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Pd nanoparticles loaded on modified chitosan-Unye bentonite microcapsules: A reusable nanocatalyst for Sonogashira coupling reaction

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ABSTRACT

This work investigates the preparation of a catalytic complex of palladium nanoparticles supported on novel Schiff base modified chitosan-Unye bentonite microcapsules (Pd NPs@CS-UN). The complex has been characterized by FT-IR, EDS, XRD, TEM, HRTEM, Raman, ICP-OES and elemental mapping analyses. Pd NPs@CS-UN was used as a catalyst for Sonogashira coupling reactions between aryl halides and acetylenes, employing K₂CO₃ as the base and EtOH as a green solvent under aerobic conditions in which it showed high efficacy. Pd NPs@CS-UN was regenerated by filtration after the completion of the reaction. This catalytic process has many advantages including simple methodology, high yields, and easy work-up. The catalytic performance does not notably change even after five consecutive runs.

1. Introduction

The Sonogashira coupling reaction (SCR) is an extremely valuable and useful reaction to form C(sp)-C(sp²) bonds for the coupling of vinyl or aryl halides with terminal alkynes, which has been broadly used in various fields including synthesis of different molecules with biological features, natural products, heterocycles, pharmaceuticals, electron conducting polymers, liquid polymer substances, etc. (Bunz, 2000; Kamali, Habibi, & Nasrollahzadeh, 2009; Negishi & Anastasia, 2003; Sonogashira, Tohda, & Hagihara, 1975). This reaction usually proceeds using toxic phosphine ligands, a homogeneous Pd catalyst, a Cu salt as the co-catalyst, and a stoichiometric quantity of a base in an organic solvent, for example, benzene, THF, DMF, or an amine under environmentally and economically disadvantageous and inert conditions (Fleckenstein & Plenio, 2007; Gholap et al., 2005; Huang, Liu, Jiang, & Chen, 2008: Lu et al., 2013: Roy & Plenio, 2010: Shylesh, Schuenemann, & Thiel, 2010; Sonogashira, 1991). A protocol for SCR of aryl halides with terminal alkynes was introduced by Fu et al. in the presence of CuBr using 1,10-phenanthroline as the ligand and tetrabutylammonium bromide (TBAB) as the phase transfer catalyst (Yang, Li, Yang, Fu, & Hu, 2011). In addition, 1,4-diphenyl-1,4-diazabuta-1,3-diene in

combination with $Cu(OAc)_2$ and TBAF was used as a ligand for the SCR of aryl iodides and bromides with terminal alkynes in 2006 (Deng, Xie, Yin, & Li, 2006). Furthermore, Li and co-workers modified the $Cu(OAc)_2$ catalyst system by replacing the ligand with a coordinating solvent (Et₃N) (Guo, Deng, & Li, 2007).

Typically, the disadvantages of Pd catalyzed SCR reactions including harsh reaction conditions, long reaction times, hard work-ups, application of toxic polar solvents, inert atmosphere conditions, expensive ligands, contamination of the environment triggered by formation of diyne as the side product and obtaining the main products with low yields limit their utilization. Therefore, the development of suitable approaches for SCR is a prominent objective (Nasrollahzadeh, Issaabadi, Tohidi, & Sajadi, 2018; Shylesh et al., 2010; Sonogashira, 1991). In SCR, copper salts assist in transmetallation by the *in situ* formation of copper acetylide. Moreover, the homocoupling of the terminal acetylene may occur as a side reaction (Sagadevan & Hwang, 2012; Shylesh et al., 2010; Sonogashira, 1991; Yamane, Miwa, & Nishikata, 2017). In addition, the utilization of amines such as triethylamine and piperidine in most SCR reactions causes bad smell and environmental hazard (Albrecht & Stephenson, 1988; Kesson, Florén, & Skerfving, 1985).

