

Synthesis and characterization of MCM-41@L-Arginine@Pd(0) and its excellent catalytic activity as recyclable heterogeneous catalyst for Suzuki-Miyaura cross-coupling reaction

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Abstract

MCM-41@L-Arg@Pd(0) has been prepared by some consequent reactions. This nano structural material has been characterized by different techniques including; X-ray diffraction (XRD), TGA, BET, EDS, SEM, ICP-OES and FT-IR analysis. The synthesis of a variety of biphenyl compounds has been successfully achieved *via* a reaction of aryl halides with arylboronic acids in the presence of this nano structure (MCM-41@L-Arg@Pd(0)) as a green, mild, and versatile catalyst. Mild reaction conditions with excellent conversions of products and simple product isolation procedure are noteworthy advantages of this new methodology and catalyst. Recyclability and reusability of the newly synthesized catalyst make this protocol environmentally benign.

Keywords: Heterogeneous catalyst; MCM-41; L-Arginine; aryl halide; cross-coupling; arylboronic acid.

Introduction

Recently, nano structure mesoporous materials have attracted much attention for the development of catalytic and adsorption systems [24-27]. Mesoporous materials have often been functionalized by adding noble ligands to improve their physical and chemical properties [1]. The mesoporous materials are synthesized *via* the polymerization of silica around periodic cationic amphiphiles (MCM-41) [2,3]. Mesoporous silica has attracted widespread interest due to their high surface

area (up to 1000 m²/g), large pore volume, and a hexagonal array of uniform pores [4]. Due to their great porosity and uniform structure of MCM-41, access to the organo-functional groups as attached to the mesopore walls is easy [5-7] and causes fast transport of the target analyte to the binding sites. The nature of MCM-41 pore structure can be used to functionalize *via* reaction with organic compounds and then incorporate the metal complexes into the channel walls [8].

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The Suzuki-Miyaura cross-coupling reaction of aryl halides with arylboronic acids is one of the most powerful and convenient synthetic protocols and a versatile method for synthesizing variegated biaryls [9,10]. The Suzuki coupling reactions have been applied extensively in the synthesis of natural products, nucleoside analogues, and pharmaceuticals [11]. Also, biaryls are versatile intermediates in organic synthesis and a recurring functional group in many natural products and bioactive compounds [12]. As a result, considerable effort has been directed toward the development of efficient and selective methods for the synthesis of biaryls.

Palladium complexes are particularly effective catalysts for such cross-coupling reactions [13-17]. However, in most cases homogeneous palladium complexes are used as the catalysts. Although homogeneous palladium catalysts have proven to be efficient, they are expensive, air-sensitive and cannot be recovered from the products [18]. Heterogenization of the existing homogeneous Pd catalysts would be an attractive solution to this problem because of their easy separation and facile recycling.

Thus, our interest in this area has attracted us to explore the immobilization of Pd(OAc)₂ on the surface of MCM-41@L-Arg. Here, we report an efficient procedure for synthesizing of coverable MCM-41@L-Arg@Pd(0) nano catalyst for the Suzuki coupling reaction in a green medium (EtOH).

Experimental

General

Synthesis of MCM-41@L-Arg@Pd(0)

MCM-41 was prepared using the Sol-gel method described by a previous

report [19]. The functionalization of MCM-41 was carried out by stirring 1.0 g of MCM-41 and 2.0 g of L-Arginine, in deionized water (50 mL) under reflux conditions for 72 h. The resulting mixture was filtered, washed with a mixture of ethanol and deionized water several times and dried under vacuum. In the next step, the functionalized material (1 g) was mixed with Pd(OAc)₂ (0.5 g) in ethanol (20 mL) under reflux for 24 h. Then, Pd (II) ions were adsorbed onto the magnetic nanoparticles and were reduced by 2 mmol NaBH₄ to produce MCM-41@L-Arg@Pd(0). Finally, the precipitate was filtered, washed with absolute ethanol and dried under vacuum to afford MCM-41@L-Arg@Pd(0) (Scheme 1).

General procedure for cross-coupling reaction of aryl halides with aryl boronic acids

A mixture of aryl halide (1 mmol), aryl boronic acid (1 mmol), 0.12 g NaOH (3 mmol), MCM-41@L-Arg@Pd(0) (3 or 5 mg) and ethanol (1 mL) as solvent was added to a 10 mL pressure-safe vial and stirred under reflux conditions and the reaction progress was monitored by TLC. After completion of the reaction, the catalyst was filtered and the reaction mixture was diluted with water. The resultant mixture was extracted with ethyl acetate to isolate the products. Then, the combined organic layers were dried over Na₂SO₄ (1.5 g), followed by the evaporation of the solvent, the crude residue was purified by column chromatography on silica gel using n-hexane/EtOAc (80/20), affording pure product in good yield. The formation of the products was confirmed by comparing the melting point, IR and NMR spectroscopy data with authentic samples and literature data.

