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**FULL PAPER**

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# Pd-SBT@MCM-41: As an efficient, stable and recyclable organometallic catalyst for C-C coupling reactions and synthesis of 5-substituted tetrazoles

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A palladium S-benzylisothiourea complex was anchored on functionalized MCM-41 (Pd-SBT@MCM-41) and applied as efficient and reusable catalyst for the synthesis of 5-substituted 1*H*–tetrazoles using [2 + 3] cycloaddition reaction of various organic nitriles with sodium azide ($NaN_3$) in poly(ethylene glycol) (PEG) as green solvent. Also this catalyst was applied as an versatile organometallic catalyst for Suzuki cross-coupling reaction of aryl halides and phenylboronic acid ($PhB(OH)_2$) or sodium tetraphenyl borate ($NaB(Ph)_4$). This nanocatalyst was characterized by thermal gravimetric analysis (TGA), X-ray Diffraction (XRD), scanning electron microscopy (SEM), inductively Coupled Plasma (ICP) and $N_2$ adsorption–desorption isotherms techniques. Recovery of the catalyst is easily achieved by centrifugation for several consecutive runs.

**KEYWORDS**
mesoporous MCM-41, organometallic catalyst, palladium, Suzuki reaction, tetrazoles

## 1 | INTRODUCTION

Recently, heterogeneous catalysts have used in various organic reactions and industrial processes.[1] Because heterogeneous catalysts have several advantages such as: stability, recoverability and recyclability.[2–4] However, they have enormous drawbacks, such as lack of activity and selectivity.[3] This drawback can be overcome by nanomaterials, because nanomaterials have high surface area resulting to high activity and selectivity.[3,4] Generally, various nano materials have been employed to fabricate heterogeneous palladium catalysts such as graphene,[5] graphitic carbon nitride[6] metal oxides,[1,7] ionic liquids,[8] clay,[9] boehmite nanoparticles,[10] molecular sieves (SBA-15 and MCM-41),[11,12] metal–organic frameworks,[13] and polymers.[14] Among them, mesoporous silica such as MCM-41 is great and useful material for the heterogenization of homogeneous catalysts because of some unique properties such as large specific surface area (>1000 $m^2/g$), ease of functionalization, homogeneous hexagonal pore arrays with pore diameters, stability in high temperature, relatively hydrophobic nature and versatile separation from reaction media.[15] Large specific surface area of MCM-41 that possesses a lot of silanol groups leads to simple modification of its surface by other functional groups.[16,17] Also high specific pore volume (up to 1.3 ml/g) of MCM-41 allows anchoring of huge molecules such as organic ligands and metal complexes into hexagonal channels.[18] Furthermore, high thermal stability of this nanostructural compound allows doing organic reaction in high temperatures.[19] On the other hand, tetrazoles are an important class of heterocycles with wide range of applications in medicinal chemistry, coordination chemistry, catalytic science technology and in material chemistry.[20–23] Recently tetrazoles and their derivatives (such as Valsartan and Losartan) were used in drugs and they are used for anti HIV drug candidate, antiviral, antibacterial and anticancer agents.[22,23] Also, C-C coupling reactions have become a powerful strategy for the preparation of complicated organic compounds, natural products, preparation of advanced materials and biologically active compounds.[24–28] The

Suzuki cross coupling reaction is one of the powerful methods for the preparation of pharmaceuticals, polymers, herbicides, liquid crystals and ligands for catalysis.[28] In continuation of our studies, [29,30] herein, we report synthesis and characterization of Pd-SBT@MCM-41 as an efficient, stable and reusable nanostructural catalyst for the preparation of 5-substituted 1*H*–tetrazole derivatives and C-C coupling reactions.

## 2 | EXPERIMENTAL

### 2.1 | Preparation of catalyst

The mesoporous MCM-41 was prepared according to the previously reported procedure.[30] Typically, 2 ml of (3-choloropropyl)triethoxysilane (CPTES) was added to 25 ml of toluene containing 2 g of MCM-41. The reaction mixture was stirred with magnetic stirrer for 24 h at 40°C. The product was separated out, washed with ethanol and dried at 50°C. Then the resulting product (MCM-41-$(SiCH_2CH_2CH_2Cl)_x$) (1 g) added to toluene (20 ml) and S-benzyl isothiourea (2 mmol) and potassium carbonate ($K_2CO_3$) (2 mmol) were added also to this mixture and stirred under reflux conditions for 24 h. The resulting SBT@MCM-41 was washed with ethanol to remove unreacted S-benzyl isothiourea. Finally Pd-SBT@MCM-41 was prepared by mixing a solution of palladium acetate ($Pd(OAc)_2$) (0.25 g) in ethanol (20 ml) with SBT@MCM-41 (0.5 g) for 24 h under reflux conditions. Subsequently sodium borohydride (0.4 mmol) was added to this mixture and kept under reflux for another 2 h. The resulting catalyst was filtered, washed by ethanol and dried at 50°C.

