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FULL PAPER

Pd(0)-guanidine@MCM-41: a very effective catalyst for rapid production of bis (pyrazolyl)methanes

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In this research, a rapid, green and efficient protocol for synthesis of bis (pyrazolyl)methane derivatives in the presence of Pd(0)-guanidine@MCM-41 catalysts under solvent-free conditions by the following two methods has been reported: (i) via the one-pot pseudo five-component reaction among phenylhydrazine (2 equivalents), ethyl acetoacetate (2 equivalents) and aromatic aldehydes (1 equivalent); and (ii) the one-pot pseudo three-component reaction between 3-methyl-1-phenyl-1H-pyrazol-5(4H)-one (2 equivalents) and aromatic aldehydes (1 equivalent). Some advantages of this protocol include: green conditions, extremely short times, high efficiency, proper one-pot operation, generality of method, easy work-up and recyclability, and reusability of the catalyst up to five times without significant loss in catalytic activity.

KEYWORDS

bis (pyrazolyl)methanes, heterogeneous catalyst, multi-component reaction, Pd(0)-guanidine@MCM-41, reusable catalyst

1 | INTRODUCTION

Nanocatalysis is one of the most exciting subfields to have emerged from nanoscience.[1–7] Its central aim is the control of chemical reactions by changing the size, dimensionality, chemical composition and morphology of the reaction center, and by changing the kinetics using nanopatterning of the reaction centers.[8–12] Nanoparticles can substitute conventional materials, and serve as active and stable heterogeneous catalysts or as support materials for various catalytic groups.[13–18] Due to their small sizes, catalytic-active nanoparticles have higher surface areas and increased exposed active sites, and thereby improved contact areas with reactants, akin to those of homogeneous catalytic systems.[19–23]

Preparation of chemical, industrial and pharmaceutical compounds by multi-component reactions (MCRs) is very significant in consideration of combinatorial chemistry.[21,24,25] In this technique, more than two starting materials react together in a one-pot reaction to form a product wherein all or most of the reactants atoms contribute.[26–29] That is important from the atom economic standpoint.[30] Environmental friendly operation via reducing the number of synthetic steps and work up, the energy consumption, reaction time, waste production, and eliminating the isolation of unstable intermediates are among the advantages of MCRs.[20,21,31–34] Over the last few decades, with increasing environmental concerns, the design of new MCRs with ecofriendly, green procedures have become increasingly useful tools, especially in the fields of drug discovery, organic synthesis and material science.[35–37] Because of the increasing concern of the harmful effects of organic solvents on the environment and human body, organic reactions that are operated with green solvents or without conventional organic solvents have aroused the attention of organic and medicinal chemists.[38–41] In the past decade, interest in solvent-free MCRs has expanded and it now encompasses wide areas of the chemical enterprise.[20,21,42–44] For reasons of economy and pollution prevention,

solvent-free methods are used to modernize classical procedures by making them cleaner, safer and easier to perform.[45–47] The demand for both clean and efficient chemical syntheses is becoming more urgent.[48] Among the proposed solutions, solvent-free conditions are becoming more popular, and it is often claimed that the best solvent is no solvent.[49] The benefits of solvent-free processes are cost savings, decreased energy consumption, reduced reaction times, a large reduction in reactor size and capital investment.[20,49]

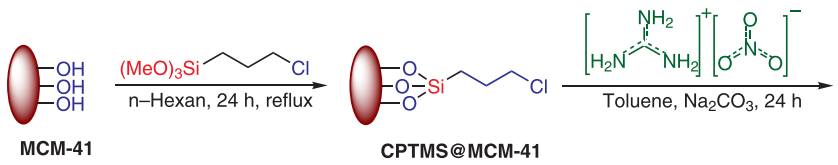
Pyrazoles or pyrazolones [e.g. bis (pyrazolyl)methanes] are a significant category of bioactive drug goals in the pharmaceutical industry that show a variety of biological and medicinal activities, such as anti-HIV,[50] antiviral,[51] gastric secretion stimulatory,[52] antifilarial,[53] antioxidant,[54] antihypertensive,[55] anticancer,[56] anti-inflammatory,[57] antimalarial,[58] antidepressant,[59] antimicrobial,[60] antipyretic[61] and antibacterial[62] properties. There are two ways to prepare bis (pyrazolyl)methanes: (i) the one-pot pseudo five-component reaction among phenylhydrazine, ethyl acetoacetate and aromatic aldehydes; and (ii) the one-pot pseudo three-component reaction between 3-methyl-1-phenyl-1H-pyrazol-5(4H)-one and aromatic aldehydes. Rare reports of this method (i) compared with the second method (ii) are provided for preparing bis (pyrazolyl) methanes.

