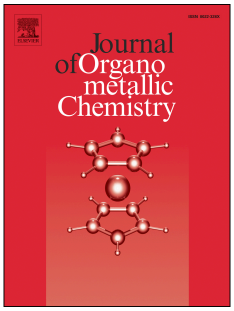

Nano–silica supported palladium catalyst: Synthesis, characterization and application of its activity in Sonogashira cross–coupling reactions

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Nano–silica supported palladium catalyst: Synthesis, characterization and application of its activity in Sonogashira cross–coupling reactions

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Abstract– This study deals about preparation of palladium(II) complex of 3,5–*bis*(2–benzothiazolyl)pyridine supported on nano silica functionalized with trimethoxysilylpropyl chloride, $Pd(II)Cl_2$–BTP@TMSP–$nSiO_2$. The synthesized heterogeneous catalyst was characterized by FT–IR, UV–Vis spectroscopies, field emission scanning electron microscopy, energy dispersive X–ray analysis, transmission electron microscopy and elemental analysis. Furthermore, the $Pd(II)Cl_2$–BTP@TMSP–$nSiO_2$ was found as a highly efficient catalyst in the Sonogashira cross–coupling of aryl halides (iodides, bromides and chlorides) with phenyl acetylene. This heterogeneous catalyst was easily recyclable and reused several times without significant loss of reactivity. Finally, its catalytic activity was compared with homogeneous catalyst to demonstrate the effect of supporting on the catalytic activity.

Keywords: *Sonogashira cross–coupling; Palladium complex; Nano silica; Aryl halide.*

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1. Introduction

The palladium catalyzed C–C coupling reactions are considerably powerful tools in synthetic organic chemistry [1]. These include Suzuki–Miyaura, Mizoroki–Heck, Sonogashira–Hagihara, Stille, Fukuyama and Negishi reactions [2]. Among them, the Sonogashira–Hagihara cross–coupling is one of the most successful methods for the carbon–carbon bond forming between sp^2–hybridized carbon atoms of aryl, heteroaryl, and vinyl halides and sp–hybridized carbon atoms of terminal acetylenes [3–10]. The products of these reactions have been widely used for the synthesis of substituted alkynes [8] natural products, pharmaceutical compounds, polymeric materials [4] and optical materials [11-13].

The traditional procedure for the Sonogashira–Hagihara reaction requires the presence of Pd–complex of phosphines as a catalyst and copper iodide salt as a co–catalyst. However, using copper salts as co–catalysts sometimes leads to the homo–coupling reaction of terminal alkynes (Glaser–type reaction) upon exposure of the copper–acetylide intermediate to air or other oxidizing agents [14–16]. However, the separation of these unpleasant by–products is difficult [17–19]. Therefore, several attempts have been done to eliminate the copper co–catalyst from the Sonogashira–Hagihara reaction [20,21]. Thus, the design and synthesis of palladium catalysts for this reaction under copper free and mild reaction conditions are highly desirable [22].

The palladium salts are expensive to purchase and therefore homogeneous palladium catalysts suffer from disadvantages such as high price, low chemical and thermal stability, and difficulties in the isolation and recovery of the catalyst from the reaction mixture. These problems limit the large–scale applications of these catalysts. A way to overcome these difficulties is to immobilize the palladium catalysts on suitable supports. In this respect, several heterogeneous palladium catalysts have been reported for Sonogashira C–C coupling reactions [2, 23–31]. Sardarian and co–workers reported the reaction of different aryl halides with alkynes in water in the presence of nanosilica dendritic polymer supported palladium nanoparticles [32]. Also, our group reported the synthesis of mono–, di–, and trialkynylaromatics by Sonogashira cross–coupling reaction in water by Pd nanoparticles immobilized on nanosilica triazine dendritic polymer as catalyst [33]. Zhang and co–workers reported the Sonogashira coupling reactions between aryl halides and aryl acetylenes at 120 °C using a novel magnetic composite nanoparticles anchored palladium nanocatalyst [34]. Also, an efficient copper and solvent free Sonogashira cross-coupling reaction catalyzed by polymer supported 3-benzoyl-1-(1-benzylpiperidin-4-yl)-2-thiopseudourea-Pd(II) complex, was reported [27].

One of the most applied supports is nano–silica due to its excellent (chemical and thermal) stability, economic aspects, good accessibility and reusability and good dispersion of catalytic active sites on it [35].

Here, we report the preparation of palladium complex of *bis*–thiazole ligand and investigation of its catalytic activity in the Sonogashira C–C coupling reaction under copper ion and phosphorous ligand free conditions. Also, the catalyst was supported on silica nanoparticles and characterized by different analytical techniques. Finally, its catalytic activity was studied in the Siniogashira reaction and the results were compared with homogeneous counterpart (Scheme 1).

Scheme 1. Sonogashira cross–coupling catalyzed by $Pd(II)Cl_2$–BTP@TMSP–$nSiO_2$.

2. Experimental

2.1. Materials and methods

All the reagents were obtained from commercial sources. The FT–IR spectra were recorded by a JASCO 6300 spectrophotometer. The UV–vis spectra were recorded by a JASCO V–670 spectrophotometer. ^1H NMR and ^{13}C NMR (400 and 100 MHz) spectra were taken on a Bruker

Avance 400 MHz spectrometer. The morphological features were obtained on a SIGMA VP–500 field emission–scanning electron microscope (FE–SEM), equipped with an energy dispersive X–ray analysis (EDAX) detector. Elemental analysis was performed on a LECO, CHNS–932 analyzer. The palladium content of the catalyst was determined by a Jarrell–Ash 1100 ICP analysis. The transmission electron microscopy (TEM) was carried out on a Zeiss EM10C transmission electron microscope operating at 100 kV. The silica nanoparticles were activated and chloropropylated by known procedures [36, 37].

2.2. Synthesis of Pd(II)Cl_2–BTB catalyst

In a 25 mL round bottom flask equipped with a condenser, a mixture of triphenylphosphite (TPP, 0.52 ml, 2 mmol), tetrabutylammonium bromide (TBAB, 0.88 g, 3 mmol), 2–aminothiophenol (0.212 ml, 2 mmol), and 1,3–benzenedicarboxylic acid (0.164 g, 1 mmol) was prepared and stirred at 100 ºC for 120 min. At the end of the reaction, MeOH (15 ml) was added to the viscous solution to precipitate the product. The resulting solid was filtered off and washed with cold MeOH to give the desired 1,3–*bis*(2–benzothiazolyl)benzene(BTB) ligand. Then, the residue was purified by recrystallization from ethanol to afford the pure product [38]. ^{1}H NMR (400 MHz, $CDCl_3$) 8.83 (t, J = 1.6, 1H), 8.25 (dd, J = 7.6, 1.6 Hz, 2H), 8.15 (d, J = 8, 2H), 7.97 (dd, J = 8, 0.4 Hz, 2H), 7.66 (t, J = 8, Hz, 1H), 7.53–7.58 (td, 2H, aromatic H), 7.43–7.47 (td, 2H, aromatic H), FT–IR (KBr disc): 1560 (m), 1424 (m), 1315 (m), 954 (s), 893 (m), 752 (s), cm^{-1}.Elemental analysis: calcd for $C_{20}H_{12}N_2S_2$ (344) C, 69.76; H, 3.49; N, 8.17; S, 18.62; found: C, 71.39; H, 3.79; N, 7.75; S, 18.66.