Among different palladium catalysts, homogeneous ones have been

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Scheme 1. Schematic representation of the procedure for the organization of Pd NPs@CS-UN microcapsules.

widely used. However, heterogeneous catalysts are cheaper, easier to separate from the reaction mixture and reusable for several runs (Fu et al., 2017; Fuku et al., 2019). In addition, their thermal stability and high catalytic activities make them suitable for application in various organic syntheses (Bahammou et al., 2016). Therefore, polymer supported palladium catalysts have been developed as efficient catalysts (Nasrollahzadeh et al., 2020). Among different polymers, chitosan (CS) was found to have a high efficacy as a support due to its biodegradability, biocompatibility, non-toxicity, positive charged, and availability (Nasrollahzadeh, Shafiei, Nezafat, Bidgoli, & Soleimani, 2020). Chitosan is a natural polymer suitable for the organization of a heterogeneous palladium catalyst (Motahharifar, Nasrollahzadeh, Taheri-Kafrani, Varma, & Shokouhimehr, 2020; Nasrollahzadeh & Shafiei, 2020).

Clays can be used as ion exchangers, adsorbents or catalysts in numerous industrial fields due to their low cost, environmental compatibility, reusability, operation simplicity and easy accessibility (Ghassemzadeh & Sahimi, 2004; Harvey & Murray, 1997; Lagaly, Ogawa, & Dékány, 2006; Murray, 2000; Zhou, Frost, He, & Xi, 2007). Any clay of volcanic source containing montmorillonite is referred to as bentonite. The crystalline structure of bentonite consists of an alumina octahedral among two tetrahedral silica layers (Eren, 2009). In comparison with other kinds of clay, it has outstanding adsorption features and contains adsorption sites in its interior layer space along with the edges and outer surface (Abollino, Aceto, Malandrino, Sarzanini, & Mentasti, 2003: Alvarez-Avuso & Garćia-Sánchez, 2003: Tabak, Afsin, Aygun, & Koksal, 2007). Unve bentonite comprises mainly of a dioctahedral smectite together with quartz, cristobalite, tridymite, and slight portions of anatase and feldspar (Caglar, Afsin, Koksal, Tabak, & Eren, 2013). The cation exchange capacity and high specific surface area of Unve bentonite and its noteworthy chemical and thermal stability afford a variety of structural and surface properties. The combination of this clay with chitosan improves the chemical, thermal, and mechanical properties of the biopolymer. It also provides a good support for metal ions in addition to its low cost and non-toxicity as it affords high dispersion and good adsorption (Abdelkrim et al., 2020). The octahedral aluminum hydroxide and tetrahedral silicon oxide sheets possessing more hydroxyl functional groups on the surface of bentonite allow chemical surface modifications, making it an appropriate stabilizer for supporting nano-scaled Pd particles (Sajjadi et al., 2020).

Herein, we report amine, ligand, and copper free conditions for SCR in ethanol as a green solvent using a Pd based nanocatalyst as a novel efficient catalyst. Pd NPs supported on Schiff base modified chitosan-Unye bentonite microcapsules (Pd NPs@CS-UN) have been designed



Fig. 1. FT-IR spectra of a) CS-UN, b) Pd NPs@CS-UN, and c) recycled Pd NPs@CS-UN.



Fig. 2. XRD patterns of a) Unye bentonite, b) Pd NPs@CS-UN, and c) recycled Pd NPs@CS-UN.





Fig. 3. TEM analysis and histogram of particle size distribution of the Pd NPs@CS-UN.



Fig. 4. HRTEM images of recycled Pd NPs@CS-UN.

following a simple surface modification process (Scheme 1). This method is mild, highly efficient and naturally benign.

2. Experimental

2.1. Material and devices

All the solvents and reagents employed in this research were provided by Merck and/or Sigma Aldrich Chemical Co. (USA) and applied as received. UN was obtained from Turkey. FT-IR (Fourier transform/infrared) spectroscopy carried out using a Perkin Elmer 100 spectro-photometer was applied to study the surface modification of the products obtained. The surface segments and EDS (energy-dispersive X-ray spectroscopy) analyses of Pd NPs@CS-UN microcapsules were performed using a FEI Quanta 450 FEG instrument. Raman spectra were recorded using a *via* Raman microscope. The X-ray spectra of Pd NPs@CS-UN microcapsules were recorded using a *via* Raman microscope. The X-ray spectra of Pd NPs@CS-UN microcapsules were recorded using a Philips model PW 1373 diffractometer (Cu K α =1.5418 Å and 2 θ = 10–90°). The size and the morphology of the nanocatalysts were studied by TEM (transmission electron microscopy, JEM-F200 JEOL). A Bruker DRX-400 AVANCE spectrometer was used to record ¹³C and ¹H NMR spectra at 100.61 and 400.13 MHz, respectively.