Now, in this report, palladium complex supported on the surface-modified MCM-41 nanoparticles [Pd(0)-guanidine@MCM-41] is introduced as a new and efficient reusable catalyst for the synthesize of bis (pyrazolyl)methanes, as a mesoporous recoverable nanocatalyst in solvent-free conditions and in a completely green environment by both methods via the following protocols: (i) the one-pot pseudo five-component reaction of phenylhydrazine (2 equivalents), ethyl acetoacetate (2 equivalents) and arylaldehydes (1 equivalent); and (ii) the one-pot pseudo three-component reaction of 3-methyl-1-phenyl-1H-pyrazol-5(4H)-one (2 equivalents) with arylaldehydes (1 equivalent).

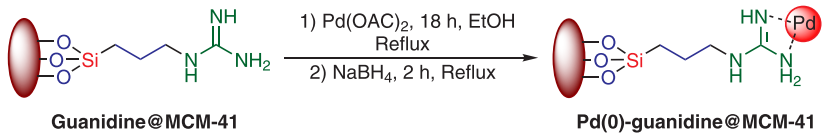
2 | EXPERIMENTAL

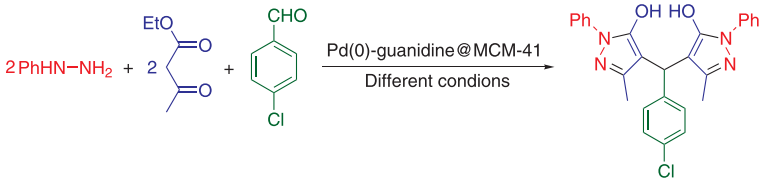
2.1 | Materials and apparatus

All starting materials, applied solvents and reagents were purchased from Fluka, Sigma-Aldrich or Merck Chemical Companies. The structures of the known compounds were recognized by the comparison of their NMR data/melting points with those reported in the literature. Thin-layer chromatography (TLC) was utilized for the observation of the reaction progress. Bruker Avance DPX FT-NMR spectrometer was applied for running the ^{1}H-NMR (500 MHz) and ^{13}C-NMR (125.7 MHz) spectra. Büchi B-545 apparatus was used for measuring the melting points in open capillary tubes. The morphologies and particle sizes of samples were characterized by field emission-scanning electron microscopy (FE-SEM), model TESCAN MIRA3 LMH. A transmission electron microscope (TEM; model Philips CM200) was used to measure the size and shape of particles.



SCHEME 1 Synthesis of MCM-41@guanidine@-Pd(0)





SCHEME 2 The pseudo five-component preparation of bis (pyrazolyl)methanes model reaction

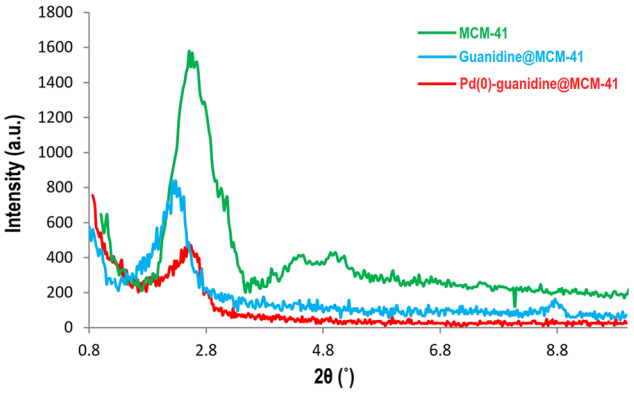


FIGURE 1 X-ray diffraction (XRD) patterns of (a) MCM-41, (b) guanidine@MCM-41 and (c) Pd(0)-guanidine@MCM-41