A mixture of 1,3–*bis*(2–benzothiazolyl)benzene, BTB, ligand (1 mmol) and $PdCl_2$ (1 mmol) in EtOH (3 mL) was stirred under reflux conditions for 5 h. After the homogeneous catalyst was synthesized, the resulting solid was filtered off and washed with EtOH to give the desired Pd(II)Cl_2–BTB complex.

2.3. Synthesis of Pd(II)Cl_2–BTP@TMSP–nSiO_2 catalyst

First, in a 25 mL round bottom flask equipped with a condenser, a mixture of triphenyl phosphite (TPP, 0.52 ml, 2 mmol), tetrabutylammonium bromide (TBAB, 0.88 g, 3 mmol), 2–aminothiophenol

(0.212 ml, 2 mmol), and pyridine–3,5–dicaboxylic acid (0.164 g, 1 mmol) was prepared and stirred at 100 ºC for 120 min. At the end of the reaction, MeOH (15 ml) was added to the viscous solution to precipitate the product. The resulting solid was filtered off and washed with cold MeOH to give the desired 3,5–*bis*(2–benzothiazolyl)pyridine, BTP, ligand. Then, the residue was purified by recrystallization from ethanol to afford the pure product [39]. ^{1}H NMR (400 MHz, $CDCl_3$) 9.42 (d, *J* = 2Hz, 2H), 9.06 (t, *J* = 2.4, 1H), 8.18 (d, *J* = 8.4, 2H), 8 (dd, *J* = 8, 0.4Hz, 2H), 7.59 (td, *J* = 8.2, 0.26 Hz, 2H), 7.47–7.51 (td, 2H, aromatic H), FT–IR (KBr disc): 1690 (s), 1417 (m), 1265 (s), 957 (m), 751 (s), 720 (s), cm^{-1}. Elemental analysis: calcd for $C_{19}H_{11}N_3S_2$ (345.18) C, 66.08; H, 3.18; N, 12.17; S, 18.55; found: C, 66.32; H, 3.67; N, 12.35;S, 18.10.

For attachment of BTP ligand to nanosilica and preparation of BTP@TMSP–nSiO_2, a mixture of chloropropylated nanosilica (1 g), BTP ligand (0.24 g, 1 mmol) and NaI (0.17 g, 1.2 mmol) in dry DMF (25 mL) was stirred under reflux conditions overnight. The yellow solid material was separated by filtration, washed with $CHCl_3$ (2×15 mL) to remove the unreacted 3,5–*bis*(2–benzothiazolyl)pyridine ligand. The final nanocatalyst, Pd(II)Cl_2–BTP@TMSP–nSiO_2, was obtained by addition of $PdCl_2$ (0.33 g, 1 mmol) to silica supported BTP@TMSP–nSiO_2 in ethanol (25 mL) under reflux conditions for 24 h. The resulting catalyst was washed with ethanol (2×15 mL) to remove the unreacted $PdCl_2$, and finally dried under air.

2.4. General Procedure for the Sonogashira cross–coupling of aryl halides with phenyl acetylene catalyzed by pd(II)Cl_2–BTP@TMSP–nSiO_2

A round–bottom flask was charged with aryl halide (1 mmol), phenylacetylene (1.1 mmol), DIPEA (1 mmol), Pd(II)Cl_2–BTP@TMSP–nSiO_2 (0.15 mol% Pd) and H_2O/DMF (0.5 mL,1:1). The reaction mixture was stirred at at room temperature for the time indicated in Table 2 and its progress was monitored by TLC (*n*–hexane/ethyl acetate, 6:1). After completion of the reaction, ethyl acetate (15 mL) was added to reaction mixture, and the catalyst was separated by centrifugation. The resulting mixture was washed with H_2O (2×10 mL). Then, the organic layer was dried over anhydrous $MgSO_4$ and the solvent was removed under reduced pressure. The residue was recrystallized from ether and ethyl acetate (3:1) to afford the pure product (Table 2).

3. Results and discussion

3.1. Preparation and characterization of catalysts

Scheme 2 demonstrates the preparation route for homogeneous catalyst. As can be seen, 1,3–*bis*(2–benzothiazolyl)benzene (BTB) was prepared by the reaction of 2–aminothiophenol with 1,3–benzenedicarboxylic acid in the presence of triphenylphosphite [38]. Then, the produced ligand reacted with $PdCl_2$ to give the Pd(II)Cl_2–BTB. The homogeneous catalyst was characterized by FT–IR, ^{1}H NMR, and UV–vis spectroscopies. From the FT–IR spectra presented in Fig. 1, the absorption band at 1690 cm^{-1} corresponds to the stretching vibration mode of imine bond in BTB. This band appears at 1585 cm^{-1} in the FT–IR spectrum of the synthesized homogeneous catalyst indicating the coordination of the ligand to the metal.

In the UV–vis absorption spectrum of the BTB ligand, two absorption peaks were observed at 260 and 300 nm (Fig. 2). Upon complexation, the Pd(II)Cl_2–BTB complex exhibits a peak at 400 nm, which is pertained to *d–d* charge transfer (Fig. 3).

The preparation path for heterogeneous catalyst is demonstrated in Scheme 3. First, the BTP ligand, 3,5–(*bis*(2–benzothiazolyl))pyridine, was prepared by the reaction of 2–aminothiophenol with 3,5–pyridinedicarboxylic acid. Then, the prepared ligand was attached to the surface of 3–chloropropylated nanosilica and finally a heterogeneous catalyst, Pd(II)Cl_2–BTP@TMSP–nSiO_2, was obtained by the reaction of the nanosilica supported BTP ligand with $PdCl_2$. The prepared heterogeneous catalyst was characterized by elemental analysis, FT–IR and UV–vis spectroscopies, SEM, TEM and ICP analyses.

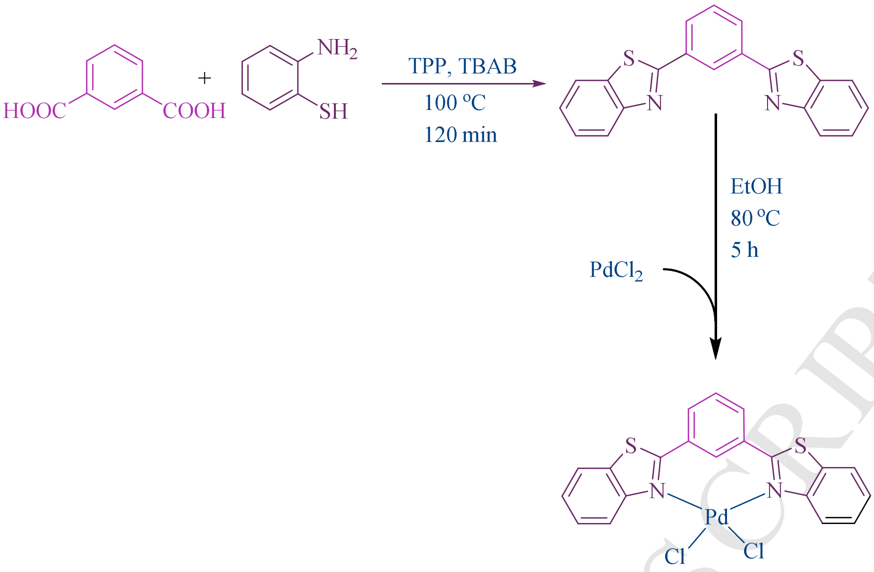
In the FT–IR spectrum, the bands at 1101 (Si–O–Si), 1427 (C=N) and 2955 cm^{-1} (C–H stretching vibration) confirmed the attachment of the catalyst on the surface of nano SiO_2 (Fig. 4).