### 2.2 | General procedure for the synthesis of 5-substituted 1H–tetrazole derivatives

A mixture of sodium azide (1.4 mmol), benzonitrile (1 mmol), and 0.03 g of Pd-SBT@MCM-41 in PEG-400 (3 ml) magnetically stirred at 120°C. After completion of the reaction (observed by tin layer chromatography (TLC)), the reaction mixture was cooled down to room temperature, and catalyst was separated by simple filtration and hydrochloric acid (HCl) (4 N, 10 ml) was added to the filtrated. The products extracted with ethyl acetate (3 × 10 ml). The organic solvent was dried over anhydrous sodium sulphate (1.5 g), and evaporated to give the corresponding solid product.

### 2.3 | General procedure for the Suzuki reaction

A mixture of aryl halide (1 mmol), phenylboronic acid (1 mmol) or sodium tetraphenyl borate (0.5 mmol), $K_2CO_3$ (3 mmol), and Pd-SBT@MCM-41 (0.010 g) were transformed into a 50 ml reaction flask containing 5 ml of PEG-400 as solvent and stirred at 80°C. The progress of the coupling reaction was monitored by TLC. After completion of the reaction, catalyst was separated and washed with diethyl ether. The reaction mixture was extracted with water and diethyl ether and organic layer dried over anhydrous sodium sulfate ($Na_2SO_4$) (1.5 g). Finally, evaporation of the solvent gives pure biphenyl derivatives.

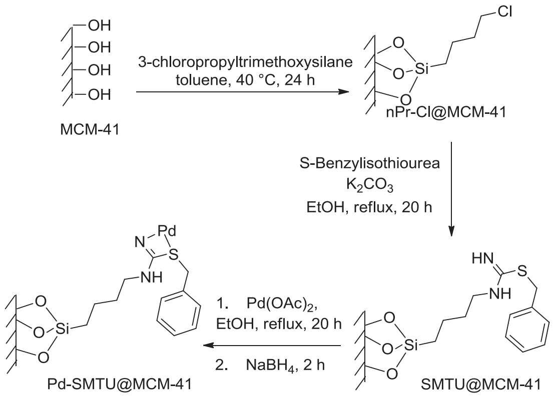
## 3 | RESULT AND DISCUSSION

### 3.1 | Catalyst preparation

Initially, the MCM-41 material has been prepared and functionalized with 3-choloropropyltriethoxysilane (CPTES) according to the previous reported procedure.[31] The immobilization of S-benzylisothiourea on MCM-41 (SBT@MCM-41) was performed by substituting replaceable NH of ligand with supported-terminal choloro groups of organic-modified MCM-41. Finally, the catalyst was prepared by reaction of SBT@MCM-41with $Pd(OAc)_2$, subsequently by reduction of Pd(II) to Pd (0) (Scheme 1). This catalyst characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), thermogravimetric analysis (TGA) and $N_2$ adsorption–desorption isotherms, and inductively coupled plasma atomic emission spectroscopy (ICP-OES).

### 3.2 | Catalyst characterization

The SEM and TEM images of the catalyst were shown in Figures 1 and 2. The Pd-SBTU@MCM-41 was observed using SEM imaging and found to be spherical with mean diameter of 80 ± 20 nm (Figure 1). Also, the catalyst sample clearly exhibits a well-ordered hexagonal type of array



