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FULL PAPER



Palladium-anchored multidentate SBA-15/di-urea nanoreactor: A highly active catalyst for Suzuki coupling reaction

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Ghodsi Mohammadi Ziarani, Department of Chemistry, Faculty of Science, University of Alzahra, Tehran, Iran. Email: gmohammadi@alzahra.ac.ir Modification of mesoporous silica was carried out by reaction of SBA-15 with di-urea-based ligand. Next, with the help of this ligand, palladium ions were anchored within the multidentate SBA-15/di-urea pore channels with high dispersion. The SBA-15/di-urea/Pd catalyst was characterized using various techniques. Theoretical calculations indicated that each palladium ion was strongly interacted with one nitrogen and two oxygen atoms from the multidentate diurea ligand located in SBA-15 channels and these interactions remained during the catalytic cycle. These results are in good agreement with those of hot filtration test: the palladium ions have very high stability against leaching from the SBA-15/di-urea support. The catalytic performance of SBA-15/di-urea/Pd nanostructure was examined for the Suzuki coupling reaction of phenylboronic acid and electronically diverse aryl halides under mild conditions with a minimal amount of Pd (0.26 mol%). Compared to previous reports, this protocol afforded some advantages such as short reaction times, high yields of products, catalyst stability without leaching, easy catalyst recovery and preservation of catalytic activity for at least six successive runs.

KEYWORDS

functionalization of SBA-15, palladium nanoparticles, SBA-15/di-urea/Pd, Suzuki coupling reaction

1 | **INTRODUCTION**

Nanoreactors are a means of creating specific nanoscale chemical environments divided from the surrounding bulk space.^[6] Because of the nanoscale confinement effect of such nanoreactors, the physical and chemical properties of catalysts can also be modulated.^[7] Higher selectivity and reactivity have been observed when reactions occur in nanoreactors.^[8] Various types of nanoreactors have been developed, including dendrimers,^[9] carbon nanotubes,^[10] metal–organic frameworks,^[11] montmorillonites,^[12] zeolites^[13] and mesoporous silicas.^[14] Among the various nanoreactors,

mesoporous silicas, particularly SBA-15, have been widely studied.^[15–17] Large surface areas, highly ordered mesoporous structures with regular channels, high hydrothermal and mechanical stability, uniform pore sizes, thick walls, wide accessibility and inert environment for immobilization of transition metal nanoparticles^[18–22] make these structures excellent carriers for many metal species.^[23]

Investigation the application of metal nanoparticles in catalysis,^[24] especially in organic synthesis, has received marked interest in research of nanocatalysis.^[25] Among them, palladium nanoparticles (Pd NPs) have attracted much attention.^[26-28] Pd NPs supported on the two-

dimensional hexagonal structure of SBA-15 can be evenly dispersed, thus efficiently preventing Pd NP aggregation.^[29,30] The inner mesochannels of SBA-15 are rich in siloxy groups; hence, these hydrophilic moieties could hinder the mass transportation of hydrophobic molecules, causing a reaction to slow down.^[31] Hybrid porous materials such as SBA-15 combined with ligands bearing organic groups would make the materials hydrophobic and hydrothermally stable and thus endow them with improved catalytic activities in applications for organic synthesis.^[32] Therefore, to extend the applicability as well as stability of Pd-decorated SBA-15 materials in air and in aqueous media, it is necessary to improve the surface using organic functional groups by suitable organic ligands as linkers between SBA-15 silica and Pd.^[5]