In the diffuse–reflectance UV–vis spectrum of the BTP@TMSP–nSiO_2, the peak at 347 nm was attributed to $n \rightarrow \pi^*$ transitions in the BTP@TMSP–nSiO_2 (Fig. 5). In the case of the Pd catalyst, the peak at 485 nm was assigned to the *d–d* transition of Pd in Pd(II)Cl_2–BTP@TMSP–nSiO_2 (Fig. 6).

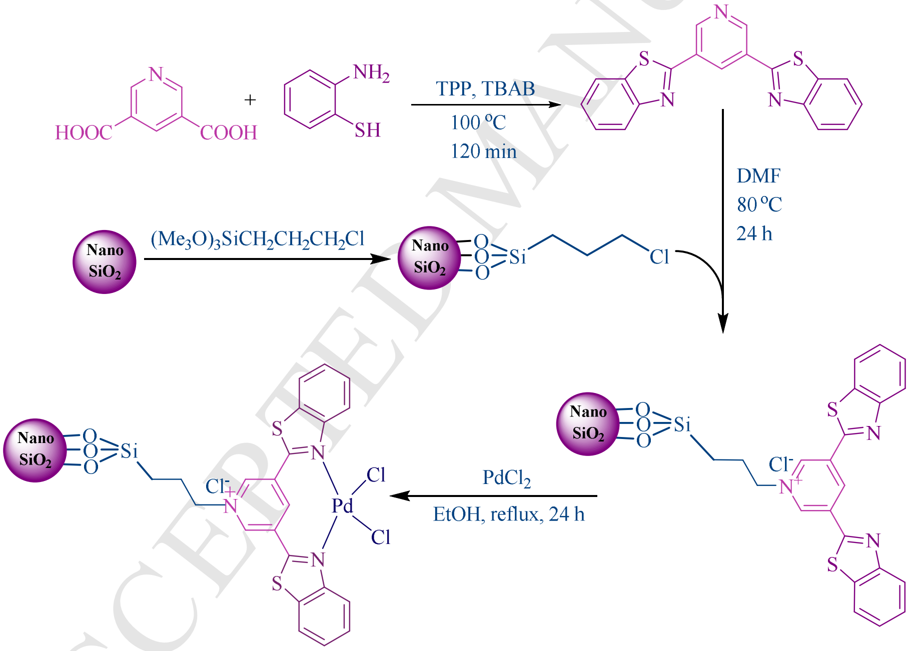
To study the morphology and particle size of the Pd(II)Cl_2–BTP@TMSP–nSiO_2, FE–SEM images of the catalyst were taken (Fig. 7). As can be seen, the nano–SiO_2 particles are spherical and have diameters in the range of 24 nm (Fig. 8). Furthermore, the energy–dispersive X–ray spectroscopy (EDX) obtained from SEM shows the presence of Pd atoms as well as, Si, N, S, and O atoms in the texture of Pd(II)Cl_2–BTP@TMSP–nSiO_2 catalyst (Fig. 9). Also, the elemental mapping showed that palladium species have been distributed uniformly in the catalyst texture (Fig. 10).

The catalyst was further characterized by transmission electron microscopy (TEM). According to the TEM images, the Pd complex has been well dispersed within the nanosilica matrix (Fig. 11).

The amount of palladium deposited on the surface of nanosilica was determined by an inductively coupled plasma (ICP) analyzer. The ICP analysis showed that the amount of Pd is about 0.31 mmol of Pd/g of the heterogeneous catalyst. The nitrogen content of the catalyst, determined by CHN ananalysis, was about 1.52%. According to this value, the amount of ligand on the nanosilica is 0.35 mmol g^{-1}.



Scheme 2. The preparation route for homogeneous catalyst



Scheme 3. The preparation route for heterogeneous catalyst

3.2. Investigation of catalytic activity of both catalysts in the C–C coupling reactions

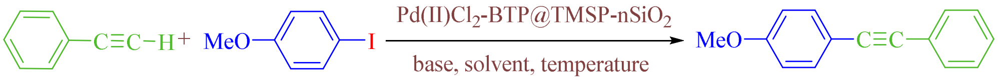
The catalytic activity of the heterogeneous catalyst was investigated in the Sonogashira–Hagihara cross–coupling of aryl halides with aliphatic alkyne. As shown in Table 1, the reaction conditions such as kind of base and solvent, and the amount of catalyst were optimized in the coupling of 4–iodoanisole with phenylacetylene in the presence of Pd(II)Cl_2–BTP@TMSP–nSiO_2 catalyst as a model reaction (Table 1).

First, a wide range of bases such as NaOH, Na_2CO_3, K_2CO_3, NEt_3 and DIPEA (*N*,*N*–diisopropylethylamine) were screened, and amongst them, DIPEA (1 mmol) was found to be the most efficient base both in terms of reaction time and yield. Note that in the absence of base, only 15% of the corresponding product was produced. This shows that the presence of base is crucial in this reaction (entries 1-6). Lower amount of base (0.75 mmol) gave lower yield but increasing it to 1.5 mmole had no significant effect on the product yield (entries 7 and 8).

To study the effect of the solvent, different solvents including H_2O, DMF, THF, EtOH, H_2O/DMF (1:1) and H_2O/EtOH (1:1) were used as reaction media in the presence of Pd(II)Cl_2–BTP@TMSP–nSiO_2 at room temperature and the highest yield obtained in H_2O/DMF (1:1)(entries 5 and 10-14).

Finally, the effect of the catalyst amount on the yield of the desired product in model reaction was investigated, and the best result was obtained with 0.15 mol% of the palladium catalyst (entries 15-17). In the absence of catalyst, no product was detected in the reaction mixture (entry 18). Consequently, from the observations summarized in Table 1, we conclude that 0.15 mol% of the catalyst, DIPEA (1 mmol) as the base, in H_2O/DMF (1:1) at room temperature, are the appropriate reaction conditions for this transformation (Table 1). To study the effect of immobilization of Pd species on its catalytic activity, the model reaction was carried out using 15 mol% of $PdCl_2$ as catalyst. The results revealed that the homogeneous $PdCl_2$ is less efficient than heterogeneous Pd(II)Cl_2–BTP@TMSP–nSiO_2 (entry 19).

Table 1. Optimization of conditions for the Sonogashira cross–coupling of 4–iodoanisole with phenylacetylene catalyzed by Pd(II)Cl_2–BTP@TMSP–nSiO_2.[a]



Entry	Catalyst amount (mol%)	Base (mmol)	Solvent	Time (h)	Yield (%)[b]
1	0.15	NaOH (1)	H_2O/DMF	6	15
2	0.15	Na_2CO_3 (1)	H_2O/DMF	6	32
3	0.15	K_2CO_3 (1)	H_2O/DMF	6	34
4	0.15	NEt_3 (1)	H_2O/DMF	6	81
5	0.15	DIPEA (1)	H_2O/DMF(1:1)	2	95
6	0.15	DIPEA (0)	H_2O/DMF(1:1)	2	15
7	0.15	DIPEA (0.75)	H_2O/DMF(1:1)	2	67
8	0.15	DIPEA (1.5)	H_2O/DMF(1:1)	2	96
9	0.15	DIPEA (1)	–	2	23
10	0.15	DIPEA (1)	H_2O	2	81
11	0.15	DIPEA (1)	DMF	3	76
12	0.15	DIPEA (1)	THF	5	51
13	0.15	DIPEA (1)	EtOH	5	60
14	0.15	DIPEA (1)	H_2O/EtOH(1:1)	5	72
15	0.3	DIPEA (1)	H_2O/DMF	2	95
16	0.06	DIPEA (1)	H_2O/DMF	5	60
17	0.04	DIPEA (1)	H_2O/DMF	5	57
18	0	DIPEA (1)	H_2O/DMF(1:1)	5	0
19[c]	0.15	DIPEA (1)	H_2O/DMF(1:1)	2	33

[a] Reaction conditions: 4–iodoanisole (1 mmol), phenylacetylene (1.1 mmol), base (1 mmol), Pd(II)Cl_2–BTP@TMSP–nSiO_2, solvent (0.5 mL), room temperature.