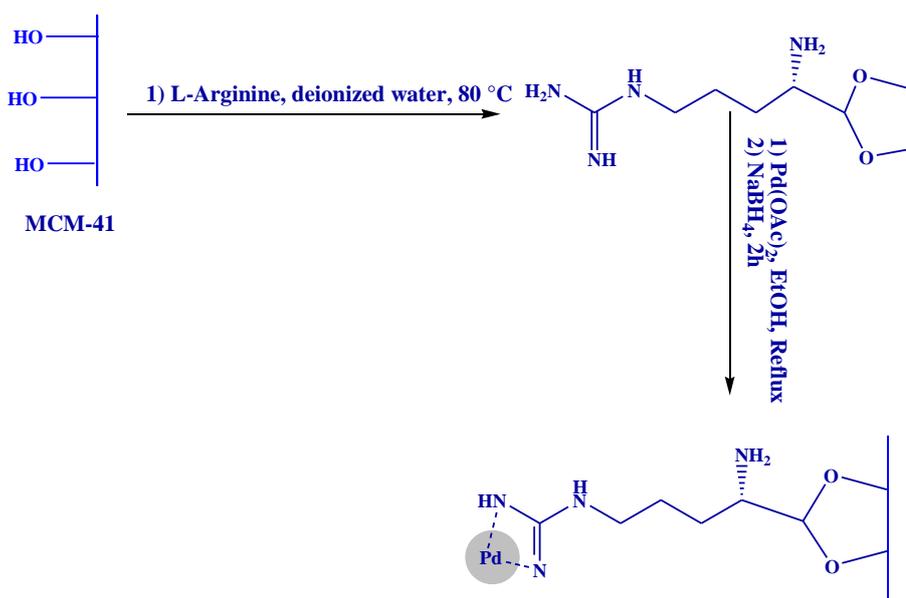
Selected spectral data

Biphenyl (Table 3, entry 1): $^1\text{H NMR}$ (400MHz, CDCl_3): $\delta = 7.40\text{-}7.44$ (t, 2H), 7.48-7.55 (t, 4H), 7.64-7.70 (d, $J=7.6$ Hz, 4H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): $\delta = 141.3, 129, 127.2, 78$.

1-Methoxy biphenyl (Table 3, entry 3): $^1\text{H NMR}$ (400MHz, CDCl_3): $\delta = 3.90$ (s, 3H), 7.0-7.10 (d, $J=7.04$ Hz, 2H), 7.34-7.40 (t, 1H), 7.45- 7.51 (t, 2H), 7.57- 7.64 (t, 4H). $^{13}\text{C NMR}$ (100

MHz, CDCl_3): $\delta = 159, 141, 134, 126.5\text{-}129, 114, 77, 55$

1-Methyl biphenyl (Table 3, entry 4): $^1\text{H NMR}$ (400MHz, CDCl_3): $\delta = 3.50$ (s, 3H), 7.33-7.40 (t, 2H), 7.41-7.47 (t, 1H), 7.51- 7.65 (m, 4H), 7.68-7.74 (d, $J=7.7$ Hz, 2H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): $\delta = 141.3, 138.5, 137, 129.6, 128.8, 127, 77, 20$.



Scheme 1. Synthesis of MCM-41@L-Arginine@Pd(0)

The FT-IR spectra of MCM-41, MCM-41@L-Arginine, and MCM-41@L-Arg@Pd(0) nano composites were recorded to confirm the modification of the MCM-41 surface with the amino acid and, then, Pd nanoparticles (Figure 1). The sharp features around 1092 cm^{-1} and the absorption peak at 467 cm^{-1} are assigned to asymmetric stretching and bending vibration of Si-O-Si. In the IR spectra of the MCM-41, a strong and a

broad band in the range of $3500\text{-}3400\text{ cm}^{-1}$ corresponds to the hydrogen bonded Si-OH groups and adsorbed water. In addition, the bands in the $2900\text{-}3000\text{ cm}^{-1}$ are attributed to the stretching of C-H bonds of the amino acid (Figure 2 b,c). Taking the above observations into consideration, it can be concluded that the MCM-41@L-Arg@Pd(0) was successfully obtained.