2.2. Preparation of CS-UN microcapsules

2 g of chitosan were dissolved in 100 mL of 2 % acetic acid solution (v:v), followed by the addition of 2 g of Unye bentonite to the reaction mixture and stirring for 3 h at ambient temperature. Subsequently, the reaction mixture was poured into an alkaline solution (water: methanol: NaOH 40 mL: 60 mL: 12 g) to provide gelatinous microcapsules. After the fabrication of gelatinous chitosan-Unye bentonite, the microcapsules were extensively washed with water to neutrality. Finally, the microcapsules were dropped into the glyoxal solution (5 mL) in methanol (50 mL) and stirred under reflux conditions for one day for cross-linking. After the cross-linking, CS-UN microcapsules were filtered, washed with methanol and dried.

2.3. Preparation of Pd NPs on CS-UN microcapsules

1 g of CS-UN microcapsules and 0.2 g of PdCl₂ were stirred in 30 mL of EtOH at 70 °C for 4 h. Upon the completion of the reaction, Pd NPs loaded on the CS-UN microcapsules were filtered, washed with EtOH, dried, and used as catalysts in organic reactions.

2.4. General process for SCR

A terminal alkyne (1.1 mmol) and an aryl halide (1.0 mmol) were vigorously stirred in a combination of Pd NPs@CS-UN (40.0 mg), K_2CO_3 (1.5 mmol), and ethanol (8.0 mL) in a glass flask under reflux conditions at 80 °C for proper durations of time. Upon the completion of the reaction (as followed by TLC), the mixture was cooled, the catalyst was separated by filtration, and the solvent was removed. The precipitate was washed with n-hexane and acetone to obtain the desired pure precipitate. All the products obtained were known and their analysis data and melting points were similar to those reported in the literature.

2.5. Characterization data of selected products

1,2-Diphenylethyne

¹HNMR (400 MHz, DMSO- d_6) $\delta_{\rm H} = 7.58 - 7.55$ (m, 2 H) 7.45-7.42 (m, 3 H); ¹³CNMR (100 MHz, DMSO- d_6) $\delta_{\rm C} = 131.8, 129.3, 129.2, 122.7, 89.7.$

1-Methoxy-4-(phenylethynyl)benzene

¹HNMR (400 MHz, CDCl₃) $\delta_{\rm H}$ = 7.55–6.89 (m, 9 H), 3.85 (s, 3 H); ¹³CNMR (100 MHz, CDCl₃) $\delta_{\rm C}$ = 159.6, 133.1, 131,4, 128.3, 127.9, 123.6, 115.4, 113.9, 89.3, 88.1, 55.31.

1-Methyl-4-(phenylethynyl)benzene

¹HNMR (400 MHz, DMSO) $\delta_{\rm H} = 7.23 - 7.55$ (m, 9 H), 2.34 (s, 3 H).

3. Results and discussion

3.1. Catalyst analysis

The structural, morphological, and physicochemical properties of Pd



Fig. 5. FFT (top) and STEM (bottom) images of the Pd NPs@CS-UN.



Fig. 6. Raman spectrum of the Pd NPs@CS-UN.



Fig. 7. EDS spectrum of the Pd NPs@CS-UN.

NPs@CS-UN were determined by FT-IR, EDS, XRD, TEM, HRTEM, Raman, ICP-OES and elemental mapping.

The reduction potential of the Pd^{2+} is very low, and it can be reduced under mild conditions without the use of any harsh reductant. High temperature, use of EtOH as the solvent, and solid support with the amine groups work as a mild reduction condition to reduce the Pd^{2+} moieties. The prepared Schiff base also assists the Pd^{2+} reduction (Choi, Shokouhimehr, & Sung, 2013; Li, Wang, & Li, 2005; Shokouhimehr et al., 2018). After the reaction was completed, it was observed that the color of the solution turned dark grey.