Pd-catalysed cross-coupling reactions are an important class of carbon-carbon bond forming reactions that remain the most broadly explored area in the field of synthetic organic chemistry.^[33] Among C-C coupling reac-Pd-catalysed Suzuki-Miyaura coupling has tions. become an exceedingly powerful synthetic method for preparing biaryl compounds.^[34,35] Biaryls have broad applications in the synthesis of natural products, advanced materials and pharmaceuticals.^[36-38] Recently various types of Pd-anchored ligand-based SBA-15 have been reported for the synthesis of biaryl compounds.^{[39–} ^{43]} Cao and co-workers described the synthesis of a Pddiimine@SBA-15 catalyst for Suzuki-Miyaura coupling through immobilizing Pd ions into the pore channels of diimine-functionalized SBA-15 mesoporous silica.^[2] Sarkar et al. prepared a thiol-modified SBA-15-supported Pd catalyst for Suzuki coupling reaction under mild reaction conditions.^[44] Ghorbani-Vaghei et al. described the synthesis of a novel SBA-15/AO/Pd(II) nanocatalyst by anchoring of amidoxime group on SBA-15 silica and followed by deposition of PdCl₂.^[45] Veisi *et al.* were able to prepare SBA-15/CCPy/Pd(II) as a heterogeneous catalyst for C-C coupling reactions through functionalization of SBA-15 with 3-aminopropyltriethoxysilane.^[46] All of the prepared Pd@functionalized SBA-15 catalysts mentioned above showed higher activity and Pd holding ability than Pd@SBA-15 in Suzuki coupling reactions. However, to improve upon these advantages, herein we report a multidentate SBA-15/di-urea with high Pd

holding ability (each Pd ion is connected to one nitrogen and two oxygen atoms per ligand based on theoretical calculations), which is expected to be favourable for Suzuki-Miyaura catalytic coupling reactions (Scheme 1).

2 | EXPERIMENTAL

2.1 | Synthesis of SBA-15 Mesoporous Silica

The SBA-15 mesoporous silica sample was prepared according to our previously published procedure.^[47]

2.2 | Synthesis of SBA-15/Di-urea

For the synthesis of SBA-15/di-urea, 3-(triethoxysilyl) propylisocyanate (2 mmol) and *o*-phenylenediamine (1 mmol) were added to dry toluene (30 ml) and the solution was refluxed for 6 h under an inert atmosphere (progress of the reaction was monitored using Fourier transform infrared (FT-IR) spectroscopy). After completion of the reaction, SBA-15 (0.4 g) was added to the solution together with stirring for 24 h under reflux. The solid product was then centrifuged, washed with ethanol and tetrahydrofuran, and dried overnight in an oven at 80 °C. The final product was denoted as SBA-15/di-urea.

2.3 | Immobilization of Pd(II) Ions on Surface of SBA-15/Di-urea

Generally, 1.0 g of as-synthesized SBA-15/di-urea and 0.056 g of $Pd(OAc)_2$ in 40 ml of ethanol were refluxed for 12 h. The brown solid obtained was separated using filtration, washed with ethanol and dried in a vacuum oven at 70 °C for 60 min. The Pd content in the SBA-15/di-urea/Pd catalyst was 3.6 wt%, as determined using inductively coupled plasma atomic emission spectrometry (ICP-AES).

2.4 | Suzuki-Miyaura Coupling Reaction

In a general method, a 25 ml two-neck round-bottom flask was charged with aryl halide (1 mmol), phenylboronic acid (1.3 mmol), potassium carbonate (3 mmol), tetrabutylammonium bromide (TBAB) as a phase transfer agent (0.5 mmol), SBA-15/di-urea/Pd



SCHEME 1 Suzuki coupling using SBA-15/di-urea/Pd

(0.005 g, 0.26 mol% Pd) and a mixture of ethanol and water (2:1, 6 ml). The solution was then stirred for the desired time at 70 °C. An aliquot was taken at arbitrary time intervals, filtered and analysed using GC–MS. After completion of the reaction, the mixture was allowed to cool to room temperature. The catalyst was easily removed via filtration and then washed with ethyl acetate and ethanol. The organic layer was separated and dried over anhydrous magnesium sulfate and evaporated under reduced pressure to afford biaryl compounds. The spectral data for selected compounds are available in the supporting information (Figures S3 and S4).