2.2 | Procedure for the production of Pd(0)-guanidine@MCM-41

The Pd(0)-guanidine@MCM-41 was synthesized according to the previously reported method.[63] For the synthesis of pure siliceous MCM-41, NaOH solution (3.5 ml of 2 M) was added to deionized water (480 ml) at 80°C. CTAB (1 g) was then added as the template. The resulting mixture was stirred at 80°C until the solution became uniform. TEOS (5 ml) was then slowly added, and the resulting solution was refluxed for 2 hr. The product was filtered off, washed with deionized water and dried in an oven at 50°C for 24 hr, followed by calcination at 550°C for 5 hr with a heating rate of 2°C/min. This procedure gave mesoporous MCM-41. Then the mesoporous MCM-41 functionalized with (3-chloropropyl)-trimethoxysilane (CPTMS @MCM-41) was prepared according to the reported procedure.[28] The above-mentioned solid (0.5 g) was refluxed with guanidine nitrate (2 mmol, 0.244 g) and sodium carbonate (2 mmol, 0.212 g) in toluene for 24 hr. The resulting solid (guanidine@MCM-41) was separated by simple filtration, washed with ethanol and dried at room temperature. Finally, to synthesize Pd(0)-guanidine@MCM-41, the guanidine@MCM-41 (0.5 g) was dispersed in ethanol and was mixed with 0.25 g of palladium acetate and refluxed for 18 hr. Then, $NaBH_4$ (0.4 mmol) was added to the reaction mixture and stirred for 2 more hours. The solid product was obtained by filtration, washed with ethanol and dried at 60°C in an oven (Scheme 1).[63]

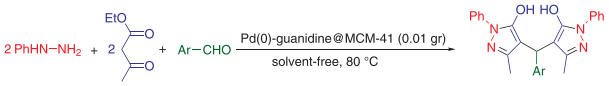
2.3 | General procedure for the synthesis of bis (pyrazolyl)methanes by the pseudo five-component reaction using Pd(0)-guanidine@MCM-41

In a 10-ml round-bottom flask, a mixture of phenylhydrazine (2 mmol), ethyl acetoacetate (2 mmol) and aldehyde(1 mmol) was stirred in the presence of Pd(0)-guanidine@MCM-41 (0.1 mol%) at 80°C under solvent-free conditions for an appropriate period of time (Scheme 2). After completion of the reaction (as monitored by TLC), and cooling the mixture to room temperature, EtOAc (10 ml) was added, and the reaction vessel was connected to a condenser, and stirred for 3 min under reflux conditions, followed by centrifugation and decantation to separate the nanocatalyst; the catalyst was washed with EtOH (2 × 4 ml), dried and used for the next run. The solvent obtained from decantation was evaporated, and the resulting precipitate was recrystallized from hot EtOH (95%) to give the pure product.

TABLE 1 The results of optimizing the catalyst quantity, temperature and solvent on the reaction of 4-chlorobenzaldehyde, phenylhydrazine and ethyl acetoacetate

Entry	Catalyst amount (mol%)	Temp. (°C)	Solvents	Time (min)	Yield[a] (%)
1	0.050	Reflux	–	14	72
2	0.075	Reflux	–	14	87
3	**0.1**	Reflux	–	14	98
4	0.1	Reflux	–	18	90
5	0.1	25	–	20	trace
6	0.1	50	–	20	67
7	0.1	70	–	20	82
8	0.1	Reflux	EtOH	40	97
9	0.1	Reflux	EtOAc	45	94
10	0.1	Reflux	CH_3CN	45	96

[a]Isolated yield.



SCHEME 3 Pd(0)-guanidine@MCM-41catalyzed the synthesis of bis (pyrazolyl)methanes

2.4 | General procedure for the synthesis of bis (pyrazolyl)methanes by the pseudo three-component reaction using Pd(0)-guanidine@MCM-41

A mixture of 3-methyl-1-phenyl-1H-pyrazol-5(4H)-one (2 mmol), aldehyde (1 mmol) and Pd(0)-guanidine@MCM-41 (0.1 mol%) was stirred at 80°C. After completion of the reaction (as monitored by TLC) and cooling the mixture to room temperature, EtOH (10 ml) was added, refluxed for 1 min, and the insoluble catalyst was separated by centrifugation and decanting [the catalyst was washed by EtOH (2 × 4 ml), dried and used for the next run]. The EtOH resulted from the decanting was evaporated, and the solid residue was recrystallized from EtOH (95%) to afford the pure product.

3 | RESULTS AND DISCUSSION

3.1 | Catalyst preparation

The presented work tries to describe a Pd-complex immobilized onto the MCM-41 as a reusable nanocatalyst. Initially, the modified MCM-41 nanoparticles with 3-choloropropyltriethoxysilane (CPTMS@MCM-41 NPs) have been prepared according to the reported procedure.[63] In order to prepare guanidine@MCM-41 NPs, guanidine has been grafted on CPTMS @MCM-41 NPs via substitution reaction of NH_2 with terminal Cl groups. Finally, the catalyst was synthesized by the reaction of guanidine@MCM-41with Pd $(OAc)_2$ (Scheme 1).