The FT-IR spectra of CS-UN, Pd NPs@CS-UN, and recycled Pd NPs@CS-UN are presented in Fig. 1. The FT-IR spectrum of CS-UN displayed typical bands of chitosan and UN at 3340 cm⁻¹ (O—H stretching), 2926 cm⁻¹ and 2871 cm⁻¹ (C—H stretching) and 1017 cm⁻¹ (C—O—C stretching). More importantly, the peak observed at 1642 cm⁻¹ is correlated to the imine bond vibration, confirming the formation of CS-UN microcapsule. As for Pd NPs@CS-UN microcapsules, the imine bond shifted to 1626 cm⁻¹ due to the strong interaction of Pd with CS-UN microcapsule (Fig. 1).

The diffraction pattern of the samples was observed by XRD. Fig. 2 demonstrates the XRD pattern of the Unye bentonite, Pd NPs@CS-UN and recycled Pd NPs@CS-UN. The specified peaks pointed by asterisks in the XRD pattern of Pd NPs@CS-UN (Fig. 2b) are related to the typical peaks of Unye bentonite (Fig. 2a) and the broad peak in the area of $2\theta = 20$ is related to the chitosan. In addition to the typical peaks of Unye bentonite and chitosan, new peaks were detected at 40.07° (111),

46.43° (200), 67.96° (220), 82.04° (311), and 86.51° (222) in the XRD spectrum of the Pd NPs@CS-UN, corresponding to the face centered cubic (*FCC*) structure of Pd (Khan et al., 2014), confirming the formation of Pd NPs on the CS-UN microcapsule.

TEM analysis of the catalyst was applied to confirm the formation of Pd NPs (Fig. 3). As observed in Fig. 3, the loading of the Pd NPs on the CS-UN microcapsules prepared has been successfully carried out. Fig. 3 (bottom) shows the particle size distribution histogram of Pd NPs@CS-UN. Moreover, the average size of NPs was estimated to be about 13 nm. The HRTEM (Fig. 4) and fast Fourier transform (FFT) (Fig. 5, top) images of the Pd NPs@CS-UN show that the nanoparticles are highly crystalline. STEM image confirms a homogeneously assembled nano-structured catalyst (Fig. 5, bottom).

The presence of the Pd NPs in the catalyst prepared was also confirmed by Raman spectroscopy (Fig. 6). The Raman peak of Pd NPs bond also verified the ambient Pd transition metal ions.

The element composition of the Pd NPs@CS-UN was determined by EDS analysis. The EDS analysis of the catalyst was carried out using a Cu grid to hold the sample. This spectrum showed the presence of Pd NPs on the CS-UN superficial (Fig. 7). In the EDS spectrum, Pd, Si, O, Cl and C peaks were observed, indicating the authenticity of Pd NPs@CS-UN.

The content of the Pd within Pd NPs@CS-UN, as determined by ICP-OES (Inductively coupled plasma-optical emission spectrometry), was found to be 14.16 wt%.

Elemental mapping of Pd NPs@CS-UN also confirmed the formation of Pd NPs (Fig. 8). These analyses strongly confirmed the immobilization of Pd NPs on the surface of the CS-UN.

The TGA analysis of Pd NPs@CS-UN (Fig. 9) showed that the catalyst had high thermal stability and is thus suitable for different organic reactions, which require high reaction temperatures. As observed in Fig. 9, the weight losses have occurred during three steps. The initial weight loss of up to 259.5 °C is attributed to the organic solvents and the water enclosed in the nanocatalyst structure (22.8 % weight loss) while the second and third steps at 424.6 °C (11 % weight loss) and 800.1 °C (3.1 % weight loss) could be related to the thermal decomposition of the glyoxal and chitosan groups, respectively.

3.2. Catalytic activity of Pd NPs@CS-UN in the SCR

The present work affords Schiff base supported Pd NPs as novel heterogeneous catalysts for the ligand and copper-free SCR. This system eliminated the need for expensive, difficult to prepare, and air and moisture sensitive ligands.