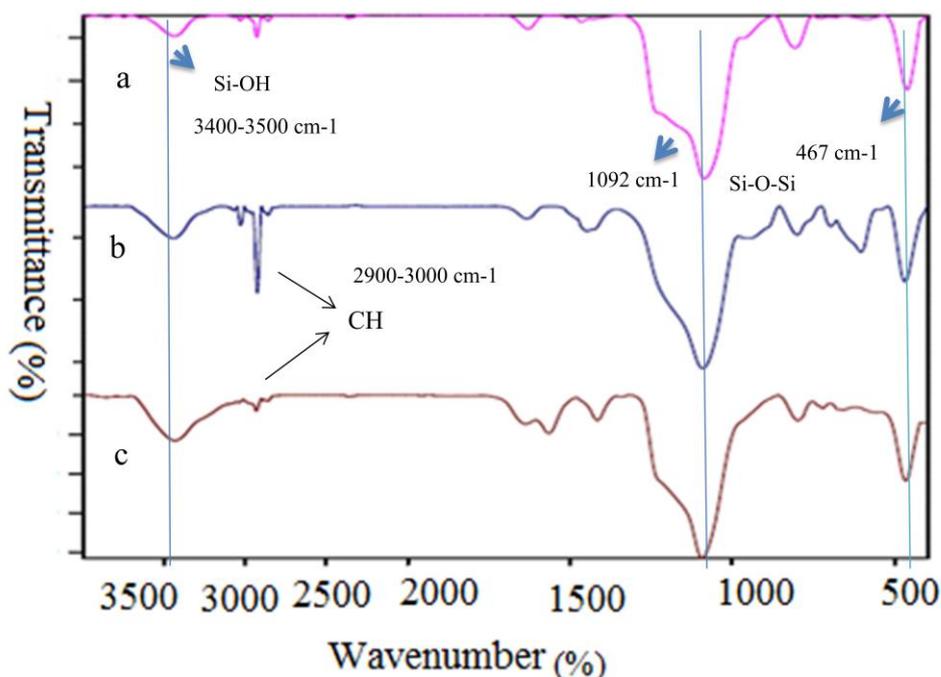


Figure 1. FT-IR spectra of (a) MCM-41, (b) MCM-41@L-Arg, (c) MCM-41@L-Arg@Pd(0)

The low angle XRD pattern of as-synthesized MCM-41@L-Arg@Pd(0) sample is shown in Figure 2. The narrow (100) peak at about 2.5° for MCM-41 indicating the mesoporous structure and high orderings of the samples. Also, the weak peaks of the planes (110) and (200) suggested the

two-dimensional hexagonal structure of all the samples indicating that the mesoporous structure of MCM-41 still remained intact after the functionalization. However, the peak intensity decreased slightly in the functionalized mesoporous material compared with pure MCM-41 [20].

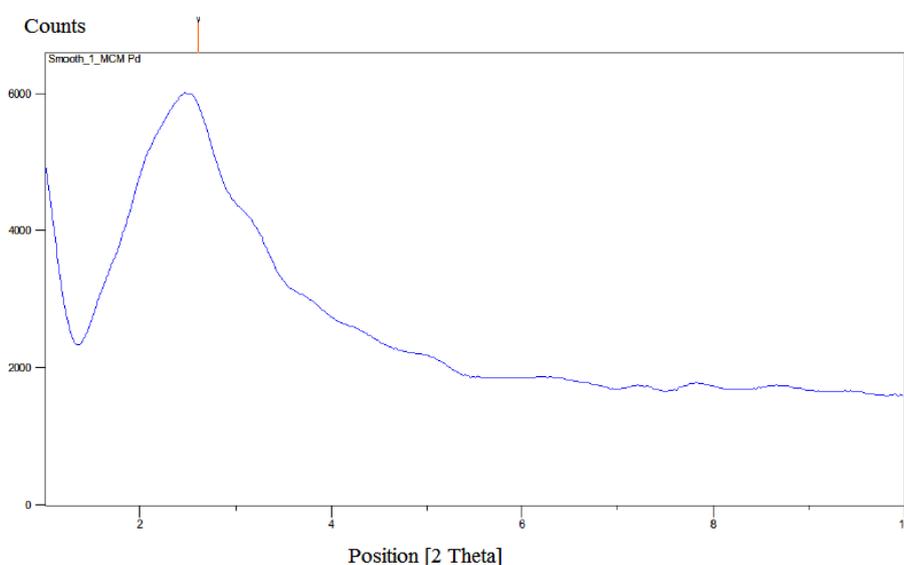


Figure 2. XRD pattern of MCM-41@L-Arg, MCM-41@L-Arginine@Pd(0)

Morphological changes of MCM-41@L-Arg@Pd(0) were investigated by scanning electron microscopy (SEM) as shown in Figure 3. As can be

seen, MCM-41@L-Arg@Pd(0) exhibited regular spherical shape particles having smooth surface morphology. MCM-41 [20].