3 | **RESULTS AND DISCUSSION**

3.1 | Catalyst Characterization

The preparation of the SBA-15/di-urea/Pd catalyst followed the steps described in Scheme 2. First, *o*phenylenediamine was reacted with 2 mol of 3isocyanatopropyltriethoxysilane via formation of C—N bond between amine and isocyanate parts to give 1,1'-(1,2-phenylene)bis(3-(triethoxysilyl)propyl)urea. Subsequently this di-urea-based ligand was reacted with ordered SBA-15 mesoporous silica to afford the di-ureafunctionalized SBA-15. Finally, the SBA-15/di-urea/Pd nanocatalyst was prepared by the reaction of $Pd(OAc)_2$ with SBA-15/di-urea.

FT-IR spectroscopy was used to investigate the preparation of SBA-15/di-urea/Pd. The FT-IR spectra of the free di-urea ligand, SBA-15, SBA-15/di-urea and SBA-15/di-urea/Pd are depicted in Figure 1. As can be seen, the characteristic absorption bands for free di-urea ligand are present at 3342 and 1741 cm⁻¹ due to the N-H and C=O stretching vibrations, respectively. The absence of a broad band at 2300 cm⁻¹ from isocyanate group and the absence of two sharp peaks of -NH₂ groups from ophenylenediamine at 3400 cm^{-1} also point to the fact that isocyanate groups successfully reacted with ophenylenediamine. The spectrum of parent SBA-15 shows the bands of symmetric and asymmetric stretching vibrations of Si-O-Si bonds at 800 and 1085 cm⁻¹, respectively, and a band at 1634 cm^{-1} due to O–H bending vibration.^[48] Furthermore in the spectrum of SBA-15 there is a weak peak at 961 cm^{-1} corresponding to the symmetric stretching vibration of Si-OH which is absent in the spectrum of SBA-15/di-urea. Compared with the spectrum of SBA-15/di-urea, it can be observed that the SBA-15/di-urea/Pd spectrum shows similar bands. Moreover, the stretching frequency at 576 cm^{-1} in the spectrum of SBA-15/di-urea/Pd is assigned to v_{Pd-N} .^[49] These results provide evidence that the SBA-15/di-urea sample was successfully functionalized with Pd species.



SCHEME 2 Schematic of SBA-15/diurea/Pd fabrication



FIGURE 1 FT-IR spectra of free di-urea ligand, SBA-15, SBA-15/ di-urea and SBA-15/di-urea/Pd

A typical scanning electronic microscopy (SEM) image of SBA-15/di-urea/Pd (Figure 2a) demonstrates rod-shaped morphology aggregated into bundles. A transmission electron microscopy (TEM) image of SBA-15/di-urea/Pd shows that the material is organized in ordered arrays of two-dimensional hexagonal mesoporous SBA-15 and the attachment of organic components inside the pore channels of SBA-15 silica has no distinct influence on the morphology of composition (Figure 2c). Moreover, the dark spots in the TEM image are the Pd NPs with diameters of about 3 nm that are clearly obvious.

The presence of Pd in the SBA-15/di-urea/Pd nanocatalyst was clearly confirmed via energy-dispersive

X-ray spectroscopy (EDS), the spectrum also showing the presence of N, C, O and Si (Figure 2b). The maps of Si, O, C, N and Pd (Figure 2d–h) are well defined with sharp contrast.

Low-angle XRD patterns of SBA-15 and the SBA-15/ di-urea/Pd catalyst are displayed in Figure 3. SBA-15 shows a strong diffraction reflection (100) and two small diffraction reflections (110) and (200).^[48] All reflections indicate that the mesoporous SBA-15 has a well-defined hexagonal symmetry and has long-range ordering of its structure. The presence of the di-urea ligand results in a minor decrease in the overall intensity of the (100), (110) and (200) reflections owing to the loading of organic moieties in the mesostructured SBA-15 material. Comparison of the diffraction patterns of SBA-15 and SBA-15/di-urea/Pd demonstrates that the ordered mesoporous structure of the sample remains intact even after incorporation of the Pd complex in the SBA-15 silica.

The results for N₂ adsorption–desorption isotherms concerning the Brunauer–Emmett–Teller (BET) surface area (S_{BET}), the total pore volume (V_{total}) and the pore diameter (D_{BJH}) of SBA-15, SBA-15/di-urea and SBA-15/di-urea/Pd are presented in Table 1.

