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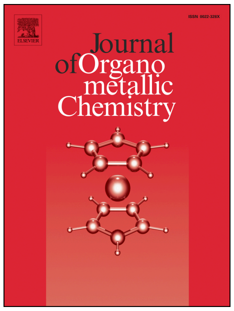

Synthesis of 3-sulfenylindoles by Pd (II) nanoclusters confined within metal−organic framework fibers in aqueous solution

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Synthesis of 3-sulfenylindoles by Pd (II) nanoclusters confined within metal−organic framework fibers in aqueous solution

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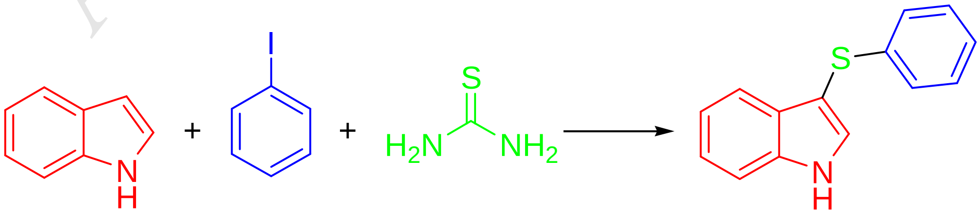
Abstract

We have found that fibrous nanosilica (KCC-1) can used as a excellent support for the synthesis of highly sparse nanoparticles. KCC-1 has high surface area that was functionalized with 1,3-bis(dimethylthiocarbamoyloxy)benzene groups acting as the strong performers so that the Pd (II) was complex without aggregation on the fibers of the KCC-1 microspheres (KCC-1/BTB/Pd). For synthesis of 3-sulfenylindoles from aryl iodide, indoles, and thiourea used from the KCC-1/BTB/Pd NPs as a catalyst that showed excellent catalytic activities under green conditions. Compared with the traditional substrate, KCC-1/BTB/Pd substantially increases protection and the accessibility of the nanoparticle sites due to its three dimensional hierarchical structure.

Keywords: KCC-1, Nano catalyst, One-pot synthesis, Green chemistry

Introduction

The metal complex have strong catalytic activities that for this property has been a topic of research.[1–5] Among the reported metal used in catalysis, palladium is the most stable catalyst, and have been widely studied because of their catalysis related properties, which can be leveraged in various usage. Among the reported metal used in catalysis, palladium is the most stable catalyst, and have been widely studied because of their catalysis related properties, which can be leveraged in various usage such as Sonogashira [6-8], Suzuki-Miyaura [9-11], Heck [12-14], Hiyama [15-17], Larock heteroannulation [18-21], degradation of pollutants,[22] hydrogenation,[23] and fuel cells. [24] In recent years, it has been proved that the use of complex functional groups either grafted or smeared on the solid supports played an important role in preventing the aggregation of metal catalysts.[25-34] Fibrous nano-silica (KCC-1), which possibilities a high surface area and easy availability through its fibers is reported by Polshettiwar et al. .[35] This would be an ideal catalyst support troth for the making of noble metal based catalysts that represent high availability of active sites and excellent catalytic activity. [36-44]
Sulfenylated indoles consist of an important class of indole derivatives and have been discovered as scaffolds possessing versatile biological relevance. According to known results, The development of general protocol for 3-sulfenylindoles formation has received significant attention because of their therapeutic value in the treatment of cancer,[45] HIV,[46] allergies,[47] heart disease,[48] and bacterial infection.[49] Various sulfenylating agents such as sulfonium salts,[50] quinone mono-O,S-acetals,[51] sulfonyl hydrazides,[52] sulfinates,[53] disulfides,[54] sulfenyl halides,[55] N-thioimides,[56] thiols[57] and arylsulfonyl chlorides[58] were smoothly coupled with indoles. These processes, though efficient, have several drawbacks including unstable and expensive reagents, lower reaction yields, unpleasant odors, uncommon solvents, requirement of inert atmosphere and excess reagent loadings as well as long reaction times. Moreover, most of these methods need preparation steps of the thiolating agent. Therefore, there is still a growing demand to develop an efficient method for the synthesis of 3-sulfenylindoles from suitable and readily available precursors. Herein, we report the synthesis of KCC-1 supported 1,3-bis(dimethylthiocarbamoyloxy)benzene-Pd(II) complex (KCC-1/BTB/Pd) and its application for investigate the one-pot synthesis of 3-sulfenylindoles from aryl iodide, indoles, and thiourea. We enthusiasm to report cross-couplings between aryl iodide, indoles, and thiourea for first time (Scheme 1).



Scheme 1 Synthesis of 3-Sulfenylindoles from aryl iodide, indoles, and thiourea in the presence of KCC-1/BTB/Pd NPs.