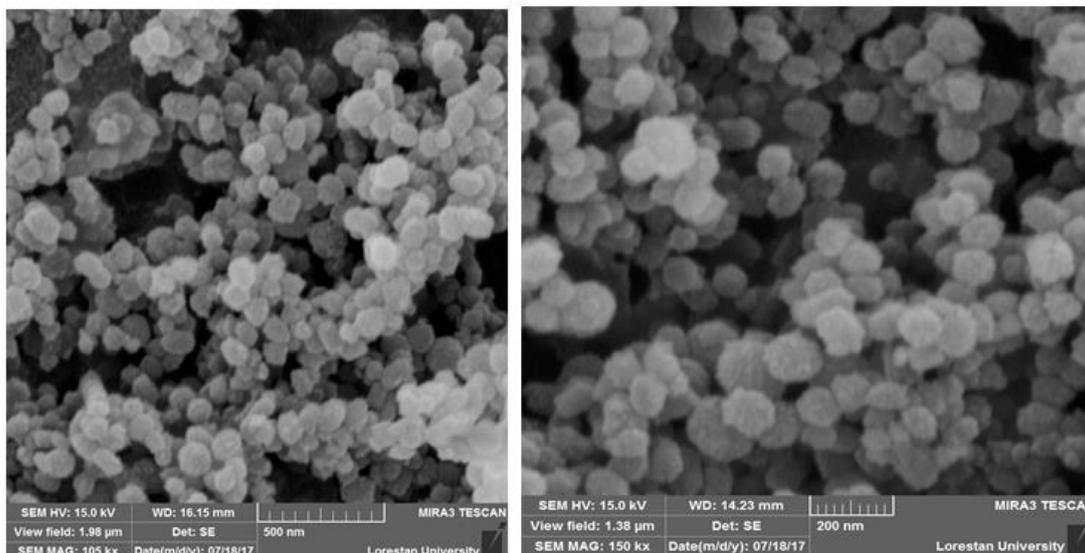
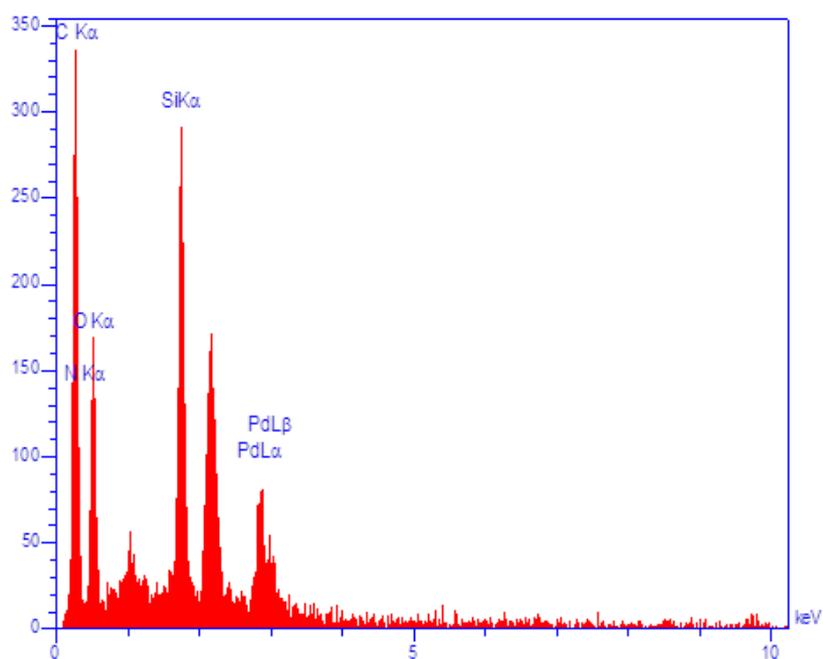


Figure 3. SEM images of MCM-41@L-Arginine@Pd(0)