The materials demonstrated a type IV nature with an H_1 hysteresis loop, characteristic of mesoporous solids with uniform cylindrical pores according to the IUPAC classification. From the data of Table 1, the incorporation of the di-urea ligand into mesoporous SBA-15 silica pores and the inclusion of Pd into this structure shifted the pore size to a smaller value and led to decreased in pore volume and surface area. S_{BET} decreased during the two functionalization processes as compared to the parent



FIGURE 2 (a) SEM image, (b) EDS spectrum, (c) TEM image and (d-h) EDS mapping images of SBA-15/di-urea/Pd. The arrows in (c) indicate Pd NPs



FIGURE 3 Low-angle XRD patterns of SBA-15 and SBA-15/diurea/Pd

SBA-15. These results confirm that the surface modification indeed occurred within the primary mesopores of SBA-15 silica which can be ascribed to the di-urea and di-urea/Pd functionalization. Additionally, Barrett– Joyner–Halenda (BJH) analysis indicated that the primary pore size of SBA-15 decreased during the functionalization process for the same reason (Figure 4).

The amount of grafted organic compounds on the mesoporous SBA-15/di-urea/Pd surface was also estimated using thermogravimetric analysis (TGA), from room temperature up to 1000 °C. The related curves are shown in Figure 5. The initial weight of SBA-15/di-urea/Pd exceeding 100% is related to the buoyancy effect.^[50] The obtained results revealed that the first weight loss (4.1%) below 200 °C can be attributed to trapped solvents and physically adsorbed compounds trapped in the SBA-15 channels pores. After that, the obvious mass change (23.1%) from 200 up to 570 °C can be assigned to covalently functionalized organic motifs (di-urea ligand) in the material. The amount was estimated to be 0.82 mmol g⁻¹ for degradation of organic



FIGURE 4 N_2 adsorption-desorption isotherms and BJH pore size distribution curves of SBA-15 and SBA/di-urea

groups. Since free silanols groups on the surface of SBA-15 can be dehydrated at high temperatures, the slight weight loss (2.2%) detected at temperatures above 570 °C can be ascribed to this phenomenon.

3.2 | Computational Details

Quantum chemical calculations were carried out with density functional theory using the ORCA 3.0.3 program.^[51] Geometries were optimized using the BP86



FIGURE 5 TGA profile of SBA-15/di-urea/Pd

TABLE 1Textural properties of SBA-15, SBA-15/di-urea and SBA-15/di-urea/Pd

Entry	Sample	$S_{\rm BET} \ ({ m m}^2 { m g}^{-1})$	D _{BJH} (nm)	$V_{\rm total}~({\rm cm}^3~{\rm g}^{-1})$
1	SBA-15	824	8.1	1.45
2	SBA-15/di-urea	518	6.5	0.81
3	SBA-15/di-urea/Pd	501	6.2	0.79

functional^[52,53] and the def2-TZVP basis sets.^[54] and the solvent effects were included in all calculations using the conductor-like screening model (COSMO).^[55] The PBE0 hybrid functional^[56] was used for single-point energy calculations. The optimized geometries of the ligand and the Pd complex (two different structures) are displayed in Figure 6, and the bond lengths, Mayer bond orders and Mulliken atomic charges are listed in Table S1. In the more symmetric structure, Pd is connected to two nitrogen atoms (bond orders ~ 0.69) and two oxygen atoms (bond orders ~ 0.40). However, this structure is less stable than the asymmetric structure, and the energy difference including zero-point energy is about 40 kJ mol $^{-1}$. In the optimized structure of the asymmetric Pd complex catalyst, Pd is connected to one nitrogen atom and two oxygen atoms through Mayer bond orders of 0.83, 0.53 and 0.49, respectively. Consequently, the C-O bond orders in carbonyl groups have been reduced from 1.87 and 1.73 in the free ligand to 1.44 and 1.28 in the SBA-15/di-urea/Pd (L-Pd) complex. The asymmetric structure of the L-Pd complex was used in subsequent calculations for the Suzuki reaction.