**SCHEME 1** Synthesis of Pd-SBT@MCM-41

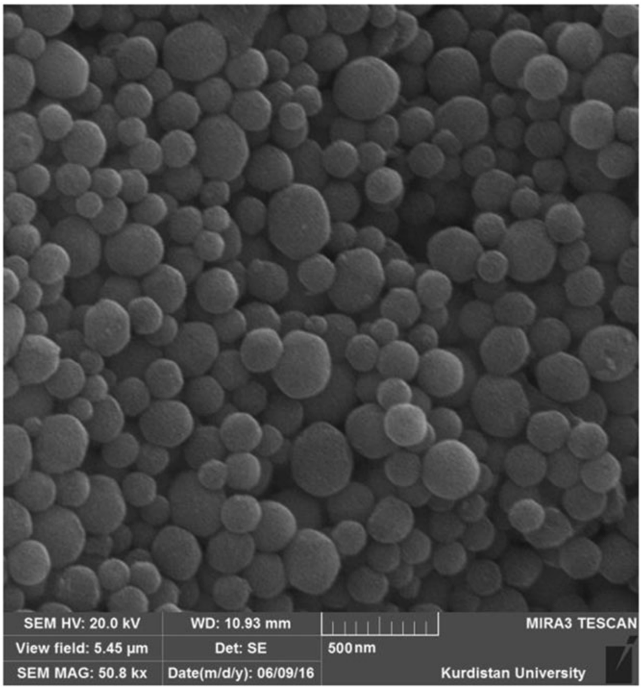


**FIGURE 1** SEM image of Pd-SBT@MCM-41

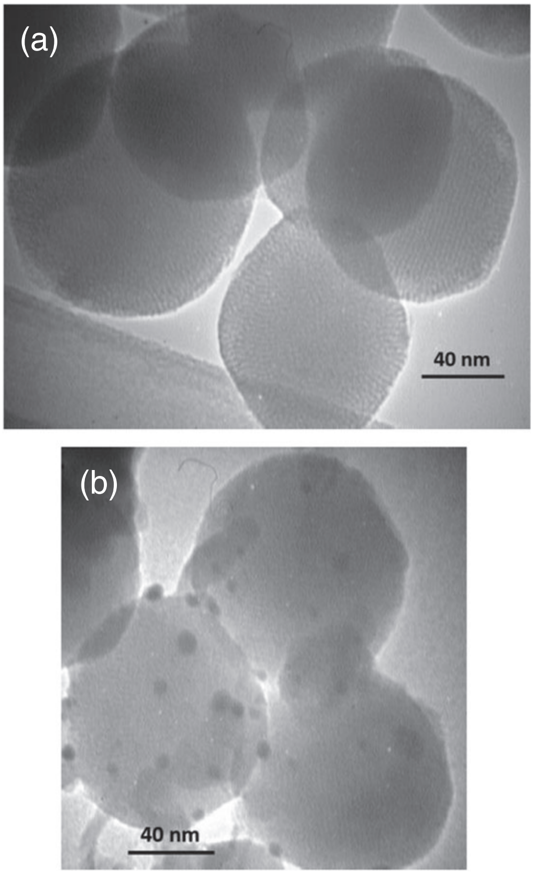


**FIGURE 2** TEM image of (a) SBTU@MCM-41 and (b) Pd-SBTU@MCM-41

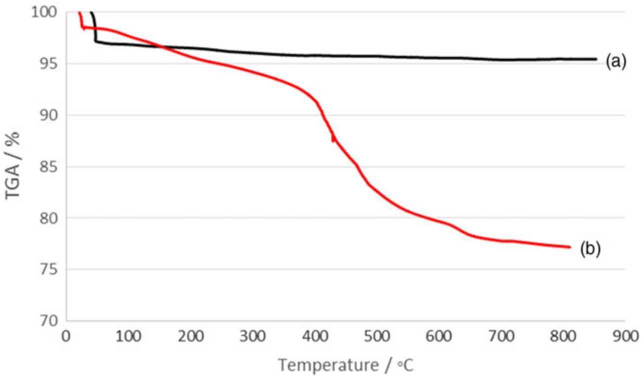


**FIGURE 3** TGA diagram of MCM-41 (a) and Pd-SBT@MCM-41 (b)

of regular hexagonal arrangement in TEM micrographs before (Figure 2a) and after (Figure 2b) of coordination of palladium. Also, TEM image revealed more accurate information on the morphology and particles size of the palladium nanoparticles. As shown in TEM image, most of the Pd particles are supported on MCM-41 with an average diameter about 4 ± 1 nm (Figure 2b). In order to estimate the exact amount of palladium loaded on the mesoporous catalyst, ICP-OES analysis was performed. The Pd amount of immobilized catalyst on MCM-41 was found to be 0.0018 mol $g^{-1.}$

In order to determine the percentage of organic moieties onto MCM-41, the TGA analysis of Pd-SBT@MCM-41was performed. TGA curves of MCM-41 and Pd-SBT@MCM-41 are shown in Figure 3. The TGA curve of MCM-41 showed a 3% weight loss from 25–250°C, which is related to desorption of water and silanol groups. TGA curve of Pd-SBT@MCM showed a two-step of weight loss. The first step of weight loss from 25–200°C (about 5%), is due to the removal of the adsorbed solvents,[32] and the second weight loss in the range of 200–400°C (approximately 23%) is related to the decomposition of supported organic spacers on the MCM-41.