3.2 | Catalyst characterizations

The as-prepared Pd(0)-guanidine@MCM-41 was previously characterized as a novel mesoporous nanocatalyst in our laboratory using Fourier transform-infrared (FT-IR), scanning electron microscopy (SEM), energy-dispersive spectroscopy, Wavelength Dispersive X-ray (WDX), Brunauer–Emmett–Teller, TEM, thermal gravimetric analysis and inductively coupled plasma (ICP)

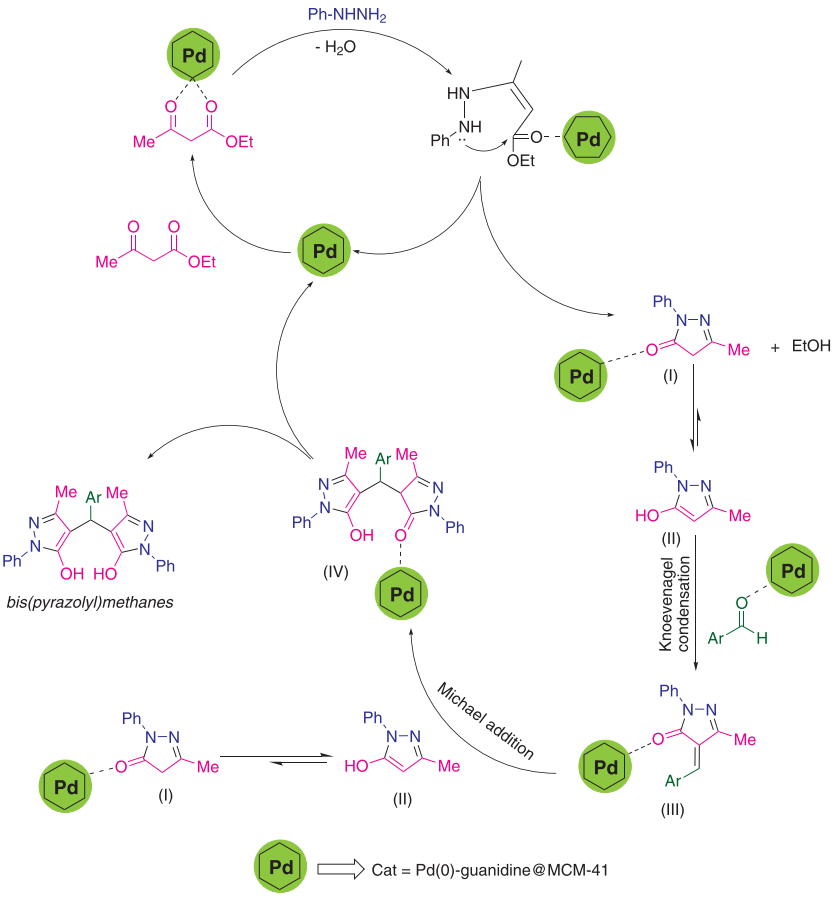
TABLE 2 The one-pot pseudo five-component production of bis (pyrazolyl)methanes using MCM-41@guanidine-Pd(0)

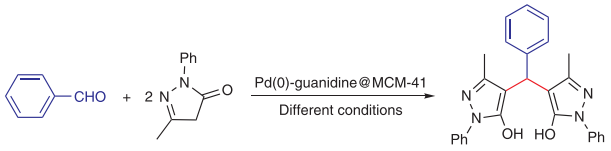
					Mp (°C)	
Comp. no	**Ar**	**Time (min)**	**Yield[a] (%)**	**TOF (min^{-1})**	**Found**	**Reported**
1	C_6H_5	15	95	63.333	165–167	166–168[66]
2	4-$O_2NC_6H_4$	17	91	53.529	230–228	229–231[66]
3	3-$O_2NC_6H_4$	18	90	50.000	149–151	148–150[66]
4	2-$O_2NC_6H_4$	17	93	54.705	220–222	221–223[67]
5	4-MeC_6H_4	20	91	45.500	197–199	198–200[66]
6	4-$MeOC_6H_4$	21	90	42.857	173–175	174–176[66]
7	3,4-$(MeO)_2C_6H_3$	27	86	31.851	191–193	191–193[66]
8	4-ClC_6H_4	14	98	70.000	209–211	208–210[66]
9	3-ClC_6H_4	17	93	54.705	150–152	151–153[66]
10	2-ClC_6H_4	15	95	63.333	241–243	240–242[66]
11	2,4-$(Cl)_2C_6H_3$	19	92	48.421	225–227	224–226[66]
12	4-FC_6H_4	20	91	45.500	175–177	175–177[67]
13	3-BrC_6H_4	21	90	42.857	173–175	172–174[67]
14	2-BrC_6H_4	22	89	40.454	252–254	251–253[66]
15[b]	4-$OHCC_6H_4$	30	84	28.000	212–214	213–216[68]