The Suzuki coupling reaction catalysed by the L–Pd complex was studied step by step. In the first step, the catalyst is coupled with phenyl iodide to yield an organopalladium complex. For the formation of this intermediate, ΔE was calculated to be -5.2 kJ mol⁻¹.



In the next step, iodide is replaced with a hydroxyl ion, and ΔE for this step was found to be -152.4 kJ mol⁻¹.



Phenylboronic acid provides another phenyl group, which is transferred to the Pd complex with $\Delta E = -181.0 \text{ kJ mol}^{-1}$.



The final step is reductive elimination in which the Pd complex eliminates the product and regenerates the catalyst. For this step ΔE was calculated to be -68.0 kJ mol⁻¹.



The optimized structures of all intermediates are displayed in Table S2 of the supporting information, and the bond lengths, bond orders and Mulliken atomic charges are listed. As evident from Table S2, Pd—O and Pd—N bond orders are relatively high in all intermediate structures of the Suzuki reaction. This indicates that Pd is strongly attached to the ligand, and the L–Pd structure remains relatively intact in the reaction cycle.

3.3 | Catalytic Activity

After characterization of the synthesized catalyst, it was investigated in the Suzuki coupling reaction. Various chemical parameters including solvent, kind of base, reaction temperature, amount of catalyst and type of aryl halide substrate were studied to determine the best possible combination. To optimize the reaction conditions, the Suzuki coupling between 4-iodobenzene and phenylboronic acid was chosen as a model reaction. To examine the influence of solvent, dimethylformamide, ethanol, water and toluene were studied. As shown in

FIGURE 6 Optimized structure of (a) asymmetric and (b) and symmetric Pd complex catalyst



FIGURE 7 Effect of base on progress of Suzuki reaction in presence of SBA-15/di-urea/Pd catalyst in EtOH-H₂O (2:1)

Figure S1, the single solvents afforded low yields for the reaction whereas the organic–aqueous co-solvent EtOH– H_2O gave high yields of products. Next the effect of various volume ratios of EtOH– H_2O as a solvent in the Suzuki reaction was studied. It was found that the optional volume ratio should be set at 2:1. The merit of the co-solvent can be attributed to the good solubility of the inorganic base and the organic reactants.

Unlike other cross-coupling reactions such as the Stille or Sonogashira reactions, the Suzuki–Miyaura reaction requires aqueous base to activate the boronate ester component. So various types of inorganic and organic bases, such as NaOH, NaHCO₃, K₂CO₃, K₃PO₄, KOH and NEt₃, were investigated in the Suzuki coupling reaction in EtOH–H₂O (2:1). Comparing all the results shown in Figure 7, it was found that an organic base like NEt₃ was less reactive than inorganic bases such as K₂CO₃ and KOH. The results indicate that stronger alkalinity could increase the product yield but the high alkalinity of KOH solution might damage the structure of the SBA-15 silica during the Suzuki coupling reaction.^[2] According to this, K_2CO_3 was selected as the best base for the reaction.

It seems that the temperature has an influence on the catalytic efficiency of SBA-15/di-urea/Pd. Based on this, increasing the temperature up to 70 °C was vital to obtain a high yield of products while no significant increase in reaction yield was observed at higher temperatures (Figure S2). It is noteworthy that when the reaction was carried out below 40 °C, only a poor yield of products was obtained.

Also, the influence of amount of catalyst on the Suzuki coupling reaction of 4-iodobenzene and phenylboronic acid was studied. It was found that 0.26 mol% of Pd was optimum in the reaction. Nevertheless, aside from the overall amount of Pd in the coupling reaction, weight percentage of Pd inside SBA-15/di-urea/Pd was also investigated. According to Figure 8, the best result was obtained with 3.6 wt% of Pd, because higher catalyst loading (4.8 wt%) led to higher Pd leaching (determined usingICP-AES).