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Experimental

Materials and Methods

Chemical materials were purchased from Fluka and Merck in high purity. Melting points were determined in open capillaries using an Electrothermal 9100 apparatus and are uncorrected. FTIR spectra were recorded on a VERTEX 70 spectrometer (Bruker) in the transmission modein spectroscopic grade KBr pellets for all the powders. The particle size and structure of nano particle was observed by using a Philips CM10 transmission electron microscope operating at 100 kV. Powder X-ray diffraction data were obtained using Bruker D8 Advance model with Cu ka radition. The thermogravimetric analysis (TGA) was carried out on a NETZSCH STA449F3 at a heating rate of 10 °C min^{-1} under nitrogen.^{1}H and ^{13}C NMR spectra were recorded on a BRUKER DRX-300 AVANCE spectrometer at 300.13 and 75.46 MHz, BRUKER DRX-400 AVANCE spectrometer at 400.22 and 100.63 MHz, respectively. Elemental analyses for C, H, and N were performed using a Heraeus CHN–O-Rapid analyzer. The purity determination of the products and reaction monitoring were accomplished by TLC on silica gel polygram SILG/UV 254 plates. Mass spectra were recorded on Shimadzu GCMS-QP5050 Mass Spectrometer.

General procedure for the preparation of comound 1

To 10 mL flask containing 5-Aminobenzene-1,3-diol hydrochloride (1 mmol) was added 5 mL dry acetonitrile and mixture was stirred at room temperature. Then triethoxy(3-isocyanatopropyl)silane (1.5 mmol) was added under argon protection and solution was stirred under argon atmosphere for 48 h at room temperature.

General procedure for the preparation of comound 2

Comound 1 (40 mmol), *N,N*-dimethylthiocarbamoyl chloride (4.94 g, 40.0 mmol) and K_2CO_3 (5.53 g, 40.0 mmol) were stirred in acetone (200 mL) and were refluxed for 2 days under a nitrogen atmosphere. After the suspension had cooled, the solvent was removed in vacuo. The resulting solid material was dissolved in chloroform, and excess K_2CO_3 was quenched with 2 M HCl. The organic phase was then separated, washed with water, 5% KOH, and saturated NaCl, and dried over anhydrous Na_2SO_4.

General procedure for the preparation of comound 3

Comound 3 structures were prepared by reaction 1 g of Comound 2 with 1 mmol of $Pd(OAc)_2$ were mixed with 20 mL of CH_2Cl_2 at room temperature for 24 h. This mixture was filtered and washed with acetonitrile to obtain BTB/Pd(II) complex.

General procedure for the preparation of KCC-1/BTB/Pd NPs

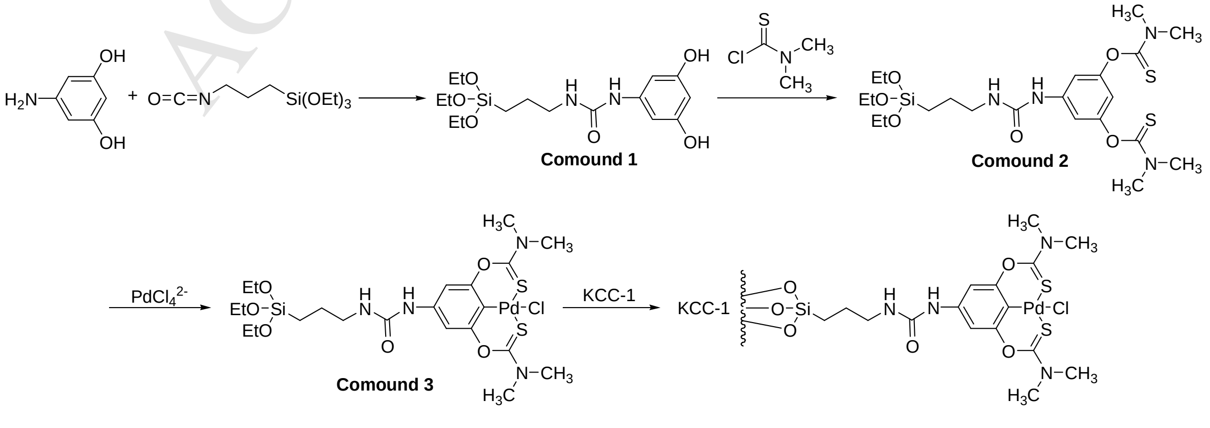
KCC-1 (2 mmol) and THF (20 mL) were mixed together in a beaker, and then NaH (20 mmol) was dispersed in to the mixture by ultrasonication. Comound 3 (22 mmol) was added drop-wise at room temperature and stirred for another 16 h at 60 ^oC. The resultant products were collected and washed with ethanol and deionized water in sequence, and then dried under vacuum at 60 ^oC for 2 h for further use.

General procedure for synthesis of 3-sulfenylindole

A mixture of aryl iodide (1 mmol), indole (1 mmol), and thiourea (1 mmol), K_2CO_3 (1 mmol), and KCC-1/BTB/Pd NPs (1 mg) was stirred heating under reflux in TFA (3 mL) for 15 min. The mixture was stirred at room temperature for 10 min under N_2 atmosphere, and then heated under reflux for 6-8 h. The catalyst was separated by filtration. Evaporation of the solvent of the filtrate under reduced pressure gave the crude products. The pure products were isolated by chromatography on silica gel eluted with petroleum ether:EtOAc (3:1).