To optimize the reaction conditions, the effects of solvents, bases and catalyst amount in the reaction of 1.1 mmol of phenylacetylene with 1.0 mmol of p-iodoanisole using Pd NPs@CS-UN catalyst, 1.5 mmol of base and 8.0 mL of solvent as the model reaction were studied. As depicted in Table 1, the SCR was first performed without any catalyst or in the presence of Unye bentonite at 80 °C (Table 1, entry 1 and 2), which resulted in no product formation. As observed in Table 1, the choice of base or solvent affects the reaction. The efficacy of Pd NPs@CS-UN (40.0 mg) as a catalyst was evaluated in the presence of various bases (K₂CO₃, NEt₃, KOH, pyridine and Na₂CO₃) and solvents (EtOH, toluene, H₂O and H₂O/EtOH). The best result was obtained using K₂CO₃ and ethanol as the base and solvent, respectively (Table 1, entry 11). Subsequently, the amount of Pd NPs@CS-UN required for the SCR was optimized. The amount of Pd NPs@CS-UN varied in the range of 20.0-50.0 mg in the presence of EtOH at 80 °C. Increasing the catalyst amount from 40.0 mg to 50.0 mg slightly increased the product yield. The reaction was



Fig. 8. STEM image and elemental mapping of Pd NPs@CS-UN.



Fig. 9. TGA analysis of Pd NPs@CS-UN.

Table 1

Optimization of reaction conditions for the SCR between *p*-iodoanisole with phenylacetylene using different solvents and bases at 80 $^{\circ}$ C for 3 h.

Entry	Catalyst (mg)	Solvent	Base	Yield (%)
1	None	EtOH	K ₂ CO ₃	0
2	Bentonite (40.0)	EtOH	K ₂ CO ₃	0
3	Pd NPs@CS-UN (40.0)	H_2O	K ₂ CO ₃	Trace
4	Pd NPs@CS-UN (40.0)	Toluene	K ₂ CO ₃	45
5	Pd NPs@CS-UN (40.0)	H ₂ O/EtOH	K ₂ CO ₃	15
6	Pd NPs@CS-UN (40.0)	EtOH	Pyridine	38
7	Pd NPs@CS-UN (40.0)	EtOH	KOH	60
8	Pd NPs@CS-UN (40.0)	EtOH	NEt ₃	63
9	Pd NPs@CS-UN (40.0)	EtOH	NaOH	42
10	Pd NPs@CS-UN (40.0)	EtOH	Na ₂ CO ₃	79
11	Pd NPs@CS-UN (40.0)	EtOH	K ₂ CO ₃	87
12	Pd NPs@CS-UN (20.0)	EtOH	K ₂ CO ₃	56
13	Pd NPs@CS-UN (50.0)	EtOH	K ₂ CO ₃	88

completed within 3 h at 80 $^\circ$ C and the product was isolated in 87 % yield. No organic co-solvent, ligand, or surfactant was required. In addition, no undesirable organization of a diyne as a homocoupling product was observed, as no copper salts were employed.

Next, under the optimized conditions, the application of Pd NPs@CS-UN was studied for the SCR between terminal acetylenes and different aryl halides containing either electron-withdrawing or donating sites. As specified in Table 2, our system is obviously general and practical for various aryl halides. Products were obtained in high yields in all the cases under the reaction conditions. To further investigate the efficacy of Pd NPs@CS-UN, the chlorobenzene reaction was also checked with phenylacetylene. Under these conditions, the desired product was obtained in 70 % yield (Table 2, entry 8).

The role of the catalyst in SCR can be accounted for by the proposed mechanism in Scheme 2, inspired from previous reports (Alinezhad, Pakzad, & Nasrollahzadeh, 2020; Gazvoda, Virant, Pinter, & Košmrlj,

2018). Here, Pd NPs@CS-UN activates the phenylacetylene terminal acetylene C—H. Potassium acetylide intermediate is then efficiently produced *via* the deprotonation of C—H using K₂CO₃. Aryl palladium halide complex (ArPdX) can be produced *via* the activation of ArX on the active sites of Pd NPs@CS-UN. Consequently, aryl palladium acetylide is generated as an intermediate. Finally, the expected coupling products are obtained by reductive elimination.