[a]Isolated yield.

[b]Reaction conditions: terephthalaldehyde (1 mmol), ethyl acetoacetate (4 mmol), phenylhydrazine (4 mmol), Pd(0)-guanidine@MCM-41 (0.1 mol%).

SCHEME 4 The suggested mechanism for the pseudo five-component preparation of bis (pyrazolyl)methanes





SCHEME 5 The pseudo three-component preparation of bis (pyrazolyl)methanes model reaction

techniques.[63] Our first goal in this report was to characterize more completely the Pd(0)-guanidine@MCM-41, so the catalyst characterizations were absolutely completed using the X-ray diffraction (XRD) technique.

XRD patterns of (a) MCM-41, (b) guanidine@MCM-41 and (c) Pd(0)-guanidine@MCM-41 are shown in Figure 1. As reported in previous works,[64,65] MCM-41 phase was identified from the XRD patterns by the three characteristic peaks related to the strong (100), smaller (110) and (200) reflections, which confirm the hexagonal pore arrangement of MCM-41. According to Figure 1, in the XRD patterns of the Pd(0)-guanidine@MCM-41, there were no well-resolved peaks corresponding to d_{100}, d_{200} and also the decrease in intensity of the peak at d_{100}, which are strong evidences revealing that the well-grafting of Pd complex into MCM-41 channels occurred.

3.3 | Catalytic studies

3.3.1 | Checking catalytic activity of Pd(0)-guanidine@MCM-41 for the synthesis of bis (pyrazolyl)methanes via the pseudo five-component reaction

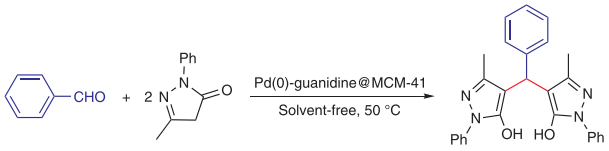
In early research to obtain optimal reaction conditions, the effect of temperature, solvent type and catalyst quantity was investigated on the condensation of phenylhydrazine (2 mmol), ethyl acetoacetate (2 mmol) and 4-chlorobenzaldehyde (1 mmol; Scheme 2). The reaction was examined at 70, 80 and 90°C, as well as under reflux conditions in ethanol, ethyl acetate and acetonitrile using 0.05, 0.075 and 0.1 mol% of Pd(0)-guanidine@MCM-41 on the basis of Pd. The best results were obtained in solvent-free conditions using 0.01 g Pd(0)-guanidine@MCM-41 at 80°C (Table 1, entry 3).

To appraise the performance and scope of the nanocatalyst, bis (pyrazolyl)methanes were synthesized by the condensation of phenylhydrazine, ethyl acetoacetate and aromatic aldehydes under the optimized reaction conditions (Scheme 3). As can be observed in this table, all aldehydes (containing benzaldehyde and arylaldehydes bearing halogens, electron-withdrawing

TABLE 3 The results of optimizing the catalyst quantity, temperature and solvent on the reaction of 4-chlorobenzaldehyde, 3-methyl-1-phenyl-1H-pyrazol-5(4H)-one

Entry	Catalyst amount (mol%)	Temp. (°C)	Solvents	Time (min)	Yield[a] (%)
1	0.05	60	–	5	98
2	0.075	50	–	5	98
3	**0.1**	**50**	–	**5**	**97**
4	0.1	40	–	18	79
5	0.1	Reflux	EtOH	40	94
5	0.1	Reflux	EtOAc	45	92
6	0.1	Reflux	CH_3CN	45	96

[a]Yield of isolated product.



SCHEME 6 The production of bis (pyrazolyl)methanes using Pd(0)-guanidine@MCM-41

groups and electron-donating groups) produced the desired derivative in a short time with high yields (Table 2). However, it is worth mentioning that the time process of the reaction of aldehydes with electron-donating groups was longer than aldehydes with electron-withdrawing groups.