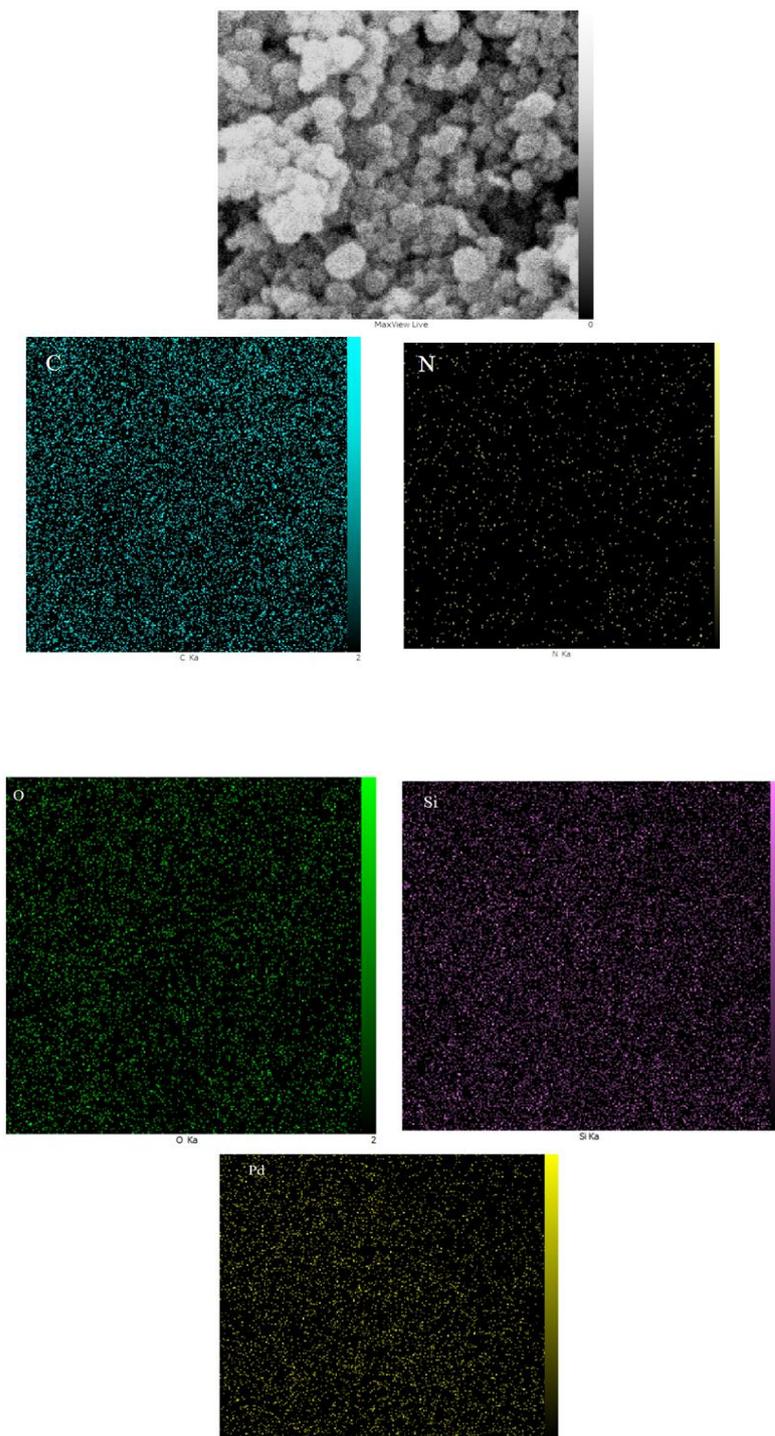


Figure 4. EDX-mapping of C, N, O, Si and PdMCM-41@L-Arginine@Pd(0)

The EDX survey of the MCM-41@L-Arg@Pd(0) (Figure 4) confirmed the presence of palladium in the mesoporous silica matrix. In addition, EDX-mapping demonstrated good dispersion of Si, C, N, O and Pd

on the surface of modified MCM-41 (Figure 5). The thermogravimetric (TG) analysis of the MCM-41@L-Arg@Pd(0) is presented in Figure 5. In the TG curve, the weight loss below 250 °C is attributed to the vaporization

of physically adsorbed water. Also, the weight loss of MCM-41@L-Arg@Pd(0) sample in the temperature range between 250 and 690 °C was ca. 10.6 %, which corresponded to the decomposition of the organic functional groups. Moreover, the content of Pd in the MCM-41@L-Arg@Pd(0) catalyst was 0.0016 mol g⁻¹ as measured by ICP-OES analysis. N₂ adsorption isotherm of the sample is recorded

(Figure 6). MCM-41@L-Arg@Pd(0) sample exhibited the type IV isotherm with distinct capillary condensation step, which can be regarded as a characteristic pattern of mesoporous materials according to the classification of the IUPAC[20]. A moderate decrease in the specific surface area and pore volume of the MCM-41@L-Arg@Pd(0) was observed after the functionalization (Table 1).

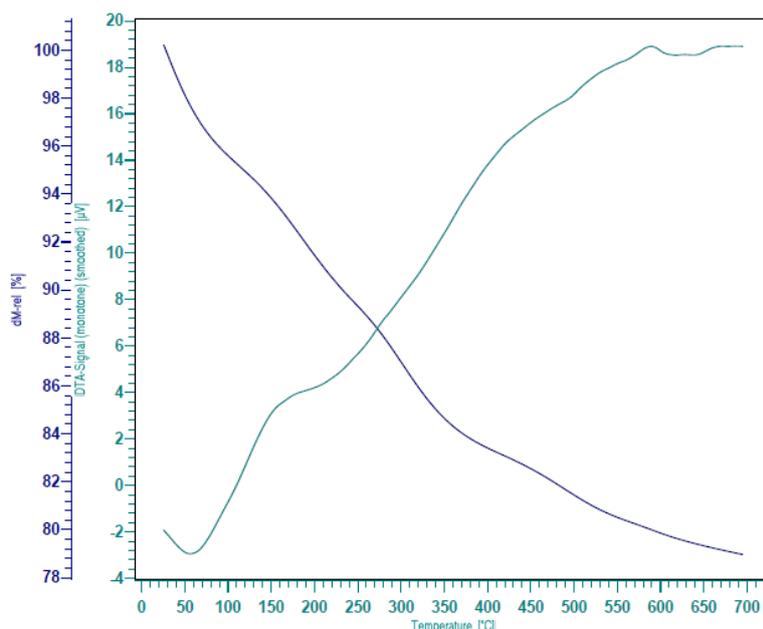


Figure 5. Thermogravimetric (TG) analysis of the MCM-41@L-Arginine@Pd(0)