Results and discussion

The synthesis of KCC-1/BTB/Pd NPs involved several steps. The fibers of KCC-1 has many Si–OH groups on thesurfaces; thus, it was expected that the KCC-1 could be easily functionalized with 1,3-bis(dimethylthiocarbamoyloxy)benzene to form KCC-1/BTB. Furthermore, 1,3-bis(dimethylthiocarbamoyloxy)benzene groups on the KCC-1/BTB could supported palladium(II) complex (Scheme 2).



Scheme 2 Schematic illustration of the synthesis for KCC-1/BTB/Pd NPs.

The structures of the synthesized KCC-1/BTB/Pd NPs were analyzed by TEM and SEM. The as prepared KCC-1/BTB/Pd NPs microspheres with fibrous structure were uniform and monodispersed (Figure 1). The average diameter of the microspheres was about 150-180 nm. TEM and SEM image shown in figure 1 further clarifies that the distance between the two fibers was about 5-10 nm.

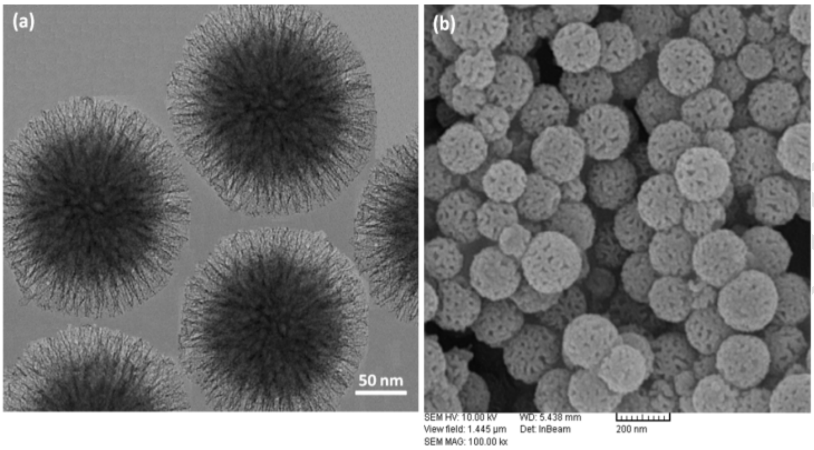


Figure 1 TEM (a), and SEM (b) images of nano KCC-1/BTB/Pd NPs.

To confirm the thermal stability of the KCC-1/BTB/Pd, the thermogravimetric analysis of this material was performed at temperatures ranging (Figure 2). Two weight loss stages were observed in flow air. The weight loss below 250 ^{o}C was ascribed to the elimination of the physisorbed and chemisorbed solvent on the surface of the silica material. In the second stage (250–400 ^{o}C), weight loss is about 11 wt%, which can be attributed to the organic group derivatives, presumably due to BTB decomposition.

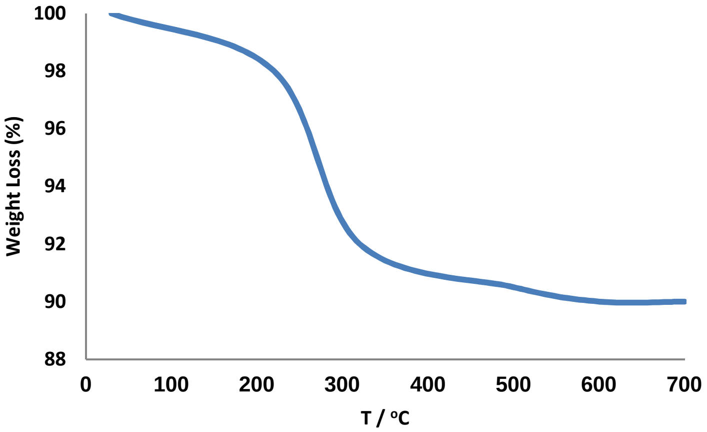


Figure 2 TGA diagram of KCC-1/BTB/Pd NPs.

XPS was used to investigate the chemical elements on the surface of KCC-1/BTB/Pd NPs. A full-scan XPS spectrum for the asprepared catalyst is illustrated in Figure 3. Peaks corresponding to Si, O, C, S, N, Cl and Pd can be clearly observed, and the presence of N 1s, S 2s, and S 2p further confirmed that KCC-1 had been successfully functionalized by the BTB. Also, XPS Pd 3d spectrum displays a doublet indicative of metallic Pd.

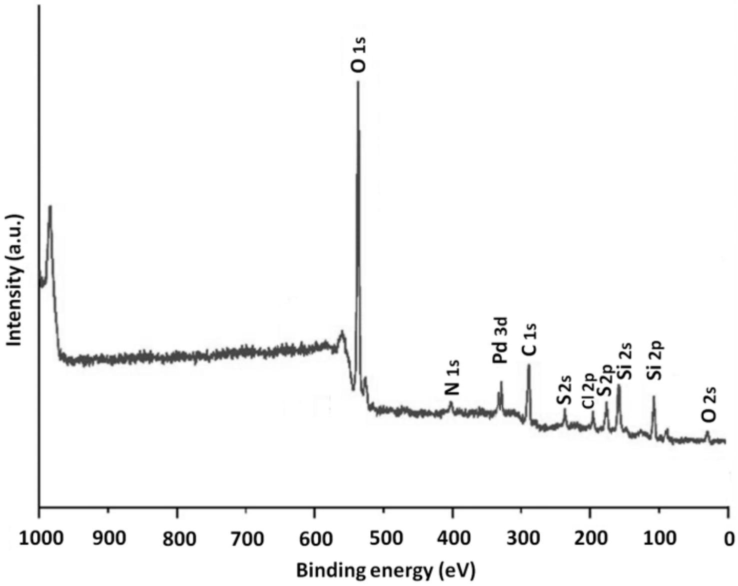


Figure 3 XPS spectra of KCC-1/BTB/Pd NPs.