The proposed mechanism for synthesis of bis (pyrazolyl)methanes using Pd(0)-guanidine@MCM-41 nanocatalyst[43] has been shown in Scheme 4. At the beginning of the reaction, palladium nanocatalyst activates carbonyl groups in the ethyl acetoacetate, and then phenyl hydrazine attacks the carbonyl groups to afford pyrazolone (I), and was further rearranged into tautomer (II). In the next step, a Knoevenagel-type of reaction takes place between activated aldehydes and tautomer (II) followed by the liberation of a water molecule to form intermediate (III). In the following, a Michael addition reaction between intermediate (III) and tautomer (II) is facilitated to form intermediate (IV). Finally, the corresponding products are formed by tautomerization and aromatization of intermediate (IV).

3.3.2 | Examining catalytic activity of Pd(0)-guanidine@MCM-41 for the synthesis of bis (pyrazolyl)methanes via the pseudo three-component reaction

After super performance of Pd(0)-guanidine@MCM-41 as catalyst in the synthesis of bis (pyrazolyl)methanes by the pseudo five-component reaction, our research team decided to evaluate its catalytic capability to accomplish the synthesis via pseudo three-component condensation. To this end, the reaction of 4-chlorobenzaldehyde (1 mmol) and 3-methyl-1-phenyl-1H-pyrazol-5(4H)-one (2 mmol) was considered as a model reaction (Scheme 5) and, like the previous method, the effects of temperature, solvent type and different values of the catalyst were tested by examining the reaction in the presence of 0.05, 0.075, 0.1 mol% of Pd(0)-guanidine@MCM-41 at 40, 50 and 60°C in solvent-free conditions, and also in some solvents (acetonitrile, ethyl acetate and ethanol). The best results were received in the absence of solvent at 50°C using 0.1 mol% Pd(0)-guanidine@MCM-41 (Table 3, entry 3).

In order to assess the generality and efficacy of Pd(0)-guanidine@MCM-41 for the production of bis (pyrazolyl)methanes, 3-methyl-1-phenyl-1H-pyrazol-5(4H)-one was reacted with arylaldehydes (with various substituents) under the optimal reaction conditions (Scheme 6). The results are summarized in Table 4. As the data in this table show, the nanocatalyst was general and highly efficient for the reaction; all aromatic aldehydes (containing electron-withdrawing substituents, electron-donating substituents and halogens) afforded the corresponding products in high yields within short reaction times.

The mechanism supported by the literature[44] for the synthesis of bis (pyrazolyl) methanes via the pseudo three-component reaction is illustrated in Scheme 7.