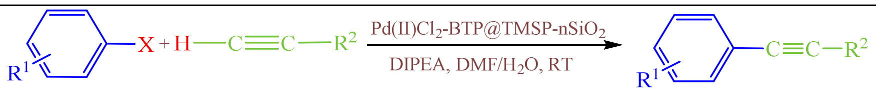
[b] Isolated yield.

[c] The $PdCl_2$ was used as catalyst.

Under the optimized reaction conditions, various aryl iodides, bromides and chlorides were cross–coupled with phenylacetylene in the presence of Pd(II)Cl_2–BTP@TMSP–nSiO_2 at room temperature to give the desired products in high yields (Table 2, entries 1–7). As expected; aryl iodides were found to be more reactive than aryl bromides and chlorides.

In order to show the effect of supports on the catalytic activity, some of the reactions were repeated using the 0.15 mol% of Pd(II)Cl_2–BTB complex (Table 2). The same trend observed for the heterogeneous catalyst was also observed for its homogeneous counterpart. Comparison of the turnover frequencies (TOFs) of both catalysts showed that the homogeneous catalyst is more reactive than the heterogeneous one. But the main disadvantage of the homogeneous catalyst is its lack of recoverability and reusability in the catalytic experiments.

Table 2. Sonogashira cross–coupling of aryl halides with phenylacetylene catalysed by Pd(II)Cl_2–BTP@TMSP–nSiO_2.[a]



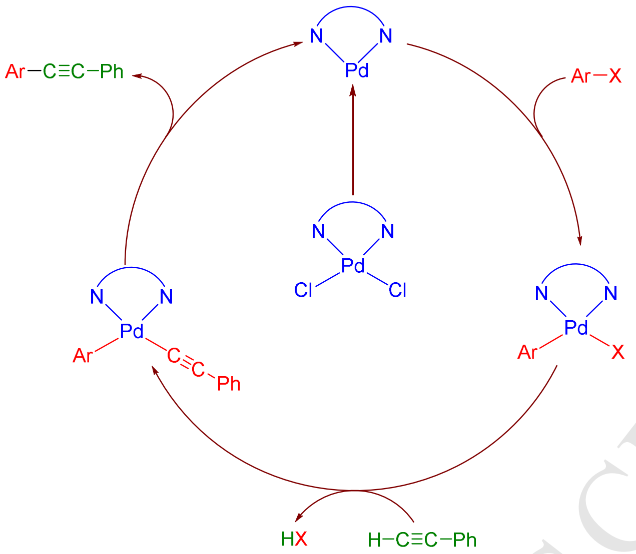
Entry	X	R^1	R^2	Time (h)[b]	Yield (%)[b,c]	TOF (h^{-1})[b]
1	I	H	Ph	2	96	320
2	I	4–MeO	Ph	2 (1.5)	95 (97)	316 (422)
3	Br	H	Ph	4	95	158
4	Br	4–MeO	Ph	4 (3)	91 (90)	152 (200)
5	Br	Ac	Ph	4 (3)	93 (94)	155 (207)
6	Cl	H	Ph	7 (5)	85 (83)	81 (111)
7	Cl	4–MeO	Ph	7 (5)	89 (90)	85 (120)

[a] Reaction conditions: aryl halides (1 mmol), phenylacetylene (1.1 mmol), DIPEA (1 mmol), Pd(II)Cl_2–BTP@TMSP–nSiO_2 (0.15 mol% Pd), H_2O /DMF (0.5 mL) at room temperature.

[b] The numbers in the parentheses refer to homogeneous catalyst.

[c] Isolated yield.

The proposed mechanism is demonstrated in Scheme 4. The first step is activation the catalyst and producing the chloride free catalytic species. Then, aryl halide is added to this active complex via an oxidative–addition process. The third step is addition of phenylacetylene and formation of a Pd-acetylide complex. The final step is formation the product via a reductive–elimination process and releasing the catalyst for the next catalytic cycle.



Scheme 4. Proposed mechanism for the Sonogashira coupling catalyzed by Pd(II)Cl_2–BTP@TMSP–nSiO_2

3.3. Catalyst recovery and reuse

As mentioned above, the homogeneous catalyst is not reusable but the main advantage of heterogeneous catalysts is their recovery and reuse. This property is important for industrial applications of catalysts. Therefore, the reusability of the catalyst was examined in the reaction of 4–iodoanisole with phenylacetylene under the optimized conditions. After completion of the reaction, the heterogeneous catalyst was separated, dried and reused for six consecutive trials without any remarkable loss of its catalytic activity (Fig. 12). Furthermore, The amount of palladium leaching from the Pd(II)Cl_2–BTP@TMSP–nSiO_2 catalyst was determined by ICP analysis. It was observed that only a trace amounts of Pd are leached in the first run.

4. Conclusion

In conclusion, we have catalyzed the Sonogashira cross–coupling of aryl halides (iodides, bromides, and chlorides) with phenylacetylene. This manner uses homogeneous and nano–silica supported palladium(II) complex derived from 3,5–*bis*(2–benzothiazolyl)pyridine (BTP) as catalysts. Both homogeneous and heterogeneous catalysts were applied in the Sonogashira cross–coupling with excellent yield. As expected, aryl iodides and bromides were more reactive than chloride ones. Despite the higher catalytic activity of the homogeneous catalyst, it could not be reused even one time while the heterogeneous catalyst can be recovered and reused, several times without significant loss of its activity.

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Reference

[1] Á. Molnár, Palladium–catalyzed coupling reactions: practical aspects and future developments, John Wiley & Sons, 2013.

[2] L. Yin, J. Liebscher, Chem. Rev. 107 (2007) 133–173.

[3] K. Sonogashira, Y. Tohda, N. Hagihara, Tetrahedron Lett. 16 (1975) 4467–4470.

[4] R. Chinchilla, C. Nájera, Chem. Rev. 107 (2007) 874–922.

[5] R. Chinchilla, C. Nájera, Chem. Soc. Rev. 40 (2011) 5084–5121.

[6] M.M. Heravi, S. Sadjadi, Tetrahedron, 65 (2009) 7761–7775.

[7] F. Bellina, M. Lessi, Synlett, 23 (2012) 773–777.

[8] H. Doucet, J.C. Hierso, Angew. Chem. Int. Ed. 46 (2007) 834–871.

[9] C. Dasaradhan, Y.S. Kumar, K. Prabakaran, F.–R.N. Khan, E.D. Jeong, E.H. Chung, Tetrahedron Lett. 56 (2015) 784–788.