The parameters of pore structure and specific surface area of the samples were calculated and summarized in Table 1. The precursor KCC-1 had a BET specific surface area of 439 m^2/g with pore volume of 1.49 cm^3/g and pore size of 14.78 nm. After grafting with BTB/Pd, KCC-1/BTB/Pd showed decreased specific surface area of 312 m^2/g with pore volume of 1.02 cm^3/g and pore size of 12.19 nm. This normally happens for the organic functionalization of BTB, which should be attributed to partial blocking of the pore channels by the introduced organic species. This could be ascribed to increased loading with the sensing probe, which occupies a large volume inside the silica spheres (Table 1).

Table 1 Structural parameters of KCC-1 and KCC-1/BTB/Pd materials determined from nitrogen sorption experiments.

Catalysts	S_{BET} (m^2 g^{-1})	V_t (cm^3 g^{-1})	D_{BJH} (nm)
KCC-1	439	1.49	14.78
KCC-1/BTB/Pd	312	1.02	12.19

The activity of described catalyst was investigated through a reaction of aryl iodide, indoles, and thiourea. Initially, we examined the synthesis of 3-sulfenylindole in different solvents, bases, time, temperature, and various catalytic amounts of KCC-1/BTB/Pd (Table 2). Five bases were tested and their reaction yields were recorded as follows; CsF (68%), Na_2CO_3 (54%), Et_3N (41%), NaOAc (35%), KOH (29%), K_3PO_4 (42%), Cs_2CO_3 (55%), *t*BuOK (14%) and K_2CO_3 (97%). We opted for K_2CO_3 because it gave high product yield and it is low-cost and available. we studied very short reaction times i.e., from 1 to 7 min and we recorded reaction yields as follows; 5 min (42%), 10 min (89%), 15 min (97%), and 20 min (97%). Increasing reaction time gradually gave higher product yield, reaching the highest value in 15 min. Longer reaction time did not much contribute to yield. Therefore, we determined optimum reaction time as 15 min. On the other hand, low amount catalyst is also responsible for producing high yield. 1 mg of catalyst gave the best result.Applying 1 mg of KCC-1/BTB/Pd and 1 mmol of K_2CO_3 as base in 5 mL TFA, is the best conditions for the reaction. Also, it was found that conventional heating under reflux in 15 min is more efficient (Table 2).

Table 2 Optimization of the reaction conditions for synthesis of 3-sulfenylindole in terms of temperature, amount catalyst, time, base, and product yield.

Entry	Solvent	Temp. (°C)	Base	Amount catalyst (mg)	Time (min)	Yield (%)[a]
1	Solvent-Free	100	K_2CO_3	1	20	-
2	TFA	Reflux	K_2CO_3	1	20	97
3	EtOH	Reflux	K_2CO_3	1	20	29
4	*i*-PrOH	Reflux	K_2CO_3	1	20	23
5	MeOH	Reflux	K_2CO_3	1	20	26
6	CH_3CN	Reflux	K_2CO_3	1	20	11
7	CH_2Cl_2	Reflux	K_2CO_3	1	20	18
8	EtOAc	Reflux	K_2CO_3	1	20	15
9	$CHCl_3$	Reflux	K_2CO_3	1	20	22
10	DMSO	Reflux	K_2CO_3	1	20	21
11	Dioxane	Reflux	K_2CO_3	1	20	-
12	Cyclohexane	Reflux	K_2CO_3	1	20	-
13	*n*-Hexane	Reflux	K_2CO_3	1	20	-
14	CCl_4	Reflux	K_2CO_3	1	20	-
15	TFA	Reflux	-	1	20	-
16	TFA	Reflux	CsF	1	15	68
17	TFA	Reflux	Na_2CO_3	1	15	54

18	TFA	Reflux	Et_3N	1	15	41
19	TFA	Reflux	NaOAc	1	15	35
20	TFA	Reflux	KOH	1	15	29
21	TFA	Reflux	K_3PO_4	1	15	42
22	TFA	Reflux	Cs_2CO_3	1	15	55
23	TFA	Reflux	*t*BuOK	1	15	14
24	TFA	60	K_2CO_3	1	20	83
25	TFA	40	K_2CO_3	1	20	57
26	TFA	Reflux	K_2CO_3	0.8	20	91
27	TFA	Reflux	K_2CO_3	0.6	20	66
28	TFA	Reflux	K_2CO_3	1	15	97
29	TFA	Reflux	K_2CO_3	1	10	89
30	TFA	Reflux	K_2CO_3	1	5	42

[a] Isolated yields.