The small angle powder X-ray diffraction patterns for MCM-41 and Pd-SBT@MCM-41 are exhibit in Figure 4. XRD pattern of MCM-41 sample illustrate typical peaks corresponding to diffraction at (100), (110) and (200) planes which are due to the hexagonal channel arrays.[33] The highest peak observed for all the samples (corresponding to 1 0 0 plane) indicated the regular order of the mesoporous silica, as expected in MCM-41 structure.[34] The XRD pattern of Pd-SBT@MCM-41 sample shows that upon post-synthetic grafting of palladium complex inside the channels of MCM-41, the $d_{110}$ and $d_{200}$ refractions were no longer observed. This result could be attributed to lower local order and increasing in the wall thickness of support materials.[35]

The $N_2$ adsorption–desorption isotherms of MCM-41 and Pd-SBT@MCM-41 are shown in Figure 5. According

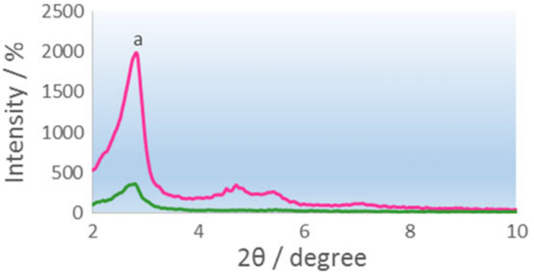


**FIGURE 4** XRD pattern of MCM-41 (a) and Pd-SBT@MCM-41 (b)

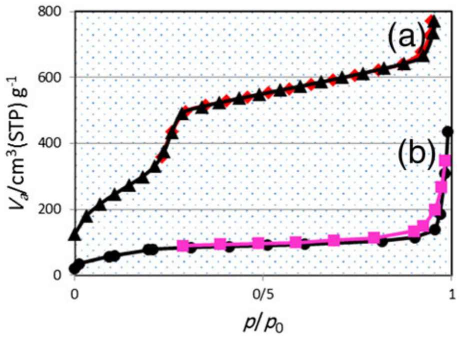


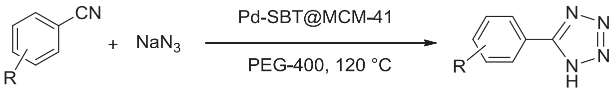
**FIGURE 5** Nitrogen adsorption–desorption isotherms of MCM-41 (a) and Pd-SBT@MCM-41 (b)

to the IUPAC classification all MCM-41 samples have type IV isotherms; this indicates that the synthesized samples have mesoporous structure.[36] The surface area of MCM-41 decreased from 1371.8 to 286.2 m$^2$ g$^{-1}$ and average pore volume decreased from 1.52 to 0.61 Cm$^3$g$^{-1}$ for Pd-SBT@MCM-41. On the other hand, an increase of the wall thickness occurred, which is show the grafting of palladium complex inside the pore channels of MCM-41.

## 3.3 | Catalytic study of Pd-SBT@MCM-41

After synthesis and characterization of described catalyst, its catalytic properties was examined in the synthesis of tetrazoles *via* [2 + 3] cycloaddition reaction of nitriles with sodium azide (Scheme 2).

In order to optimize reaction conditions, various parameters such as solvent (PEG, dimethylsulfoxide (DMSO), N,N-dimethylformamide (DMF), water and ethanol), temperature, amount of $NaN_3$ and catalyst were examined in the [2 + 3] cycloaddition reaction of benzonitrile with $NaN_3$. The result of this study is summarized in Table 1. As shown in Table 1, 0.03 g of Pd-SBT@MCM-41, 1.4 mmol of $NaN_3$ in PEG-400 at 120°C was found to be the best conditions for the synthesis of 5-substituted 1*H*–tetrazoles.