[10] E.–I. Negishi, L. Anastasia, Chem. Rev. 103 (2003) 1979–2018.

[11] P. Gautam, R. Maragani, R. Misra, Tetrahedron Lett. 55 (2014) 6827–6830.

[12] N. Balsukuri, S. Das, I. Gupta, New. J. Chem. 39 (2015) 482–491.

[13] C. Resta, G. Pescitelli, L. Di Bari, Macromolecules, 47 (2014) 7052–7059.

[14] J.–H. Li, Y. Liang, Y.–X. Xie, J. Org. Chem. 70 (2005) 4393–4396.

[15] F. Yang, X. Cui, Y.–n. Li, J. Zhang, G.–r. Ren, Y. Wu, Tetrahedron, 63 (2007) 1963–1969.

[16] P. Siemsen, R.C. Livingston, F. Diederich, Angew. Chem. Int. Ed. 39 (2000) 2632–2657.

[17] H. Huang, H. Liu, H. Jiang, K. Chen, J. Org. chem. 73 (2008) 6037–6040.

[18] O. Vechorkin, D. Barmaz, V. Proust, X. Hu, J. Am. Chem. Soc. 131 (2009) 12078–12079.

[19] A. John, M.M. Shaikh, P. Ghosh, Dalton Trans. (2009) 10581–10591.

[20] X. Wang, W. Qin, N. Kakusawa, S. Yasuike, J. Kurita, Tetrahedron Lett. 50 (2009) 6293–6297.

[21] J.–Z. Jiang, C. Cai, J. Colloid Interface Sci. 307 (2007) 300–303.

[22] J. F. Cívicos, D. A. Alonso, C. Nájera, Adv. Synth. Catal. 355 (2013) 203–208.

[23] M. Lamblin, L. Nassar-Hardy, J.C. Hierso, E. Fouquet, F.X. Felpin, Adv. Synth. Catal. 352 (2010) 33–79.

[24] A. Köllhofer, H. Plenio, Chem. Eur. J. 9 (2003) 1416–1425;

[25] T. Suzuka, Y. Okada, K. Ooshiro, Y. Uozumi, Tetrahedron 66 (2010) 1064–1069.

[26] Y. He, C. Cai, J. Organomet. Chem. 696 (2011) 2689–2692.

[27] S. Thogiti, S.P. Parvathaneni, S. Keesara, J. Organomet. Chem. 822 (2016) 165–172.

[28] M. Bakherad, B. Bahramian, S. Jajarmi, J. Organomet. Chem. 749 (2014) 405-409.

[29] M. Navidi, N. Rezaei, B. Movassagh, J. Organomet. Chem. 743 (2013) 63-69.

[30] N. Iranpoor, H. Firouzabadi, A. Riazi, J. Iran. Chem. Soc. 12 (2015) 155-165.

[31] K. Niknam, A. Deris, F. Panahi, M.R.H. Nezhad, J. Iran. Chem. Soc. 10 (2013) 1291-1296.

[32] M. Esmaeilpour, A. Sardarian, J. Javidi, Catal. Sci. Technol. 6 (2016) 4005–4019.

[33] A. Landarani Isfahani, I. Mohammadpoor-Baltork, V. Mirkhani, A.R. Khosropour, M. Moghadam, S. Tangestaninejad, Eur. J. Org. Chem. 2014 (2014) 5603–5609.

[34] W. Li, X. Jia, B. Zhang, L. Tian, X. Li, H. Zhang, Q. Zhang, New. J. Chem. 39 (2015) 2925–2934.

[35] P.M. Price, J.H. Clark, D.J. Macquarrie, J. Chem. Soc., Dalton Trans. (2000) 101–110.

[36] B. Karimi, A. A. Safari, J. Organomet. Chem. 693 (2008) 2967–2970.

[37] M. E. Mahmoud, M. M. El–Essawi, S. A. Kholeif, E. M. Fathalla, Anal. Chim. Acta 525 (2004) 123–132.

[38] S. Meghdadi, M. Amirnasr, P.C. Ford, Tetrahedron Lett. 53 (2012) 6950–6953.

[39] Z. Dehbani, M. Moghadam, S. Tangestaninejad, V. Mirkhani, I. Mohammadpoor-Baltork, Polyhedron (2017) http://dx.doi.org/10.1016/j.poly.2017.08.032