For further investigation the efficiency of the catalyst, different control experiments were performed and the obtained information is shown in Table 3. Initially, a standard reaction was carried out using KCC-1 showed that any amount of the desired product was not formed after 15 min of reaction time (Table 3, entries 1). Also, when KCC-1/BTB was used as the catalyst, a reaction was not observed (Table 3, entries 2). The BTB could not give the satisfactory catalytic activity under mild reactions. Based on these disappointing results, we continued the studies to improve the yield of the product by added the Pd (II). Notably, there was not much difference in the reaction yields when reaction was carried out using KCC-1/BTB/Pd NPs and $Pd(OAc)_2$ catalyst (Table 3, entries 3 and 5), however, $Pd(OAc)_2$ is not recoverable and reusable for the next runs. These observations show that the reaction cycle is mainly catalyzed by Pd (II) species complexed on the KCC-1/BTB nanostructure. The nano-sized particles increase the exposed surface area of the active site of the catalyst, thereby enhancing the contact between reactants and catalyst dramatically and mimicking the homogeneous catalysts. As a result, KCC-1/BTB/Pd was used in the subsequent investigations because of its high reactivity, high selectivity and easy separation. Also, the activity and selectivity of nano-catalyst can be manipulated by tailoring chemical and physical properties like size, shape, composition and morphology. To assess the exact impact of the presence of KCC-1 in the catalyst, the KCC-1/BTB/Pd NPs compared with SiO_2/BTB/Pd NPs. To check this, we looked at SiO_2/BTB/Pd and KCC-1/BTB/Pd NPs, which have the same compositions and different structures. When SiO_2/BTB/Pd was used as the catalyst, the yield of the desired product was fair to average, but the yield for KCC-1/BTB/Pd was good (Table 3, entries 3 and 4). The loading amount of Pd (II) in KCC-1/BTB/Pd and SiO_2/BTB/Pd NPs as determined by inductively coupled plasma mass spectrometry (ICP-MS). The amount of Pd (II) in KCC-1/BTB/Pd was almost than double the amount of Pd (II) in SiO_2/BTB/Pd NPs (Table 5, entries 1 and 2).

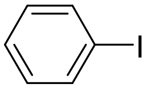
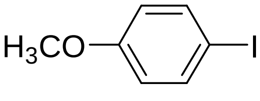
Table 3 Influence of different catalysts for synthesis of 3-sulfenylindole.[a]

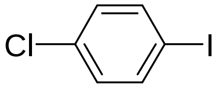
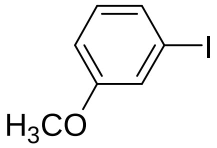
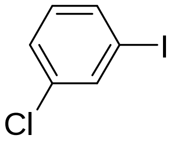
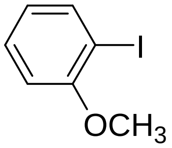
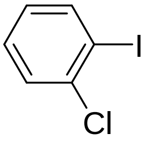
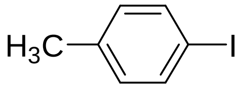
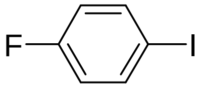
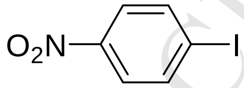
Entry	Catalyst	Yield (%)[b]
1	KCC-1	-
2	KCC-1/BTB	-
3	KCC-1/BTB/Pd	97
4	SiO_2/BTB/Pd	59
5	$Pd(OAc)_2$	98

[a] Reaction conditions: aryl iodide (1 mmol), indole (1 mmol), and thiourea (1 mmol), KCC-1/BTB/Pd NPs (1 mg), K_2CO_3 (1 mmol), and catalyst (1 mg) was stirred heating under reflux in TFA (3 mL) for 15 min.
[b] Isolated yield.

To examine the scope of the catalytic properties of the catalyst for synthesis of 3-sulfenylindole, various types of aryl iodides were reacted with indole, and thiourea in the presence of a catalytic amount of KCC-1/BTB/Pd NPs. Furthermore, electron rich and electron poor aryl iodides react smoothly with indole, and thiourea in similar reaction conditions. Highest 3-sulfenylindole yield was obtained from the reactions of indole, and thiourea with iodobenzene or 1-fluoro-4-iodobenzene; 97 and 99%, respectively. Electron-withdrawing groups such as $-NO_2$ or -Cl gave high product yield. For example, aryl iodide with *para*-substituted $-NO_2$ had high product yield; 96%. Aryl iodide with *meta, ortho or para*-substituted -Cl gave product yield of 91%, 93% and 96%, respectively. The catalyst was generally more effective in reactions with *para*-substituted substrates than with *ortho*- and *meta*-substituent of aryl halides for electron-withdrawing groups. We observed relatively good product yield in reactions with electron-donor groups. For example, *para*-substituted $-CH_3$ aryl iodides and *meta, ortho, or para*-substituted $-OCH_3$ produced 3-sulfenylindole yield of 90%, 92%, 89% and 91%, respectively. The catalyst was generally more effective in reactions with *met*a-substituted substrates than with *ortho*- and *para*-substituent of aryl halides for electron-donor groups. (Table 4)

Table 4 Synthesis of 3-sulfenylindoles in the presence of KCC-1/BTB/Pd NPs.[a]

Entry	Allylarene	Yield (%)[b]	Entry	Allylarene	Yield (%)[b]
1		97	6		91

2		96	7		92
3		91	8		89
4		93	9		90
5		98	10		96

[a] Reaction conditions: aryl iodides (1 mmol), indole (1 mmol), and thiourea (1 mmol), K_2CO_3 (1 mmol), and KCC-1/BTB/Pd NPs (1 mg) was stirred heating under reflux in TFA (3 mL) for 15 min.
[b] Isolated yields (%).