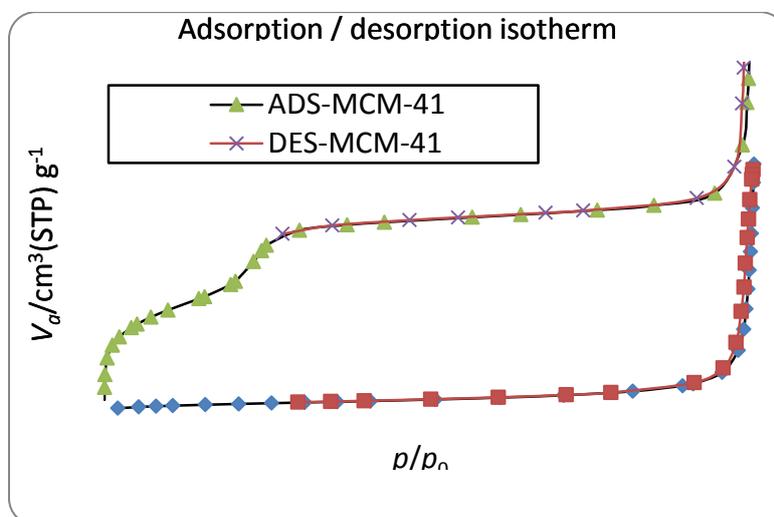


Figure 6. N₂ sorption isotherm of MCM-41@L-Arginine@Pd(0)

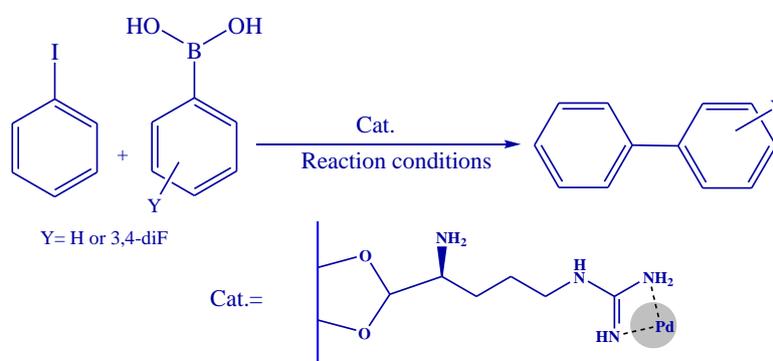
Table 1. Textural properties of synthesized materials obtained by nitrogen adsorption-desorption analysis

Sample name	S _{BET} (m ² g ⁻¹)	D _{BJH} (nm)	V _{Total} (cm ³ g ⁻¹)
MCM-41	1008.9	1.42	1.61
Catalyst	65.998	3.28	0.634

Catalytic activity of MCM-41@L-Arg@Pd(0)

The activity of the prepared catalyst was next evaluated for the synthesis of biaryl compounds. At first, the reaction of iodobenzene with phenylboronic acid was chosen as a model reaction to optimize the reaction conditions such as molar ratio of the catalyst, temperature, base, and solvent (Scheme 2, Table 2). It was found that the best yield of the product was obtained in EtOH under

reflux conditions, in the presence of 0.003 g (5×10^{-4} mol%) of MCM-41@L-Arg@Pd(0) and NaOH as a base (Table 2, Entry 3). Also, the effects of substituent on the reactivity of phenylboronic acid were probed. As evident from Table 2, the best yield of the product was obtained in the same condition but in the presence of 0.005 g (8×10^{-4} mol%) of MCM-41@L-Arg@Pd(0) (Table 2, Entry 14).

**Scheme 2.** Synthesis of biphenyl in the presence of MCM-41@L-Arginine@Pd(0)**Table 2.** Optimization of reaction condition for synthesis biphenyl under different conditions^a

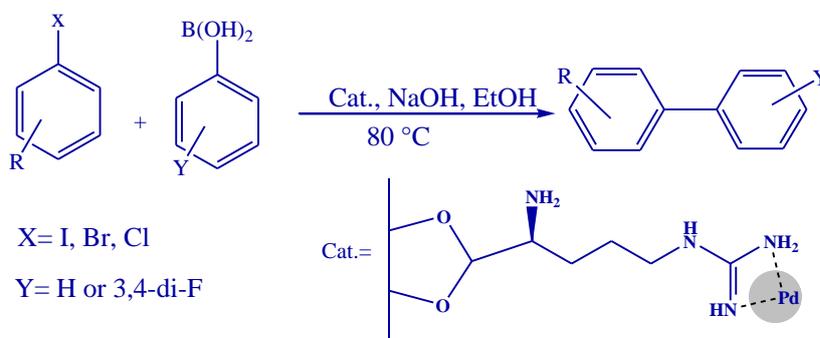
Entry	Catalyst (g)	Solvent	Base	Temperature (°C)	Time (min)	Yield ^a (%)
1	-	EtOH	NaOH	reflux	120	N.R
2	0.002	EtOH	NaOH	reflux	50	70
3	0.003	EtOH	NaOH	reflux	60	83
4	0.003	PEG	NaOH	110	40	53
5	0.003	DMF	NaOH	110	40	50
6	0.003	DMSO	NaOH	100	40	50

7	0.003	EtOH	KOH	reflux	0.	8.
8	0.003	EtOH	Na ₂ CO ₃	reflux	6.	70
9	0.003	EtOH	K ₂ CO ₃	reflux	6.	73
10	-	EtOH	NaOH	reflux	120	N.R
11 ^c	0.002	EtOH	NaOH	reflux	48.	4.
12 ^c	0.003	EtOH	NaOH	reflux	48.	00
13 ^c	0.004	EtOH	NaOH	reflux	36.	62
14 ^c	0.005	EtOH	NaOH	reflux	30.	68

^aIodobenzene (1 mmol), Phenylboronic acid (1 mmol), Base (3 mmol). ^bIsolated yield. ^cReaction in the presence of 3,4-difluoroboric acid (1 mmol).