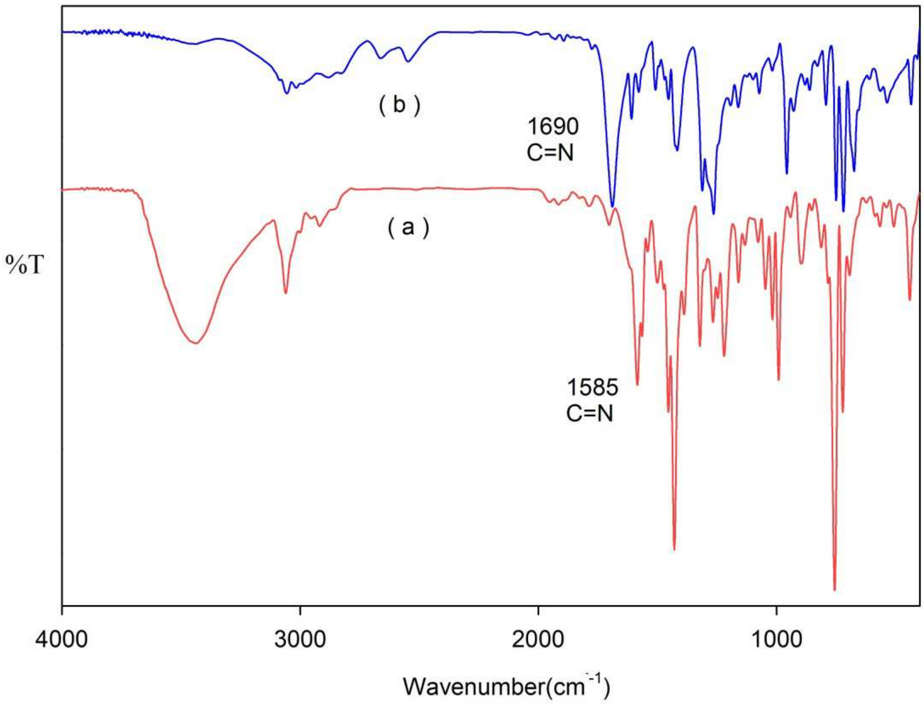


Fig. 1. The FT–IR spectra of: a) Pd(II)Cl$_2$–BTB; b) BTB ligand

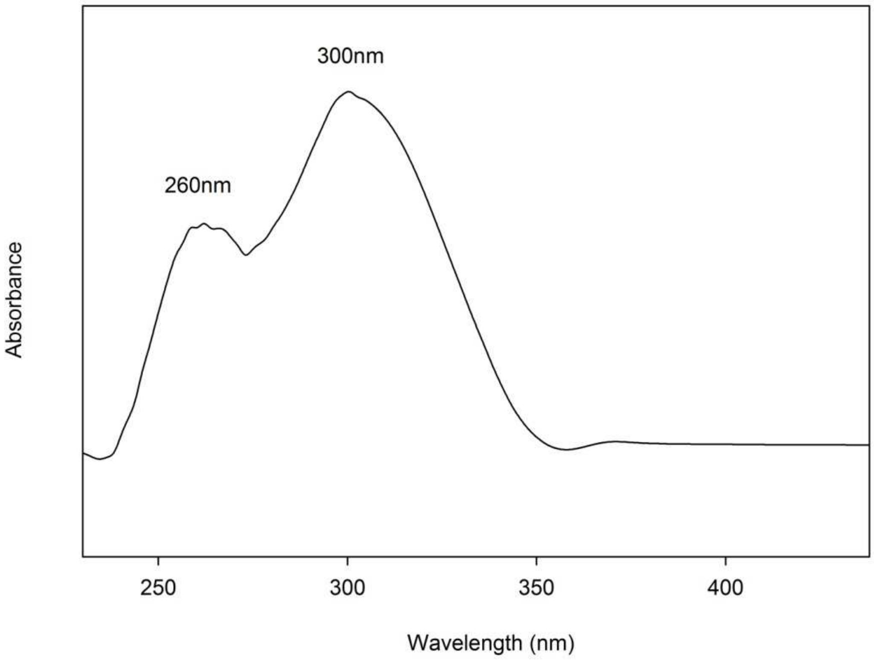


Fig. 2. The UV–vis spectrum of the BTB ligand

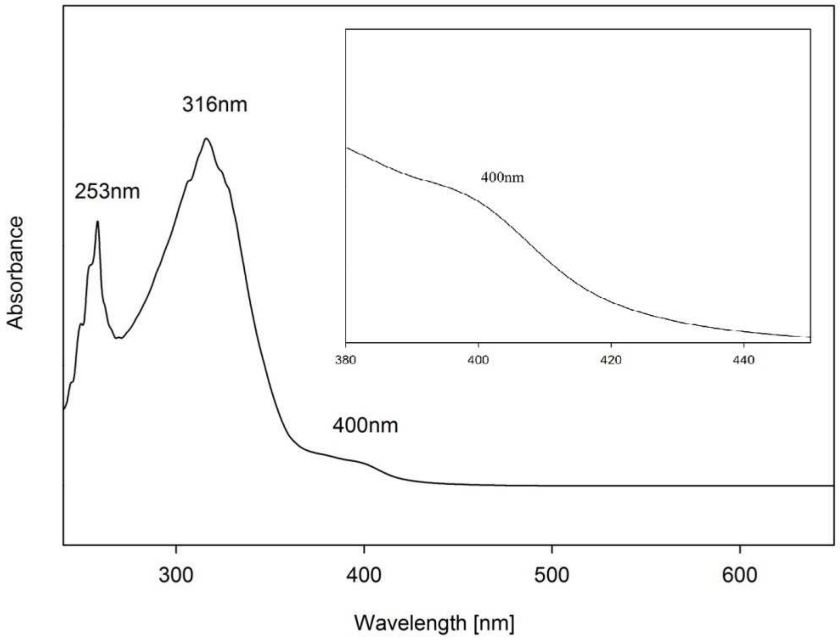


Fig. 3. The UV–vis spectrum of the Pd(II)Cl_2–BTB complex

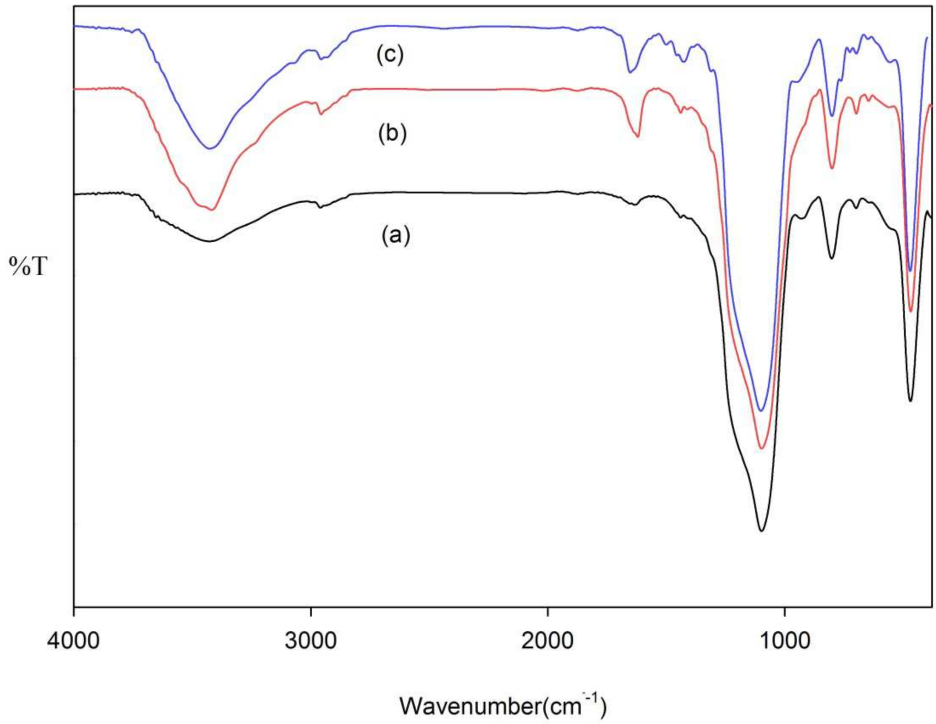


Fig. 4. The FT–IR spectra of: a) TMSP–nSiO_2; b) BTP@TMSP–nSiO_2; c) Pd(II)Cl_2–BTP@TMSP–nSiO_2