In an effort to make the synthesis more applicable, the reusability of the catalyst was also examined for the standard reaction of aryl iodide, indole, and thiourea. After completion of the reaction, the mixture was filtered, the catalyst was washed with distilled water and methanol, and dried under reduced pressure. The KCC-1/BTB/Pd NPs was found to be effectively reused in up to ten consecutive cycles while maintaining high activity and selectivity. The catalytic activity did not reduction extremely after ten catalytic cycles, it shows that the catalyst is stable and can be regenerated for repeated use (Figure 4). Pd(II) leaching was studied by the ICP-MS analysis of the catalyst, after ten cycles of reactions. The loading amount of Pd(II) was found to be 2.8 wt %, which shows negligible Pd(II) leaching. These results confirmed the high recyclability of Pd(II) nanocatalyst (Table 5).

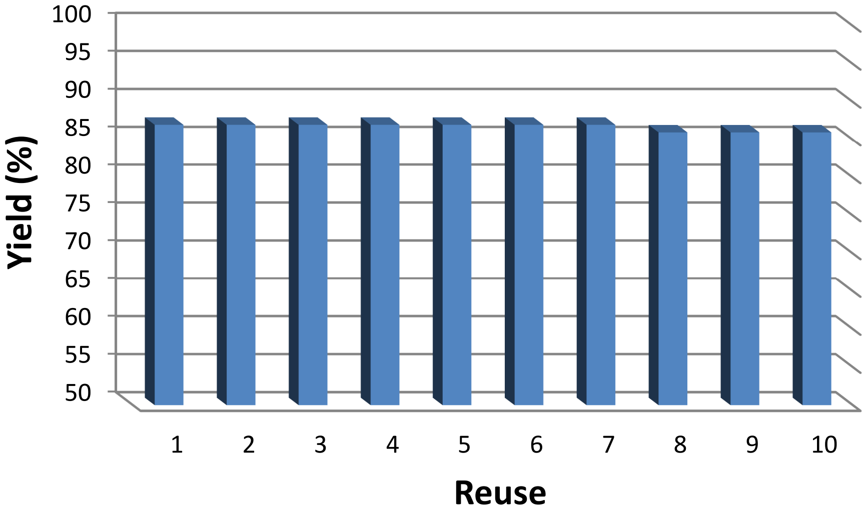


Figure 4 The reusability of catalysts for synthesis of 3-sulfenylindoles.

Table 5 The loading amount of Pd(II) in KCC-1/BTB.

Entry	Catalyst	wt %
1	SiO_2/BTB/Pd	1.8
2	KCC-1/BTB/Pd	2.9
3	KCC-1/BTB/Pd after ten reuses	2.8

Conclusions

In summary, a novel class of short-fibr KCC-1 mesoporous silica functionalized with 1,3-bis(dimethylthiocarbamoyloxy)benzene groups ligands was synthesized for selective capturing of palladium ions, that exhibited excellent catalytic activity for synthesis of 3-sulfenylindoles from aryl iodide, indoles, and thiourea in good yields.

TEM, SEM, TGA, ICP-MS, XPS, and BET surface area analysis studies suggested the functionalization of Pd(II) in the surface of the mesopores silica. In addition, the catalyst was easily recoverable and reusable. Such a rational design for single-site catalysts with full utilization of each Pd active site, as well as excellent recyclability and negligible metal leaching could coincide with the concepts of green chemistry. Thus, the study of KCC-1/BTB/Pd nanocatalyst may provide a potential platform for the fabrication of other complex metal with easy accessibility, which would be highly efficient in various complex metal based catalytic reactions. This process may be used in the future to develop additional nanocatalysts that possess favorable properties, such as efficiency and ease of reuse.