**SCHEME 2** Synthesis of 5-substituted 1H–tetrazoles catalysed by Pd-SBT@MCM-41

After optimization of the reaction condition, the catalytic activity of Pd-SBT@MCM-41 was extend for various nitriles and the obtained results are summarized in Table 2. As shown in Table 2, benzonitriles with both electron-withdrawing and electron-donating substituents have been successful converted to corresponding tetrazoles in good yields. Interestingly, malononitrile and terephthalonitrile afforded the mono cycloaddition products (Table 2, entries 10, 11).

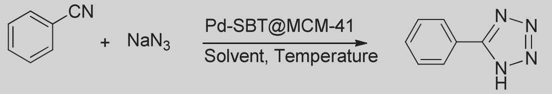
Also, we examined the catalytic activity of Pd-SBT@MCM-41 in the Suzuki cross coupling reaction of aryl halides with $PhB(OH)_2$ or $NaB(Ph)_4$ (Scheme 3).

It is well known the Suzuki cross-coupling reaction is considerably affected by the nature of catalyst, the added base and type of solvent. Therefore, the proper choice of reaction conditions is very important to do this reaction.

In order to optimize the reaction conditions, the effect of different parameters such as kind of solvent and base, temperature and the amount of Pd-SBT@MCM-41 were examined in the reaction of iodobenzene and $PhB(OH)_2$ as a model reaction (Table 3). When, 0.005 g of catalyst was used in model reaction, the corresponding biphenyl product was isolated in 46% yield after 70 min. When the amount of catalyst has been increased from 0.005 to 0.008 g, biphenyl was obtained in 69% yield after 70 min and the best perfomance was obtained when 0.010 g of Pd-SBT@MCM-41 was used. Moreover, the model reaction was carried out in the absence of catalyst: moderate yield of the product was obtained after long time (5 h). Also, the coupling of iodobenzene with $PhB(OH)_2$ was examined in various solvent such as DMSO, PEG-400, DMF, ethanol and water (Table 3, entries 3–7). Studies of solvent effect on the activity of catalyst reveal that the model reaction could proceed better in PEG-400 (Table 3, entry 3). The effect of various bases and temprature (Table 3, entries 7–11) on the performance of catalyst was also studied and the best results were obtained at 80°C using 3 mmol of $K_2CO_3$.

After the optimization of the reaction conditions, we extended the catalytic activity of Pd-SBT@MCM-41 for other aryl halide including electron-donor and electron-withdrawing functional groups (Table 4). Various aryl iodides, aryl bromides and aryl chlorides were successfully coupled with phenylboronic acid and corresponding biphenyls were obtained in good to excellent yields. However, the

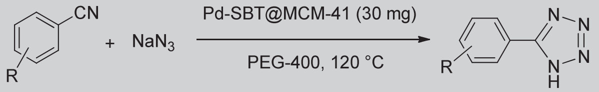
**TABLE 1** Optimization of reaction conditions for synthesis of 5-substituted 1H–tetrazole derivatives in the presence of Pd-SBT@MCM-41



| Entry | Catalyst (mg) | Solvent | $NaN_3$ (mmol) | Temperature (°C) | Time (h) | Yield (%)[a] |
|---|---|---|---|---|---|---|
| 1 | 30 | PEG | 1.2 | 120 | 8 | 60 |
| 2 | 30 | PEG | 1.3 | 120 | 8 | 63 |
| 3 | 30 | PEG | 1.4 | 120 | 8 | 96 |
| 4 | 35 | PEG | 1.4 | 120 | 6.75 | 97 |
| 5 | 25 | PEG | 1.4 | 120 | 8 | 56 |
| 6 | 20 | PEG | 1.4 | 120 | 8 | 40 |
| 7 | 30 | DMF | 1.4 | 120 | 6 | 93 |
| 8 | 30 | DMSO | 1.4 | 120 | 6.2 | 95 |
| 9 | 30 | ethanol | 1.4 | Reflux | 8 | 22 |
| 10 | 30 | water | 1.4 | Reflux | 8 | 31 |
| 11 | 30 | PEG | 1.4 | 100 | 8 | 66 |

[a] Isolated yield.