After optimization of the reaction condition, a variety of aryl halide, possessing both electron-donating and electron-withdrawing groups, was employed for the synthesis of biaryls

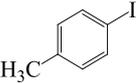
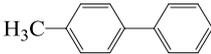
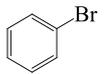
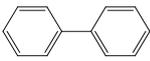
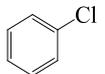
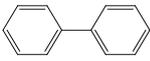
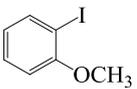
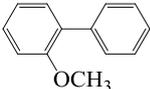
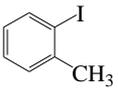
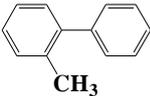
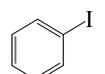
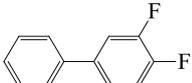
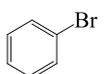
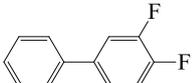
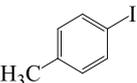
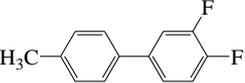
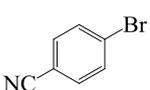
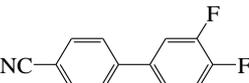
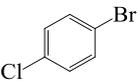
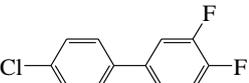
(Scheme 3), and the results indicated that bearing different functional groups, the reaction proceeded smoothly in all cases (Table 3).



Scheme 3. Synthesis of biphenyl compounds

Table 3. MCM-41@L-Arg@Pd(0)-catalyzed cross-coupling reaction of aryl halides with arylboronic acids^a

Entry	Aryl halide	Phenylating reagent	Product	Time (min)	Yield (%) ^b	m.p. (Ref.)
1		C ₆ H ₅ B(OH) ₂		0.	83	69 [21]
2		C ₆ H ₅ B(OH) ₂		9.	7.	46 [21]
3		C ₆ H ₅ B(OH) ₂		60	8.	79-82 [21]

4		$C_6H_5B(OH)_2$		90	78	43-46 [21]
5		$C_6H_5B(OH)_2$		70	73	72 [21]
6		$C_6H_5B(OH)_2$		90	70	68 [21]
7		$C_6H_5B(OH)_2$		80	73	Oil [22]
8		$C_6H_5B(OH)_2$		120	70	Oil [22]
9 ^c		3,4-diF- $C_6H_3B(OH)_2$		300	78	39 [23]
10 ^c		3,4-diF- $C_6H_3B(OH)_2$		480	00	38-40 [23]
11 ^c		3,4-diF- $C_6H_3B(OH)_2$		480	78	oil
12 ^c		3,4-diF- $C_6H_3B(OH)_2$		480	70	80-83
13 ^c		3,4-diF- $C_6H_3B(OH)_2$		480	00	oil

^aReaction condition: Aryl halide (1 mmol), phenylboronic acid or 3,4-diF-boronic acid (1 mmol), NaOH (3 mmol), Solvent:EtOH, Catalyst (0.003 g, 5×10^{-4} mol%). ^bIsolated yield. ^c Catalyst (0.005, 8×10^{-4} mol% g)

Recovery and reuse of MCM-41@L-Arg@Pd(0)

The recycling of the catalysts is important from economic and environmental points of view. Thus, the reusability of our new catalytic system was then probed in the model reaction under the optimized reaction

conditions. After the completion of the reaction, the reaction mixture was diluted with water and ethyl acetate, and the catalyst was easily and rapidly separated from the product by filtration. As can be seen, this catalytic system was recycled and reuse four times with only 5% loss of reactivity (Figure 7).

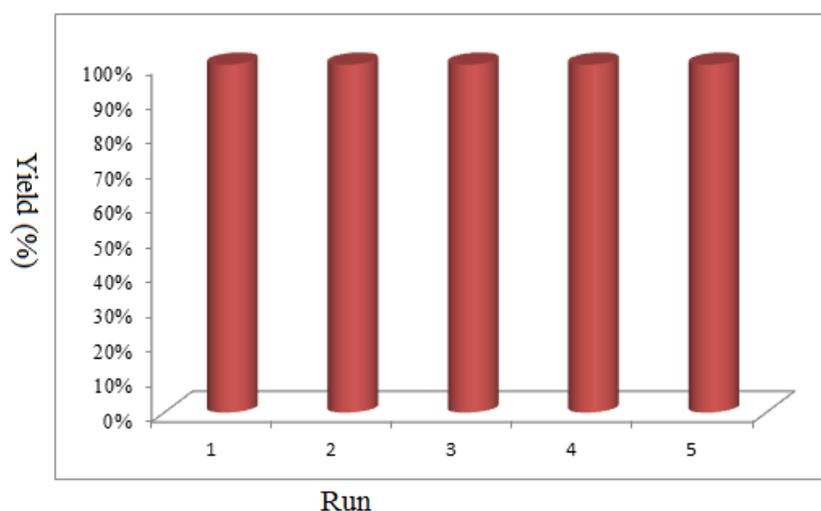


Figure7. Reusability and recycling of MCM-41@L-Arginine@Pd(0) for the synthesis of biphenyl

Conclusion

In summary, a highly efficient and reusable catalytic system for the Suzuki-Miyaura cross-coupling reaction has been developed. MCM-41@L-Arg@Pd(0) efficiently promote the cross-coupling of aryl halides with arylboronic acids under mild reaction conditions. Mild reaction conditions, commercially available, eco-friendly, high yields, short reaction time, operational simplicity, practicability, product purity and applicability to various substrates are among the advantages of this protocol.