The comparison of the results of the present study with those of some recent surveys regarding the catalytic SCR further confirms the efficacy of our proposed system as the reaction is performed in a suitable time and gives products in good to excellent yields. Table 3 briefly represents the catalytic systems for SCR.

3.3. Catalyst recyclability

The recyclability of a catalyst is one of the vital properties, which makes the catalyst advantageous for commercial applications. The recyclability of Pd NPs@CS-UN catalyst was studied by model SCR for phenylacetylene with p-iodoanisole. This catalyst was used in five consecutive cycles under similar reaction conditions (Fig. 10). The catalyst presented good yields of the products even on the fifth reaction sequence for SCR. The microcapsule form and heterogeneous nature of our catalyst allowed its easy separation from the reaction mixture. Upon the completion of SCR, the catalyst is separated via filtration, washed with EtOAc, dried at 100 $^\circ \mathrm{C}$ for 4 h in a hot air oven and then used in the next cycle. As shown in Fig. 10, the catalytic performance of Pd NPs@CS-UN remained the same for the first cycle and then decreased slightly in the next few cycles. To check the heterogeneity of this catalyst, which is an important factor, the filtrate of each cycle was also analyzed by ICP technique. Very low palladium contamination was observed during these experiments. The content of the Pd within the recycled Pd NPs@CS-UN was found to be 13.18 %, according to the ICP-OES analysis. The XRD, TEM and FT-IR analyses exhibited no significant changes in the size, shape, crystallinity and functional group of the

Table 2

Substrate scope for Pd NPs@CS-UN catalyzed SCR of terminal alkynes with various aryl halides^a.

R +	R' 2	$\frac{\text{Pd NPs@CS-UN}}{\text{K}_2\text{CO}_3, \text{EtOH, 80 °C}} R$	R'				
X = Cl, Br d	& I						
Entry	R	Aryl halide	Product	Time (h)	Yield (%) ^b	TON	TOF (h^{-1})
1	Ph	I	Ph	3	90	1800	600
2	Ph	І-ОМе	Ph — OMe	3	87	1740	580
3	Ph	I————Me	PhMe	3	88	1760	586.6
4	Ph			2.5	90	1800	720
5	Ph	Br	Ph	4.5	77	1540	342.2
6	Ph	Br Me	Ph — Me	4.5	73	1460	324.4
7	Ph	Br-NO ₂		4.5	80	1600	355.5
8	Ph	ci	Ph	5.5	70	1400	254.5
9	Me-(CH ₂) ₅ -	I	Me(CH ₂) ₅	8	82	1640	205
10	Me-(CH ₂) ₅ -	I	Me(CH ₂) ₅ ———————————————————————————————————	8	78	1560	195
11	Me-(CH ₂) ₅ -		Me(CH ₂) ₅ -NO ₂	8	83	1660	207.5
12	Me-(CH ₂) ₅ -	Br	Me(CH ₂) ₅ — Me	8	71	1420	177.5

 a Reaction conditions: Aryl halide (1.0 mmol), terminal acetylene (1.1 mmol), K₂CO₃ (1.5 mmol), catalyst (40.0 mg), EtOH (8 mL), 80 °C. b Isolated yield.



Scheme 2. Proposed pathway for the SCR using Pd NPs@CS-UN.

reused Pd NPs@CS-UN after the 5th recycle (Figs. 1c, 2c and 11). We have also checked the particle size distribution of the reused catalyst (Fig. 11). The average size of Pd NPs calculated from the TEM images is found to be about 14 nm. In addition, the FT-IR spectrum of the reused Pd NPs@CS-UN also shows peaks which assigned to the catalyst (Fig. 1c). The XRD results also confirmed that the structure of the reused Pd NPs@CS-UN is similar to the fresh catalyst (Fig. 2c). Thus, it is

sufficient to indicate that the Pd NPs@CS-UN catalyst exhibits high chemical and thermal stability.

4. Conclusion

In summary, SCR has been carried out in ethanol as a green solvent using Pd NPs@CS-UN catalyst. Several characterization methods

Table 3

Comparison of recent reports on SCR.

