCl $_3$ (3 × 3 mL) and dried at 70°C. The solid (1 g) was stirred with ethyl acrylate (400 mg, 4 mmol) in methanol (10 mL) at 50°C for 4 days and then was detached with an external magnet, washed with methanol (3 × 3 mL) and dried at 60°C for 1 h (MNPs@MCM-41-NE $_2$, Scheme 3-III). For lengthening the dendrimer chain, MNP@MCM-41-NE $_2$ (1 g) was reacted with ethylenediamine (300 mg, 5 mmol) and *p*-toluenesulfonic acid (246 mg, 1.4 mmol) in ethanol (10 mL) at 60°C for 2 days. The resulting material was detached with an external magnet, washed with ethanol (3 × 3 mL) and dried at 60°C for 1 h (MNPs@MCM-41-NE $_2$ -EDA, Scheme 3-IV). Finally the Pd-complex was synthesized by addition of MNPs@MCM-41-NE $_2$ -EDA (1 g) to a solution of palladium chloride (100 mg, 0.57 mmol) in ethanol:acetone:HCl (5 mL:5 mL:1 drop) and stirring of the mixture at ambient temperature for about 2 days. The resulting solid was detached with an external magnet, washed with ethanol (3 × 3 mL) and dried at 60°C for 1 h (MMNP, Scheme 3-V).

General procedure for the Heck reaction

A 5 mL round bottom flask was charged with MMNP (10 mg), an appropriate amount of DMF (1 mL), aryl halide (1.0 mmol), olefin (2.5 mmol) and TEA (303 mg, 3.0 mmol) and a magnetic stir bar. The mixture was stirred for an appropriate time under reflux condition. The reaction progress was monitored by TLC (*n*-hexane:acetone, 80:20 as eluent). After the reaction completion, the mixture

was cooled to ambient temperature and the catalyst was detached from the reaction mixture with an external magnet. The resultant remaining mixture was diluted with H₂O (9 mL) followed by extraction with chloroform (3 × 3 mL). The organic layer was dried over Na₂SO₄ and the solvent was evaporated under reduced pressure to obtain crude product. The corresponding pure products were obtained by preparative thin layer chromatography on silica gel using *n*-hexane:ethylacetate (95:5) as eluent or by recrystallization (ethanol:water).

Physical and spectroscopic data for selected compounds

Ethyl (E)-3-(4-nitrophenyl)acrylate: Yield: 95%, cream solid, mp: 134–136°C (Lit: (Movassagh and Rezaei, 2015) 135–138°C). FT-IR (KBr); $\bar{\nu}$ (cm⁻¹): 979 (C–H *trans*-alkene bend.), 1030 (C–O), 1341 (NO₂ symmetric), 1517 (NO₂ asymmetric), 1450 and 1597 (C=C aromatic), 1645 (C=C alkene), 1713 (C=O Ester), 2851, 2936, 2984 (C–H aliphatic), 3079 (C–H alkene stretch.), 3108 (C–H aromatic stretch.). ¹H NMR (500 MHz, CDCl₃): δ (ppm) = 1.39 (t, 3H, *J* = 7.0 Hz, CH₃), 4.33 (q, 2H, *J* = 7.0 Hz, CH₂), 6.59 (d, 1H, *J* = 16.5 Hz, CH), 7.72 (d, 2H, *J* = 8.5 Hz, Ar–H), 7.62 (d, 1H, *J* = 16.5 Hz, CH), 8.28 (d, 2H, *J* = 8.5 Hz, Ar–H). ¹³C NMR (125 MHz, DMSO-*d*₆): δ (ppm) = 14.98, 61.27, 123.29, 124.74, 130.27, 141.32, 142.60, 148.89, 166.51.

(E)-1-Nitro-4-styrylbenzene: Yield: 98%, Orang solid, mp: 154–155°C, (Lit: (Farjadian et al., 2015) 155–157°C). FT-IR (KBr); $\bar{\nu}$ (cm⁻¹): 970 (C–H *trans*-alkene bend.), 1344 (NO₂ symmetric), 1509 (asymmetric), 1447, 1591 (C=C aromatic), 1631 (C=C alkene), 3076 (C–H alkene stretch.), 3102 (C–H aromatic stretch.). ¹H NMR (250 MHz, CDCl₃): δ (ppm) = 8.6 (d, 2H, *J* = 7.5 Hz, *p*-Ar–H), 7.57 (d, 2H, *J* = 7.5 Hz, *p*-Ar–H), 7.49 (d, 2H, *J* = 7.5 Hz, Ar–H), 7.26–7.36 (m, 3H, Ar–H), 7.21 (d, 1H, *J* = 15.0 Hz, CH), 7.07 (d, 1H, *J* = 15.0 Hz, CH). ¹³C NMR (62.50 MHz, CDCl₃): δ (ppm) = 143.8, 133.3, 128.9, 128.8, 128.7, 127.0, 126.9, 126.4, 124.1, 121.9.

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