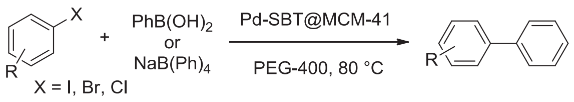
**TABLE 2** Synthesis of 5-substituted 1*H*–tetrazole derivatives in the presence of Pd-SBT@MCM-41



| Entry | Nitrile | Product | Time (h) | Yield (%)[a] | M.P. (°C) |
|---|---|---|---|---|---|
| 1 | benzonitrile | 5-phenyl-1H-tetrazole | 8 | 96 | 214–216 |
| 2 | 4-nitrobenzonitrile | 5-(4-nitrophenyl)-1H–tetrazole | 4 | 92 | 217–219 |
| 3 | 4-hydroxybenzonitrile | 5-(4-hydroxyphenyl)-1H–tetrazole | 5 | 93 | 232–234 |
| 4 | 4-acetylbenzonitrile | 5-(4-acetylphenyl)-1H–tetrazole | 24 | 88 | 174–176 |
| 5 | 3-nitrobenzonitrile | 5-(3-nitrophenyl)-1H–tetrazole | 8.5 | 86 | 148–151 |
| 6 | 3-chlorobenzonitrile | 5-(3-chlorophenyl)-1H–tetrazole | 8 | 88 | 130–132 |
| 7 | 4-bromobenzonitrile | 5-(4-bromophenyl)-1H–tetrazole | 14 | 87 | 263–265 |
| 8 | 2-chlorobenzonitrile | 5-(2-chlorophenyl)-1H–tetrazole | 4 | 90 | 180–182 |
| 9 | 2-hydroxybenzonitrile | 5-(2-hydroxyphenyl)-1H–tetrazole | 6 | 90 | 225–227 |
| 10 | malononitrile | 2-(1H–tetrazol-5-yl)acetonitrile | 24 | 76[b] | 114-117 |
| 11 | terephthalonitrile | 4-(1H–tetrazol-5-yl)benzonitrile | 7 | 80 | 253–256 |
| 12 | 4-chlorobenzonitrile | 5-(4-chlorophenyl)-1H–tetrazole | 8 | 91 | 260–263 |

[a] Isolated yield has been obtained using nitrile (1 mmol), NaN3 (1.4 mmol) in PEG-400 (2 ml) in the presence of Pd-SBT@MCM-41 (0.03 g) at 120°C,

[b] the reaction has been carried out at 130°C.

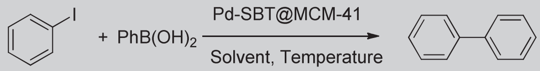


**SCHEME 3** C-C coupling reaction catalysed Pd-SBT@MCM-41

completing reaction including aryl chlorides was slower than aryl iodides and bromides ones.

We also applied optimized reaction conditions for the coupling of aryl halides with sodium tetraphenyl borate.

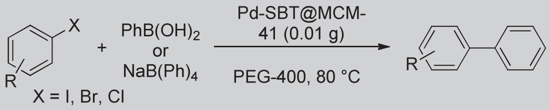
**TABLE 3** Optimization of reaction conditions for C-C coupling reaction in the presence of Pd-SBT@MCM-41



| Entry | Catalyst (mg) | Solvent | Base | Temperature (°C) | Time (min) | Yield (%)[a] |
|---|---|---|---|---|---|---|
| 1 | - | PEG | $K_2CO_3$ | 80 | 300 | - |
| 2 | 5 | PEG | $K_2CO_3$ | 80 | 70 | 46 |
| 3 | 8 | PEG | $K_2CO_3$ | 80 | 70 | 69 |
| 4 | 10 | PEG | $K_2CO_3$ | 80 | 60 | 98 |
| 5 | 10 | DMF | $K_2CO_3$ | 80 | 45 | 94 |
| 6 | 10 | DMSO | $K_2CO_3$ | 80 | 50 | 92 |
| 7 | 10 | Ethanol | $K_2CO_3$ | 80 | 60 | 64 |
| 8 | 10 | Water | $K_2CO_3$ | 80 | 60 | 69 |
| 9 | 10 | PEG | $Et_3N$ | 80 | 70 | 46 |
| 10 | 10 | PEG | NaOEt | 80 | 70 | 15 |
| 11 | 10 | PEG | KOH | 80 | 70 | 32 |
| 12 | 10 | PEG | $K_2CO_3$ | 60 | 70 | 66 |

[a] Isolated yield.