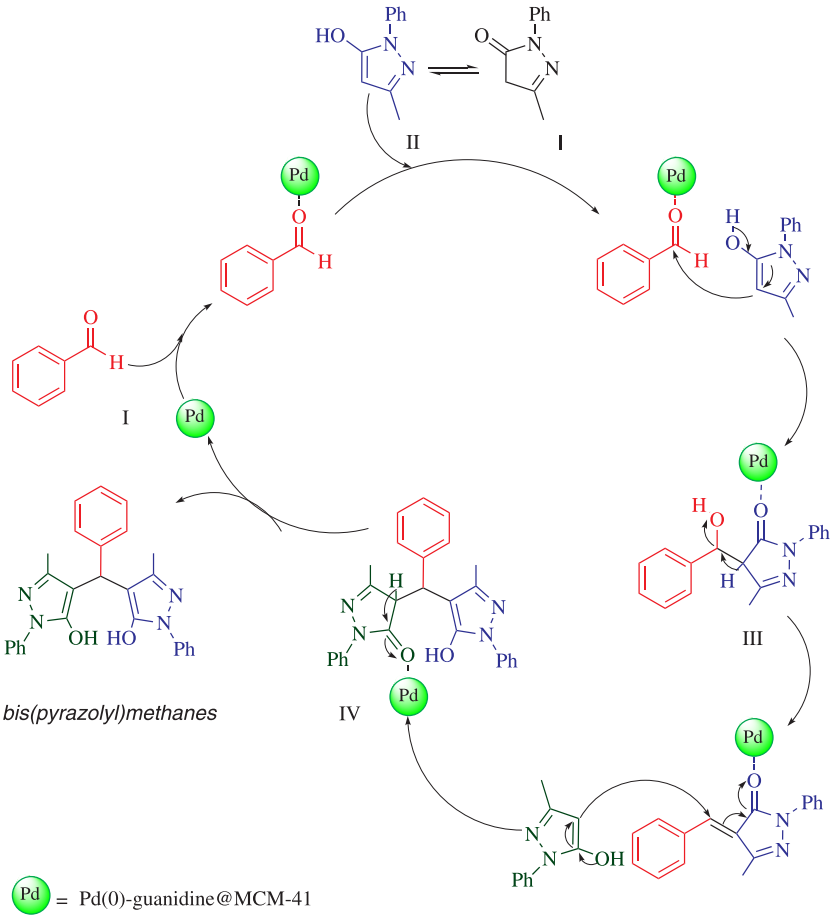
3.4 | Recyclability of the catalyst

The recovery capability of Pd(0)-guanidine@MCM-41 was considered for the synthesis of compound **8** in pseudo three-component condensation methods. The results showed that our catalysts were reusable in the pseudo three-component condensation (Figure 2) for six

TABLE 4 The one-pot pseudo three-component production of bis (pyrazolyl)methanes using Pd(0)-guanidine@MCM-41

Comp. no	Ar	Time (min)	Yield[a] (%)	TOF (min)	Mp (°C)	
					Found	Reported
1	C_6H_5	5	96	192	165–167	166–168[66]
2	4-$O_2NC_6H_4$	5	95	190	222–220	229–231[66]
3	3-$O_2NC_6H_4$	5	96	192	149–151	148–150[66]
4	2-$O_2NC_6H_4$	5	96	192	228–230	221–223[67]
5	4-MeC_6H_4	6	93	155	198–200	198–200[66]
6	4-$MeOC_6H_4$	7	92	131	175–177	174–176[66]
7	3,4-$(MeO)_2C_6H_3$	9	90	100	190–192	191–193[66]
8	4-ClC_6H_4	5	97	194	222–224	208–210[66]
9	3-ClC_6H_4	5	95	190	239–241	151–153[67]
10	2-ClC_6H_4	5	95	190	242–244	240–242[66]
11	2,4-$(Cl)_2C_6H_3$	7	93	186	207–209	224–226[66]
12	4-FC_6H_4	6	94	156	176–178	175–177[67]
13	3-BrC_6H_4	9	91	101	250–252	172–174[67]
14	2-BrC_6H_4	8	93	116	249–251	251–253[66]
15[b]	4-$OHCC_6H_4$	15	87	58	214–216	213–216[68]

[a]Isolated yield.
[b]Reaction conditions: terephthalaldehyde (1 mmol), 3-methyl-1-phenyl-1H-pyrazol-5(4H)-one (4 mmol), Pd(0)-guanidine@MCM-41 (0.1 mol%).



SCHEME 7 The suggested mechanism for the pseudo three-component preparation of bis (pyrazolyl)methanes

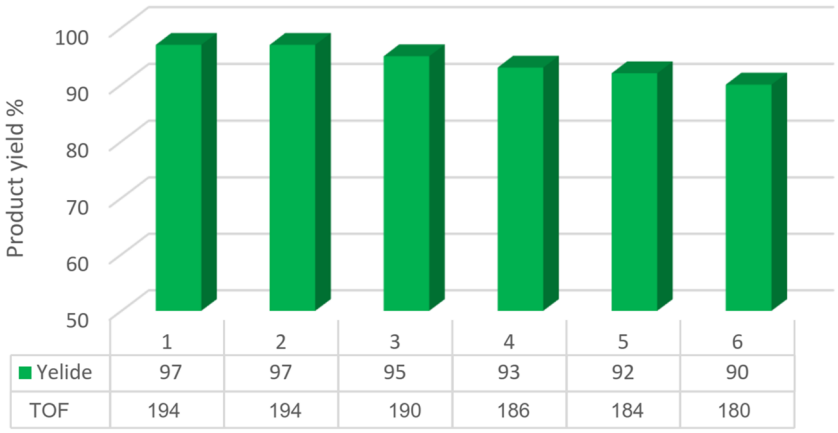


FIGURE 2 The recycling experiment of Pd(0)-guanidine@MCM-41 in the production of bis (pyrazolyl)methanes in the pseudo three-component condensation