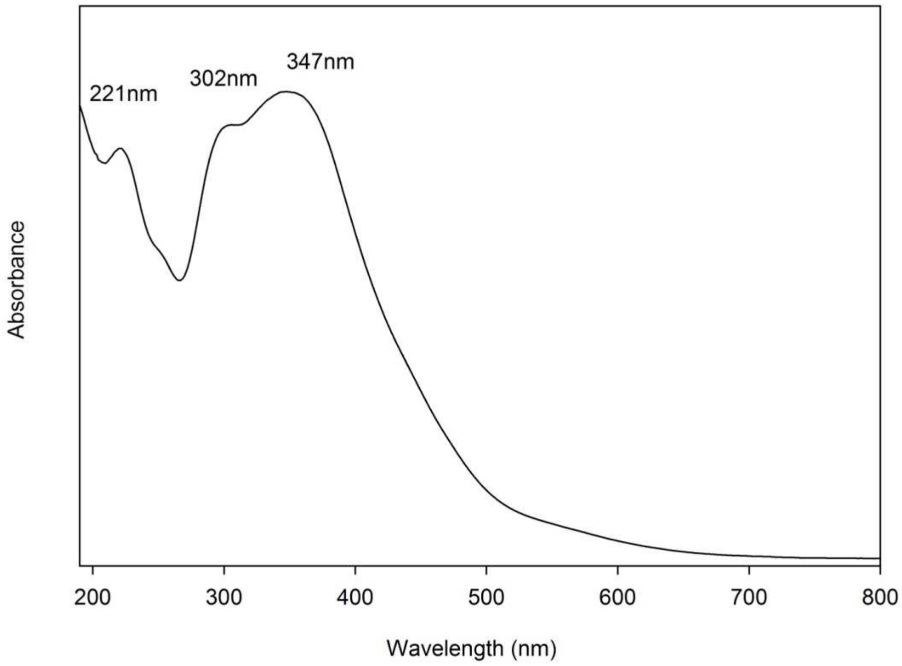


Fig. 5. Diffuse–reflectance UV–vis spectrum of the BTP@TMSP–nSiO$_2$

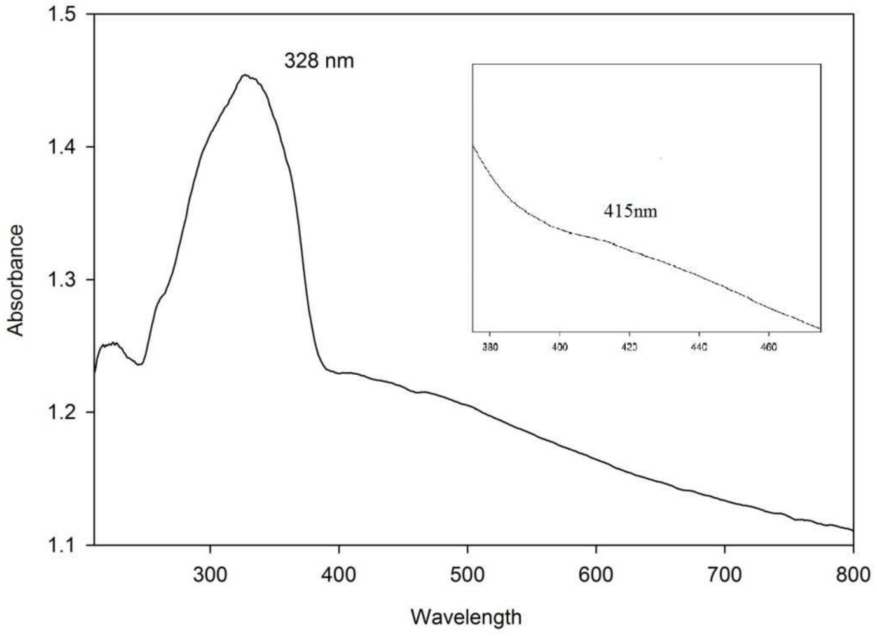


Fig. 6. Diffuse–reflectance UV–vis spectrum of the Pd(II)Cl$_2$–BTP@TMSP–nSiO$_2$

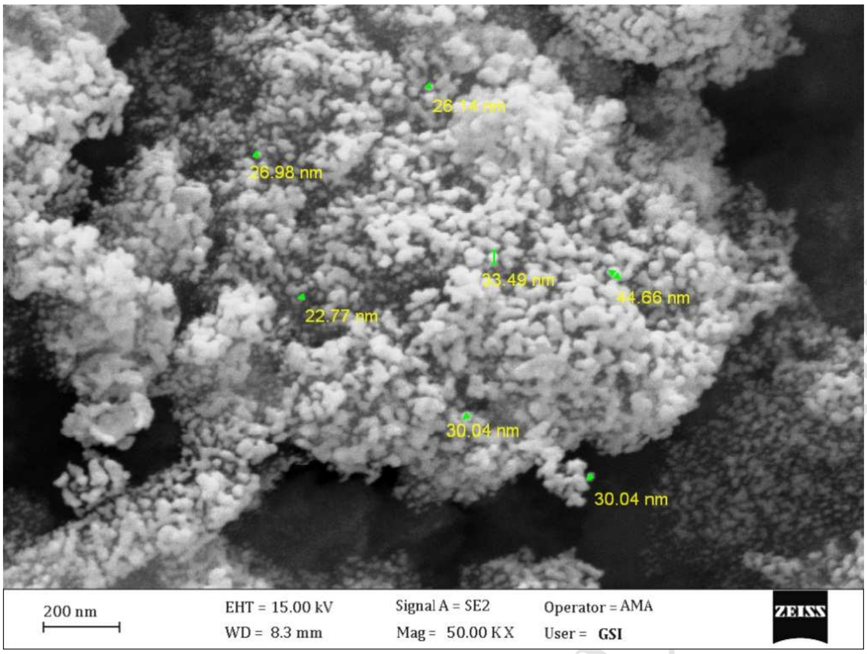


Fig. 7. SEM images of catalyst.

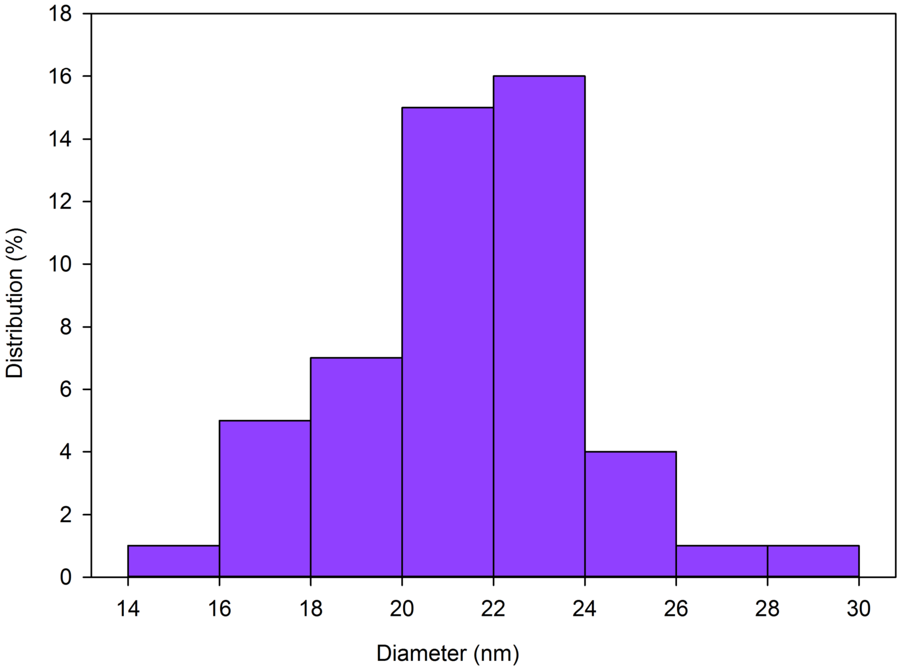


Fig. 8. Particle size distribution of catalyst

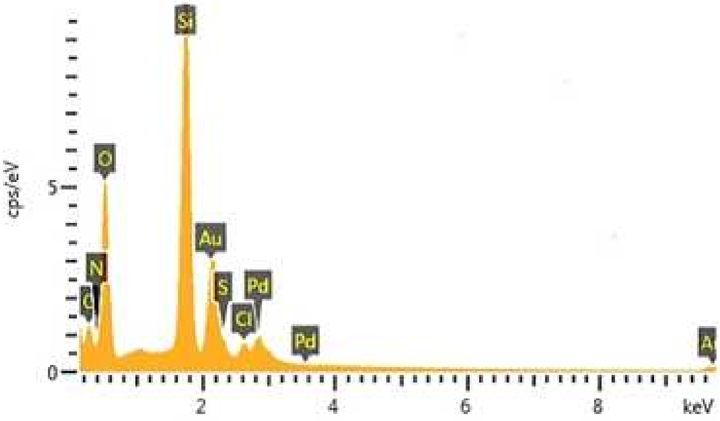
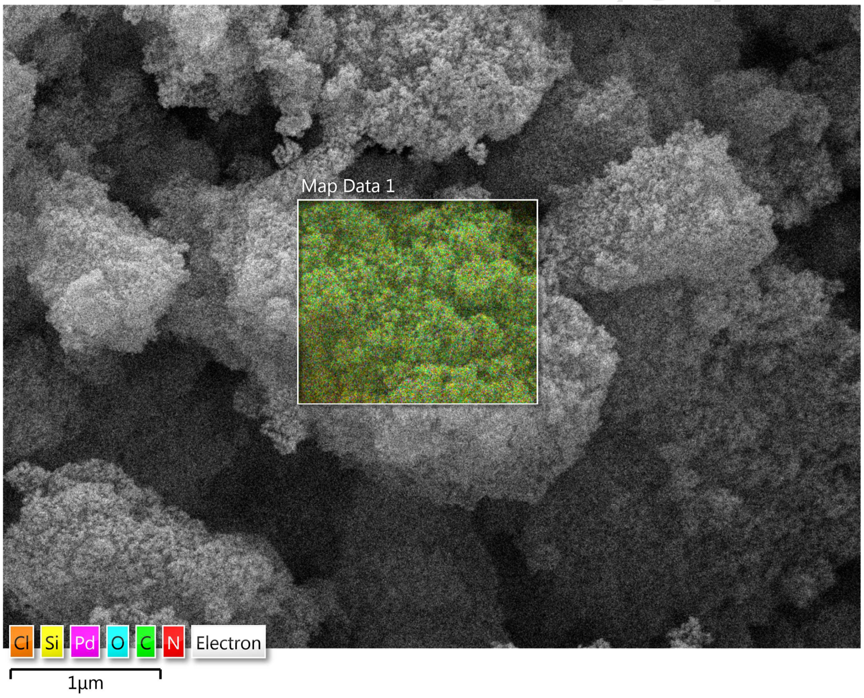