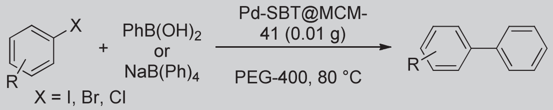
**TABLE 4** C-C coupling reaction in the presence of Pd-SBT@MCM-41



| Entry | Aryl halide | Phenylatig reagent | Time (min) | Yield (%)[a] | M.P. (°C) |
|---|---|---|---|---|---|
| 1 | Iodobenzene | $PhB(OH)_2$ | 60 | 98 | 67–68 |
| 2 | 4-Iodotoluene | $PhB(OH)_2$ | 70 | 91 | 42–44 |
| 3 | 2-Iodotoluene | $PhB(OH)_2$ | 300 | 93 | Oil |
| 4 | 4-Iodoanisole | $PhB(OH)_2$ | 175 | 96 | 81–84 |
| 5 | Bromobenzene | $PhB(OH)_2$ | 70 | 92 | 64–67 |
| 6 | 4-Bromotoluene | $PhB(OH)_2$ | 90 | 97 | 41–44 |
| 7 | 4-Bromonitrobenzene | $PhB(OH)_2$ | 50 | 95 | 112–114 |
| 8 | 4-Bromobenzonitrile | $PhB(OH)_2$ | 45 | 93 | 82–84 |
| 9 | 4-Bromochlorobenzene | $PhB(OH)_2$ | 45 | 92 | 72–74 |
| 10 | 4-Chloronitrobenzene | $PhB(OH)_2$ | 250 | 87 | 111–114 |
| 11 | 4-Chlorobenzonitrile | $PhB(OH)_2$ | 280 | 88 | 80–83 |
| 12 | Iodobenzene | $NaB(Ph)_4$ | 65 | 97 | 66–68 |
| 13 | 4-Iodotoluene | $NaB(Ph)_4$ | 80 | 95 | 42–43 |
| 14 | 4-Iodoanisole | $NaB(Ph)_4$ | 180 | 90 | 80–83 |
| 15 | Bromobenzene | $NaB(Ph)_4$ | 80 | 90 | 66–69 |
| 16 | 4-Bromotoluene | $NaB(Ph)_4$ | 100 | 94 | 41–44 |
| 17 | 4-Bromonitrobenzene | $NaB(Ph)_4$ | 45 | 96 | 112–114 |

(*Continues*)

**TABLE 4** (Continued)



| Entry | Aryl halide | Phenylatig reagent | Time (min) | Yield (%)[a] | M.P. (°C) |
|---|---|---|---|---|---|
| 18 | 4-Bromobenzonitrile | $NaB(Ph)_4$ | 60 | 90 | 81–84 |
| 19 | 4-Bromochlorobenzene | $NaB(Ph)_4$ | 60 | 93 | 72–73 |
| 20 | 4-Chloronitrobenzene | $NaB(Ph)_4$ | 275 | 89 | 110–113 |

[a] Isolated yield.

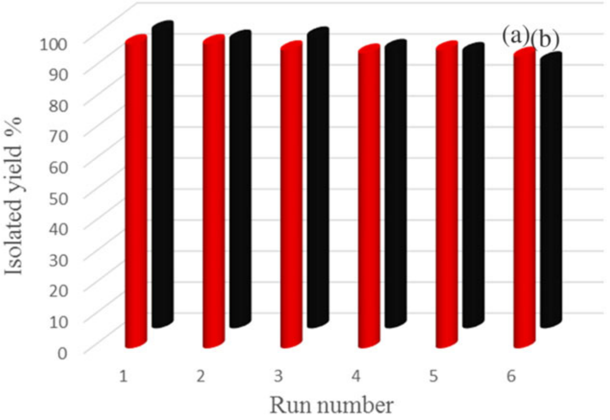
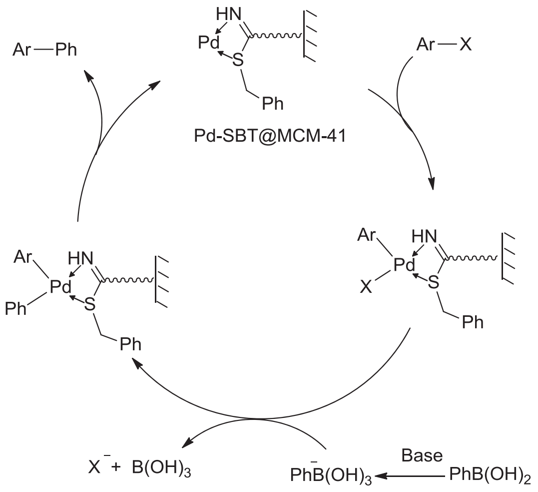


**FIGURE 6** Recyclability of Pd-SBT@MCM-41 in the (a) coupling of iodobenzene with $PhB(OH)_2$ and (b) synthesis of 5-phenyl-1H-tetrazole

In this regard, wide range of aryl halides with electron-donor and electron-withdrawing functional groups reacted with sodium tetraphenyl borate and the corresponding biphenyl was obtained in the good to excellent yields (Table 4, entries 12–20). Therefore, these results revealed that this methodology is effective for a wide range of aryl halides and phenylboronic deriavatives.