Entry	Catalyst	Reaction conditions	Time (h)	Yield	Ref.
				(%)	
1	Pd NPs@CS-UN (40.0 mg)	K ₂ CO ₃ , EtOH, 80 °C	2.5 - 8	70-90	Current study
2	Polymer supported Pd triazene complex (3.0 mol% Cat.)	CuI, dioxane, r.t.	16	71	Bräse, Dahmen, Lauterwasser, Leadbeater, &
					Sharp, 2002
3	PS ^a -Pd(II) -anthra complex (0.5 mol% Pd)	Et ₃ N, DMF, 90 °C	12 - 24	14-96	Islam, Mondal, Tuhina et al., 2010
4	Polystyrene anchored Pd(II) azo complex (0.5 mol% Pd)	Et ₃ N, H ₂ O, TBAB, 70-80 °C	8 - 12	68-96	Islam, Mondal, Roy, Mondal, Mobarak et al., 2010
5	PS ^a -PPDOT ^b -Pd(II) (1.0 mol% Cat.)	Et ₃ N or pyridine, r.t.	3	23-99	Bakherad, Keivanloo, Bahramian, & Jajarmi,
					2010
6	PS ^a -PEG ^c resin bound triarylphosphine ligand (5.0 mol %	Et ₃ N or CsOH, H ₂ O, N ₂ ,	6-24	13 - 99	Suzuka, Okada, Ooshiro, & Uozumi, 2010
	Pd)	40–100 °C			
7	Pd(II) Schiff base complex (3.72 mol% Pd)	CuI, Et ₃ N, H ₂ O, 70 °C	8-20	32-99	Islam, Mondal, Roy, Mondal, & Hossain, 2010
8	FDU ^d -NHC ^e /Pd(II) complex (1.0 mol% Cat.)	CuI, K ₂ CO ₃ , DMA, 100 °C	1 - 24	10-94	Tao et al., 2011
9	Polymer-supported Schiff base palladium complex (0.5	Piperidine, H ₂ O, 100 °C	0.5 - 12	35-99	He et al., 2011
	mol% Pd)				
10	Fe ₃ O ₄ @SiO ₂ -polymer-imid-Pd (0.03 g)	Et ₃ N, DMF, 80 °C	0.5 - 10	87-96	Esmaeilpour, Javidi, Mokhtari, & Nowroozi, 2014
11	Pd-NHC@SP-PS or Pd-NHC@PS ^f (1.0 mol% Cat.)	Et ₃ N, 90 °C	1.5 - 7	75-95	Jadhav, Kumbhar, Mali, Hong, & Salunkhe, 2015
12	Ps[PdCl-(SeCSe)] ^g (0.3 mol% Pd)	NMP ^h , TBAF, 70 °C	0.25 - 24	23 - 95	Mohammadi et al., 2018

^a Polystyrene-supported.

^b 1-Phenyl-1,2-propanedione-2-oxime thiosemi-carbazone.

^c Poly-(ethylene glycol).

- ^d (Fudan University)-15 mesopolymer.
- ^e *N*-Heterocyclic carbene.

^f Polymer supported air-stable palladium NHC complex with a spacer (Pd-NHC@SP-PS) and without a spacer (Pd-NHC@PS).

^g Palladium complex of polystyrene-supported SeCSe pincer ligand.

h N-Methylpyrolidone.



Fig. 10. Reusability of Pd NPs@CS-UN in SCR.

including FTIR, EDS, XRD, Raman, ICP-OES, elemental mapping and TEM were used to characterize this Schiff base modified heterogeneous catalyst. It was shown that the catalyst comprised Pd NPs with a particle size of about 14 nm. The catalyst appeared to be extremely efficient, stable and recyclable for five runs in SCR. The present catalyst was prepared keeping in mind the low cost and the benefits of chitosan and Unye bentonite based materials and the usefulness of solid acid catalysts. A range of different substituted aryl halides and terminal acetylenes were employed to obtain products in high yields. The easy separation, eminent reusability and low cost of this catalyst make it even more attractive for catalytic applications in various chemical transformations.





Fig. 11. TEM images and histogram of particle size distribution of recycled Pd NPs@CS-UN.

Declaration of Competing Interest

Authors declare no conflict of interest.

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