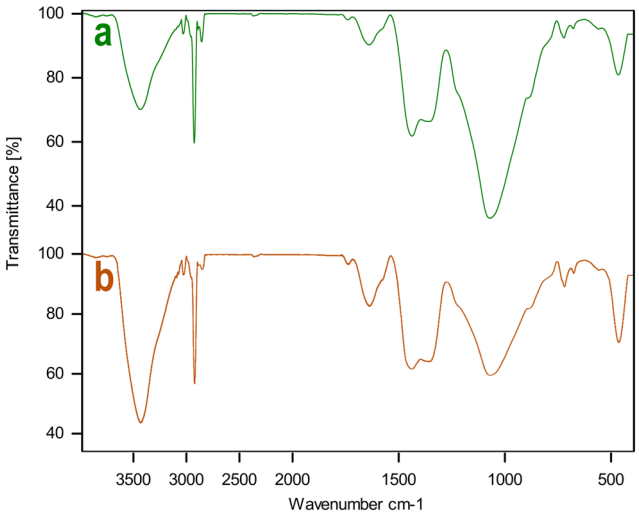


FIGURE 3 Fourier transform-infrared (FT-IR) spectrums of Pd(0)-guanidine@MCM-41 and recovered catalyst

times, with insignificant loss of activity. The nanocatalyst was recycled in both ways as described in the Experimental section.

Also, in order to examine the stability of the catalyst after recycling, the recycled catalyst has been characterized using the FT-IR technique.

The FT-IR spectrums of the recycled catalyst are shown in Figure 3. The results show that good agreement was observed for FT-IR of fresh Pd(0)-guanidine@MCM-41 (Figure 3a) and recycled catalyst (Figure 3b). Therefore, Figure 3 shows good stability of Pd(0)-guanidine@MCM-41 after recycling.

3.5 | Leaching study

In order to consider the leaching of Pd into the reaction media, ICP-atomic emission spectroscopy analysis was performed. In this sense, the palladium content in the reaction media and in the synthesis of product **7** was found to be 0.87%. The results show that the leaching of Pd during the reaction process is negligible.

3.6 | Comparison

In order to demonstrate the superiority of our catalyst to other reported catalysts for the synthesis of bis (pyrazolyl)methanes, the results of the reaction of 4-chlorobenzaldehyde with phenylhydrazine and ethyl acetoacetate for the pseudo five-component reaction

TABLE 5 Comparison results of Pd(0)-guanidine@MCM-41 with other catalysts reported in the literature

Catalyst	Conditions	Type of reaction	Time (min)	Yield (%)	TON	TOF (min^{-1})	Ref.
MCM-41@ guanidine-Pd(0)	Solvent-free, 80°C	i	14	98	75.3	5.38	–
MCM-41@ guanidine-Pd(0)	Solvent-free, 50°C	ii	5	97	74.6	14.92	–
Aspirin	EtOH/H_2O, 60°C	i	30	92	6.1	0.20	[69]
AP-SiO_2	CH_3CN, rt	ii	5	97	3.2	0.64	[70]
DCDBTSD	Solvent-free, 80 °C	i	40	80	8.0	0.20	[71]
$CuFe_2O_4$	Solvent-free, 80°C	i	8	96	24.0	3.00	[72]
[Pyridine–SO3H]Cl	Solvent-free, 50°C	ii	8	94	94	11.75	[73]
SASPSPE	EtOH, Reflux	ii	132	85	25	0.18	[74]
Ni-guanidine@MCM-41 NPs	Acetonitrile, 80°C	ii	20	90	11.2	0.56	[34]

(i) as well as the outcomes of the reaction of 4-chlorobenzaldehyde with 3-methyl-1-phenyl-1H-pyrazol-5(4H)-one for the pseudo three-component reaction (ii) are presented in Table 5. As it can be seen in Table 5, Pd(0)-guanidine@MCM-41 was better than the other catalysts in terms of two or more of these factors: TON, TOF, the reaction temperature, time and yield.

4 | CONCLUSION

In summary, we used Pd(0)-guanidine@MCM-41 as a heterogeneous and recyclable catalyst for the synthesis of bis (pyrazolyl)methane derivatives by the two following methods: (i) the one-pot pseudo five-component reaction of phenylhydrazine, ethyl acetoacetate and arylaldehydes; and (ii) the one-pot pseudo three-component reaction of 3-methyl-1-phenyl-1H-pyrazol-5(4H)-one with aromatic aldehydes. The advantages of this protocol are the use of excellent yields of the products, short reaction times, generality, cleaner reaction profile, ease of product isolation and relatively inexpensive reactants.

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