References

1 M.L. Wang, T.T. Jiang, Y. Lu, H.J. Liu, Y. Chen, J. Mater. Chem. A 1 (2013) 5923–5933.
2 X. Zhang, Z. Su, Adv. Mater. 24 (2012) 4574–4577.
3 Z.M. de Pedro, E. Diaz, A.F. Mohedano, J.A. Casas, J.J. Rodriguez, Appl. Catal. B:Environ. 103 (2011) 128–135.
4 Y.M. Liu, H. Tsunoyama, T. Akita, S.H. Xie, T. Tsukuda, ACS Catal. 1 (2011) 2–6.
5 X. Yang, C. Huang, Z.Y. Fu, H.Y. Song, S.J. Liao, Y.L. Su, L. Du, X.J. Li, Appl. Catal.B: Environ. 140 (2013) 419–425.
6 E. Negishi, L. Anastasia, Chem. Rev. 103 (2003) 1979-2017.
7 D.H. Lee, Y.H. Lee, J.M. Harrowfield, I.M. Lee, H.I. Lee, W.T. Lim, Y. Kim, M.J. Jin, Tetrahedron 65 (2009) 1630-1634.
8 K. Sonogashira, J. Organomet. Chem. 653 (2002) 46-49.
9 K. Pomeisl, A. Holy, R. Pohl, K. Horska, Tetrahedron 65 (2009) 8486-8492.
10 P. Tapolcsanyi, G. Krajsovszky, R. Ando, P. Lipcsey, G. Horvath, P. Matyus, Z. Riedl, G. Hajos, B.U.W. Maes, G.L.F. Lemiere, Tetrahedron 58 (2002) 10137-10143.
11 T.E. Nielsen, S.L. Quement, M. Meldal, Tetrahedron Lett. 46 (2005) 7959-7962.
12 F. Miyazaki, K. Uotsu, M. Shibasaki, Tetrahedron 54 (1998) 13073-13078.
13 C. Kalinski, M. Umkehrer, J. Schmidt, G. Ross, J. Kolb, C. Burdack, W. Hillerb, S.D. Hoffmann, Tetrahedron Lett. 47 (2006) 4683-4686.
14 A. Garcia, D. Rodriguez, L. Castedo, C. Saa, D. Dominguez, Tetrahedron Lett. 42 (2001) 1903-1905.
15 A. Gordillo, E.D. Jesus, C.L. Mardomingo, Org. Lett. 8 (2006) 3517-3520.
16 S.E. Denmark, J.D. Baird, Chem. Eur. J. 12 (2006) 4954-4963.
17 A. Csapo, A. Bodor, J. Rabai, J. Fluor. Chem. 137 (2012) 85-92.
18 C. Wang, J. Sperry, Tetrahedron 69 (2013) 4563-4577.
19 R.C. Larock, E.K. Yum, M.D. Refvik, J. Org. Chem. 63 (1998) 7652-7662.
20 R.C. Larock, E.K. Yum, J. Am. Chem. Soc. 113 (1991) 6689-6690.
21 L. Joucla, N. Batail, L. Djakovitch, Adv. Synth. Catal. 352 (2010) 2929-2936.
22 M.-Q. Yang, X. Pan, N. Zhang and Y.-J. Xu, CrystEngComm, 15 (2013) 6819–6828.
23 Z. Dong, X. Le, C. Dong, W. Zhang, X. Li and J. Ma, Appl.Catal., B, 162 (2015) 372–380.
24 E. Antolini, Energy Environ. Sci., 2 (2009) 915–931.
25 L. Zhou, C. Gao, W. Xu, Langmuir 26 (2010) 11217–11225.
26 Z. Chen, L. Zhou, F. Zhang, C. Yu, Z. Wei, Applied Surface Science 258 (2012) 5291–5298.
27 Q. Du, W. Zhang, H. Ma, J. Zheng, B. Zhou, Y. Li, Tetrahedron 68 (2012) 3577–3584.
28 M. Bazarganipour, M. Salavati-Niasari, Chemical Engineering Journal. 286 (2016) 259-265.
29 Fatemeh Mohandes, Fatemeh Davar, Masoud Salavati-Niasari, Kamal Saberyan, *Current Nanoscience, 7 (*2011*)* 260-266.
30 M. Salavati-Niasari, F. Mohandes, F. Davar, M. Mazaheri, M. Monemzadeh, N. Yavarinia, Inorganica Chimica Acta 362 (2009) 3691–3697.
31 M. S. Morassaei, S. Zinatloo-Ajabshir, M. Salavati-Niasari, Journal of Molecular Liquids 220 (2016) 902–909.
32 S. Zinatloo-Ajabshir, M. S. Morassaei, M. Salavati-Niasari, Journal of Colloid and Interface Science. 497 (2017) 298-308.
33 B. Barfi, M. Rajabi, M. Morshedi Zadeh, M. Ghaedi, M. Salavati-Niasari, R. Sahraei, Microchimica Acta. 182 (2015) 1187-1196.
34 M. S. Morassaei, S. Zinatloo-Ajabshir, M. Salavati-Niasari, Journal of Materials Science: Materials in Electronics. 27 (2016) 11698-11706.
35 V. Polshettiwar, D. Cha, X. Zhang, J. M. Basset, Angew. Chem. Int. Ed. 49 (2010) 9652-9656.
36 S.M. Sadeghzadeh, R. Zhiani, S. Emrani, M. Ghabdian, RSC Adv., 7 (2017) 50838–50843.
37 S.M. Sadeghzadeh, R. Zhiani, M. Khoobi, S. Emrani, Microporous and Mesoporous Materials 257 (2018) 147-153.
38 S.M. Sadeghzadeh, Microporous and Mesoporous Materials 234 (2016) 310-316.
39 S.M. Sadeghzadeh, Journal of Molecular Liquids 223 (2016) 267–273.
40 S.M. Sadeghzadeh, Journal of Molecular Catalysis A: Chemical 423 (2016) 216–223.
41 S.M. Sdeghzadeh, Catal. Sci. Technol., 6 (2016) 1435–1441.
42 S.M. Sadeghzadeh, Catal. Commun., 72 (2015) 91–96.
43 S.M. Sadeghzadeh, Green Chem., 17 (2015) 3059–3066.
44 S.M. Sadeghzadeh, R. Zhiani, S. Emrani, RSC Adv., 7 (2017) 32139–32145.
45 G. La Regina, M.C. Edler, A. Brancale, S. Kandil, A. Coluccia, F. Piscitelli, E. Hamel, G. De Martino, R. Matesanz, J.F. Diaz, A.I. Scovassi, E. Prosperi, A. Lavecchia, E. Novellino, M. Artico, R. Silvestri, J. Med. Chem. 50 (2007) 2865.