A plausible catalytic cycle for this C–C bond coupling reaction in the presence of Pd-SBT@MCM-41 was shown in Scheme 4.[10,37,38]

The reusability of the Pd-SBT@MCM-41 was studied in coupling of iodobenzene with $PhB(OH)_2$ and synthesis of 5-phenyl-1H-tetrazole (Figure 6). As shown in Figure 6, the catalyst was reused over 6 times without any significant palladium leaching or loss of its catalytic activity. The average isolated yield for 6 successive cycles in coupling of 4-Iodotoluene with $PhB(OH)_2$ and synthesis of 5-phenyl-1H-tetrazole is 91% and 91.3% respectively, which clearly demonstrates the practical recyclability of this catalyst.



**SCHEME 4** Plausible mechanism for the C-C coupling reaction in the presence of Pd-SBT@MCM-41

Also, to examine if Pd is leaching out from the catalyst during reactions, the amount of palladium in Pd-SBT@MCM-41 was determined by ICP-OES. The amount of Pd in Pd-SBT@MCM-41 was found to be $1.63 \times 10^{-3}$ mol $g^{-1}$ after 4 times recycled. This amount was comparable with fresh catalyst ($1.85 \times 10^{-3}$ mol $g^{-1}$). The obtained result confirmed that the palladium leaching is negligible in these reactions.

In order to indicate the efficiency of this catalyst, the obtained results for synthesis of the 5-phenyl-1*H*-tetrazole in the presence of Pd-SBT@MCM-41 was compared with previously reported methods for this cycloaddition reaction (Table 5). As shown in Table 5, Pd-SBT@MCM-41 has a better catalytic activity in synthesis of 5-substituted 1*H*–tetrazoles. Also Pd-SBT@MCM-41 is comparable with previously reported catalysts in terms of non-toxicity, price, stability, catalyst recycling and easy separation.

**TABLE 5** Comparison results of Pd-SBT@MCM-41 with other catalysts for synthesis of 5-phenyl-1*H*-tetrazole

| Entry | Catalyst | Condition | Time (h) | Yield (%)[a] | Ref. |
|---|---|---|---|---|---|
| 1 | CoY zeolite | DMF, 120°C | 14 | 90 | [22] |
| 2 | Cu–Zn alloy nanopowder | DMF, 135°C | 10 | 95 | [39] |
| 3 | $B(C_6F_5)_3$ | DMF, 120°C | 8 | 94 | [40] |
| 4 | $Fe_3O_4$/ZnS HNSs | DMF, 120°C | 24 | 81.1 | [41] |
| 5 | Mesoporous ZnS | DMF, 120°C | 36 | 86 | [42] |
| 6 | $LiB(N_3)_4$ | NH4OAc (15 mg), DMF/MeOH (9/1), 120°C | 8 | 86 | [43] |
| 7 | $CuFe_2O_4$ | DMF, 120°C | 12 | 82 | [44] |
| 8 | $FeCl_3$–$SiO_2$ | DMF, 120°C | 12 | 79 | [45] |
| 9 | Nano ZnO/$Co_3O_4$ | DMF, 120–130°C | 12 | 90 | [46] |
| 10 | Pd-SBT@MCM-41 | Peg, 120°C | 8 | 96 | This work |

[a] Isolated yield.

## 4 | CONCLUSION

Covalently functionalization of Pd-SBT complex onto the MCM-41 surface was successfully achieved by post-synthetic grafting procedure. A novel and highly efficient method was developed for synthesis of 5-substituted 1*H*–tetrazole derivatives by treatment of nitriles with sodium azide in the presences of Pd-SBT@MCM-41 as catalyst. Also, a simple and efficient procedure for Suzuki cross-coupling reaction between aryl halides and $PhB(OH)_2$ or $NaB(Ph)_4$) in the presence of Pd-SBT@MCM-41 in PEG-400 as green solvent was developed. This new protocol has the advantage of easy availability, easy handling, high stability and reusability of the catalyst, short reaction times, simple experimental and work up procedure.

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