Fig. 9. EDX spectrum of catalyst



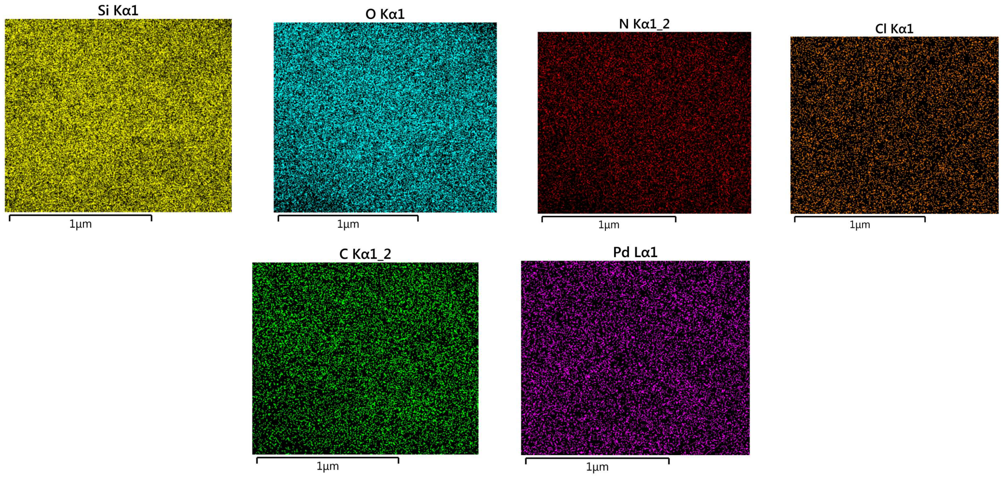


Fig. 10. Elemental Mapping of The catalyst

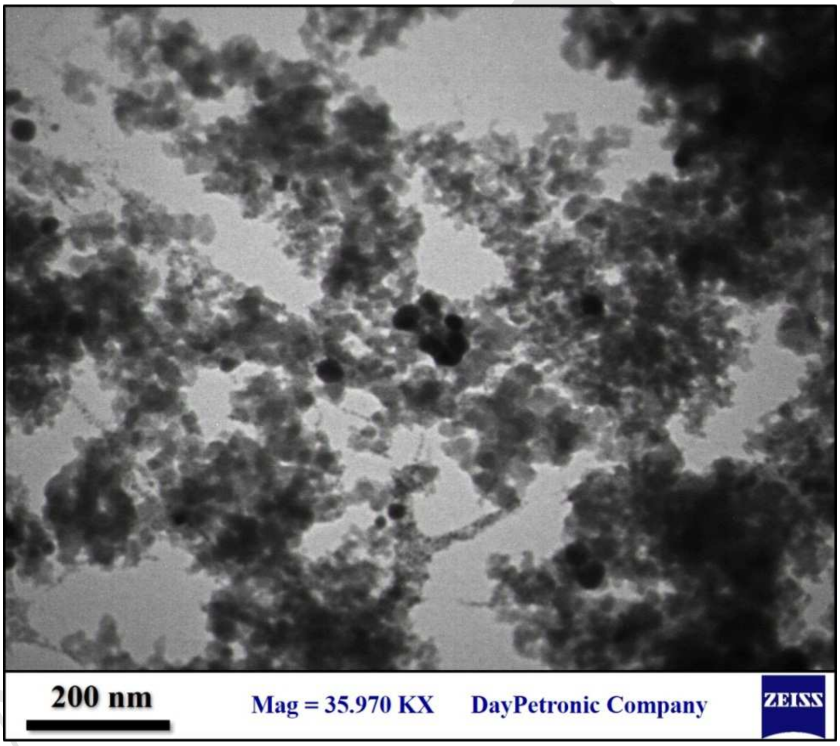


Fig. 11. TEM image of catalyst

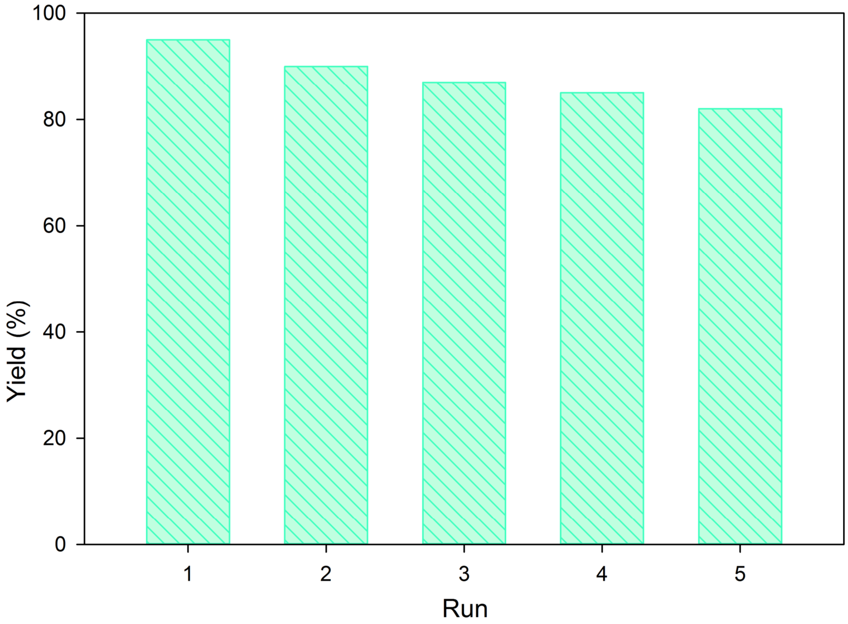


Fig. 12. Reusability of the Pd(II)Cl_2–BTP@TMSP–nSiO_2 catalyst in the reaction of 4–iodoanisole with phenylacetylene

▶ A new palladium complex supported on nano–silica was prepared ▶ This heterogeneous catalyst was used for Sonogashira C-C coupling reaction ▶ The results of heterogeneous catalyst was compared with homogeneous counterpart ▶ The heterogeneous catalyst was reusable.