46 R. Silvestri, G. De Martino, G. La Regina, M. Artico, S. Massa, L. Vargiu, M. Mura, A.G. Loi, T. Marceddu, P. La Colla, J. Med. Chem. 46 (2003) 2482.

47 P.C. Unangst, D.T. Connor, S.R. Stabler, R.J. Weikert, M.E. Carethers, J.A. Kennedy, D.O. Thueson, J.C. Chestnut, R.L. Adolphson, M. Conroy, J. Med. Chem. 32 (1989) 1360.

48 C.D. Funk, Nat. Rev. Drug Disc. 4 (2005) 664.

49 S.S. Khandekar, D.R. Gentry, G.S. Van Aller, P. Warren, H. Xiang, C. Silverman, M.L. Doyle, P.A. Chambers, A.K. Konstantinidis, M. Brandt, R.A. Daines, J.T. Lonsdale, J. Biol. Chem. 276 (2001) 30024.

50 S. Jain, K. Shukla, A. Mukhopadhyay, S. N. Suryawanshi, D. S. Bhakuni, Synth. Commun. 20 (1990) 1315.

51 (a) M. Matsugi, K. Murata, H. Nambu, Y. Kita, Tetrahedron Lett. 42 (2001) 1077. (b) M. Matsugi, K. Murata, K. Gotanda, H. Nambu, G. Anilkumar, K. Matsumoto, Y. Kita, J. Org. Chem. 66 (2001) 2434.

52 F.L. Yang, S.-K. Tian, Angew. Chem. 125 (2013) 5029.

53 F.H. Xiao, H. Xie, S. W. Liu, G. J. Deng, Adv. Synth. Catal. 356 (2014) 364.

54 (a) W. Ge, Y. Wei, Synthesis (2012) 934. (b) W. Ge, Y. Wei, Green Chem. 14 (2012) 2066. (c) Z. Li, J. Hong, X. Zhou, Tetrahedron 67 (2011) 3690. (d) X.-L. Fang, R.-Y. Tang, P. Zhong, J.-H. Li, Synthesis (2009) 4183. (e) C.C. Browder, M.O. Mitchell, R.L. Smith, G. Stdayman, Tetrahedron Lett. 34 (1993) 6245.

55 (a) P. Hamel, J. Org. Chem. 67 (2002) 2854; (b) H.M. Gilow, C.S. Brown, J.N. Copeland, K.E. Kelly, J. Heterocycl. Chem. 28 (1991) 1025; (c) M. Raban, L.-J. Chern, J. Org. Chem. 45 (1980) 1688.

56 (a) E. Marcantoni, R. Cipolletti, L. Marsili, S. Menichetti, R. Properzi, C. Viglianisi, *Eur.* J. Org. Chem. (2013) 132. (b) C.C. Silveira, S.R. Mendes, L. Wolf, G.M. Martins, Tetrahedron Lett. 51 (2010) 2014. (c) M. Tudge, M. Tamiya, C. Savarin, G.R. Humphrey, Org. Lett. 8 (2006) 565.

57 (a) J.S. Yadav, B.V.S. Reddy, Y.J. Reddy, K. Praneeth, Synthesis (2009) 1520. (b) G. Wu, J. Wu, J. Wu, L. Wu, Synth. Commun. 38 (2008) 1036. (c) J.S. Yadav, B.V.S. Reddy, Y.J. Reddy, Tetrahedron Lett. 48 (2007) 7034. (d) Y. Maeda, M. Koyabu, T. Nishimura, S. Uemura, J. Org. Chem. 69 (2004) 7688. (e) K.M. Schlosser, A.P. Krasutsky, H.W. Hamilton, J.E. Reed, K. Sexton, Org. Lett. 6 (2004) 819. (f) J.A. Campbell, C.A. Broka, L. Gong, K.A.M. Walker, J.-H. Wang, Tetrahedron Lett. 45 (2004) 4073.

58 Q. Wu, D. Zhao, X. Qin, J. Lan, J. You, Chem. Commun. 47 (2011) 9188.

Highlights

1- Pd (II) complex modified fibrous nano-silica material KCC-1 for the first time.

2- It was used as a recyclable catalyst for synthesis of 3-sulfenylindoles.

3- High catalytic activity and ease of recovery from the reaction mixture by filtration.