Upon optimization of the reaction conditions, the catalytic activity of SBA-15/di-urea/Pd for Suzuki coupling reactions of various aryl halides and phenylboronic acid was investigated, and the results are presented in Table 2. It is evident that aryl iodides versus aryl bromides exhibited more activity towards products (Table 2, entries 2 and 5) but, with the reaction of aryl chlorides, a low yield of products was obtained because of the strength of the C-Cl bond. In most cases of Suzuki reaction, oxidative addition is the rate-determining step of the catalytic cycle. During this step, coupling reactions involving halogenated substrates typically decrease in the order R-I > R-Br > R-Cl. This may be explained according to the R-X bond dissociation enthalpies. For example, the X-Ph bond dissociation enthalpies range from $65.0 \pm 1 \text{ kcal mol}^{-1}$ (X = I) to $80.4 \pm 1.5 \text{ kcal mol}$ $^{-1}$ (X = Br) and 95.5 ± 1.5 kcal mol⁻¹ (X = Cl).^[57]



FIGURE 8 Influence of weight percentage of Pd in SBA-15/di-urea/Pd

TABLE 2Suzuki coupling reactions of various aryl halides andphenylboronic acid over SBA-15/di-urea/Pd catalyst^a

Entry	R	x	Time (h)	Yield (%) ^b	TON ^c	TOF (h ⁻¹) ^d
1	Н	Ι	20 min	>99	385	1283
2	4-0CH ₃	Ι	30 min	>99	385	770
3	$2-NH_2$	Ι	1	88	338.5	338.5
4	Н	Br	1	98	377	377
5	4-OCH_3	Br	2	95	365	183
6	4-COCH ₃	Br	1.5	97	371	249
7	4-CHO	Br	2	96	369	185
8	3-CHO	Br	5	86	331	66
9	4-NO ₂	Br	3	93	358	119
10	4-OH	Br	5	82 ^e	315	64
11	4-NH ₂	Br	5.5	80	308	56
12	2-NO ₂	Br	7	78	300	43
13	4-Br	Br	4	92^{f}	354	89
14	Н	Cl	8	80	308	38
15	4-NH ₂	Cl	12	72	277	24
16	4-CH ₂ -Cl	Cl	12	70	270	22

^aReaction conditions: ArX (1 mmol), PhB(OH)₂ (1.3 mmol), K_2CO_3 (3 mmol), TBAB (0.5 mmol), EtOH-H₂O (2:1, 6 ml) in the presence of catalyst (0.005 g, 0.26 mol% Pd) at 70 °C.

^bGC-MS yield.

^cTurnover number, calculated as: moles of product/moles of active sites.

^dTurnover frequency, calculated as TON/time.

^eIsolated yield.

^fIsolated yield using ArX (2 mmol), PhB(OH)₂ (2.5 mmol), K₂CO₃ (5 mmol).

Therefore monosubstituted aryl halides iodobenzene, bromobenzene and chlorobenzene with phenylboronic acid gave yields of biphenyl of >99, 98 and 80%, respectively (Table 2, entries 1, 4 and 14). In the case of iodobenzene and bromobenzene, the corresponding products were obtained with high turnover frequencies (TOFs) of 1283 and 377 h^{-1} . When aryl halides containing both electron-withdrawing and electron-donating groups were coupled with phenylboronic acid, the corresponding biphenyl products were obtained in excellent yields. Moreover, para-substituted aryl halides afforded high yields of the desired biaryls whereas sterically hindered ortho-substituted halides provided moderate yields of products. For example, the Suzuki coupling reaction of 4- and 3-bromobenzaldehyde with phenylboronic acid gave 96 and 86% yields after 2 and 5 h (Table 2, entries 7 and 8). Additionally, meta-substituted aryl halides led to lower yield than the para-substituted derivatives such as in the case of 4- and 2-nitrobenzaldehyde, where the corresponding products were obtained in yields of 93 and 78%, respectively (Table 2, entries 9 and 12).