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References

- [1] M.H. Mallah, M. Ghannadi Maragheh, A. Badiei, R. HabibzadehSbo, J. Radioanal, *Nucl. Chem.*, **2010**, 283, 597–601.
- [2] D.Y. Zhao, Q.S. Huo, J.L. Feng, B.F. Chmelka, G.D. Stucky, *J. Am. Chem. Soc.*, **1998**, 120, 6024.
- [3] D. Zhao, J. Feng, Q. Huo, N. Melosh, G.H. Fredrickson, B.F. Chmelka, G.D. Stucky, *Science.*, **1998**, 279,548.
- [4] W.U. Yong, Y. Zhang, J. Cheng, Z. Li, H. Wang, Q. Sun, B. Han, Y. Kong, *Microporous Mesoporous Materials.*, **2012**, 162, 51–59.
- [5] R. Martin, S.L. Buchwald, *J. Chem. Res.*, **2008**, 41, 1461.
- [6] M.B. Thathagar, J. Beckers, G. Rothenberg, *J. Am. Chem. Soc.*, **2002**, 124, 11858.
- [7] D. Zim, D.V.R. Lando, J. Dupont, A.L. Monteiro, *Org. Lett.*, **2001**, 3, 3049.
- [8] J.Y. Ying, C.P. Mehnertand, M.S. Wong, *Angew. Chem, Int. Ed.*, **1999**, 38, 56-77.
- [9] J. Han, Y. Liu, R. Guo, *J. Am. Chem. Soc.*, **2009**, 131, 2060–2061.
- [10] S.W Kim, M. Kim, W.Y. Lee, T. Hyeon, *J. Am. Chem. Soc.*, **2002**, 124, 7642-7643.
- [11] a) J.H. Li, W.J. Liu, *Org. Lett.*, **2004**, 6, 2809-2811. b) S. Pratihari, R. Pegu, A. KantiGuha, B. Sarma, *D. Trans.*, **2014**, 43, 17136-17144.
- [12] J. Sun, Y. Fu, G. He, X. Sun, X. Wang, *Appl Catal B. Environmental.*, **2015**, 165, 661–667.
- [13] T.N. Mitchell, *Synth. Commum.*, **1992**, 9, 803-815.
- [14] N. Miyaura, A. Suzuki, *Chem. Rev.*, **1995**, 95, 2453-2483.

- [15] J.M. Saa, G. Martorell, *J. Org. Chem.*, **1993**, 58, 1963-1966.
- [16] M. Rottlander, N. Palmer, P. Knochel, *Synlett.*, **1996**, 6, 573-575.
- [17] S. Riggelman, P. DeShong, *J. Org. Chem.*, **2003**, 68, 8106-8109.
- [18] Q. Xu, P.P. Wang, M. ZhongCai, *Chin. Chem. Lett.*, **2007**, 18, 387-389.
- [19] A. Ghorbani-Choghamarani, F. Nikpour, F. Ghorbani, F. Havasi, *Rsc. Adv.*, **2015**, 5, 33212-33220.
- [20] A. Ghorbani-Choghamarani, F. Ghorbani, Z. Yousofvand, G. Azadi, *J. Porous Mat.*, **2015**, 22, 665-673.
- [21] G. Azadi, A. Ghorbani-Choghamarani, *Appl. Organomet. Chem.*, **2016**, 30, 360-366.
- [22] A. Ghorbani-Choghamarani, B. Tahmasbi, N. Noori, R. Ghafouri-nejad, *J. Iran Chem Soc.*, **2017**, 14, 681-693.
- [23] A. Ghorbani-Choghamarani, B. Tahmasbi, P. Moradi, *Rsc. Adv.*, **2016**, 6, 43205-43216.
- [24] S. Sajjadifar, Z. Arzehgar, A. Ghayuri, *J. Chin. Chem. Soc.*, **2017**, 65, 205-211.
- [25] S. Sajjadifar, Z. Arzehgar, S. Khoshpoori, *J. Inorg. Organomet. Polym. Mater.*, **2018**, 28, 837-846
- [26] Z. Arzehgar, S. Sajjadifar, H. Arandiyan, *Asian J. Green Chem.*, **2019**, 3, 43-52.
- [27] M. Soleiman-Beigi, Z. Arzehgar, *Synlett.*, **2018**, 29, 986-992.

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