Based on the results discussed above and also the computational details (Section 3.2), a proposed mechanism for the Suzuki coupling reaction over SBA-15/diurea/Pd can be described through a catalytic cycle which involves three fundamental steps: oxidative addition, transmetalation and reductive elimination (Scheme 3). The oxidative addition of aryl halides to Pd(0) complex is the initial step to give intermediate **1**, a Pd(II) species. With the participation of base, an organoborane compound reacts with intermediate **1** in transmetalation to give intermediate **2**. This is followed by reductive elimination to produce the corresponding biphenyl product and regeneration of the original Pd(0) species.

3.4 | Catalyst Leaching and Recyclability

3.4.1 | Hot filtration test

To test if Pd was leached out from the catalyst during the reaction, a hot filtration test for the model Suzuki reaction under the optimal conditions was carried out. In this method, hot reaction mixture was filtered after 10 min and the coupling reaction was permitted to continue under the same conditions with the supernatant solution. No increase in the product was observed (determined using GC–MS measurements) and no Pd could be detected in the hot filtered solution using ICP-AES. This result showed that the Pd NPs were firmly grafted on the SBA-15/di-urea nanoreactor because of the excellent affinity between Pd NPs and di-urea ligand.

3.4.2 | Reusability of catalyst

The recyclability of catalysts is one of the most important advantages of heterogeneous catalytic systems from an economic point of view. The process of recycling of the SBA-15/di-urea/Pd catalyst was performed for the Suzuki coupling reaction of 4-iodobenzene and phenylboronic acid under optimized reaction conditions. After the completion of each cycle, the solid catalyst was filtered off from the reaction, washed with ethyl acetate and hot ethanol followed by drying under vacuum overnight and reused in a subsequent run. The results in Figure 9 demonstrate that the supported catalyst was highly reusable under the examined reaction conditions, preserving almost unaltered its initial catalytic performance after six uses. The ICP analysis results for fresh and reused Pd catalyst were 3.6 and 3.4 wt%, respectively.

3.5 | Comparison

Several reports on the use of Pd-based SBA-15-catalysed Suzuki coupling reactions have appeared in the



SCHEME 3 Proposed mechanism of Suzuki coupling reaction



FIGURE 9 Recycling study of SBA-15/di-urea/Pd

literature.^[1-5] Table 3 presents a comparison of the catalytic activity of SBA-15/di-urea/Pd in the coupling of bromobenzene and phenylboronic acid with that of other supported Pd catalysts. As is evident, the SBA-15/di-urea/Pd catalyst showed a higher performance than some of

the previously reported catalysts in terms of shorter reaction times, higher stability and also better isolated yields.

4 | CONCLUSIONS

In summary, the present work reports a highly stable and recyclable mutidentate SBA-15/di-urea/Pd nanoreactor as heterogeneous catalyst for Suzuki–Miyaura cross-coupling reactions of aryl halides with phenylboronic acid in mixed EtOH– H_2O solvent under mild conditions. Theoretical calculations indicated that each Pd ion was interacted with one nitrogen and two oxygen atoms from the multidentate di-urea ligand located in SBA-15 channels. Moreover these calculations suggested that the interactions of Pd with nitrogen and oxygen atoms remained during catalytic cycle. It is noteworthy that the high stability and activity of the presented

TABLE 3 Comparison of catalytic activity of various catalysts in the coupling of bromobenzene and phenylbo	oronic acid
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Entry	Catalyst	Temp. (°C)	Time (h)	Yield (%)	Ref.
1	D-2PA-Pd(II)@SBA-15	120	5	85	[1]
2	Pd-Diimine@SBA-15	80	12	87	[2]
3	Pd@SBA-15/IL _{DABCO}	80	12	95	[3]
4	Pd ⁰ /SBA-15	110	4	80.2	[4]
5	SBA-15-EDTA-Pd	120	8	83	[5]
6	SBA-15/di-urea/Pd	70	1	98	This work

nanoreactor system could be directly assigned to the nature of the applied mutidentate di-urea ligand, which is not only an inherently air- and moisture-stable ligand, but also acts to stabilize active Pd species to protect Pd NPs against agglomeration and Pd black formation. Additionally, the SBA-15/di-urea/Pd catalyst could be easily separated by filtration and reused at least six times without significant decrease of catalytic activity.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

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