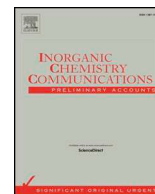




ELSEVIER

Contents lists available at ScienceDirect

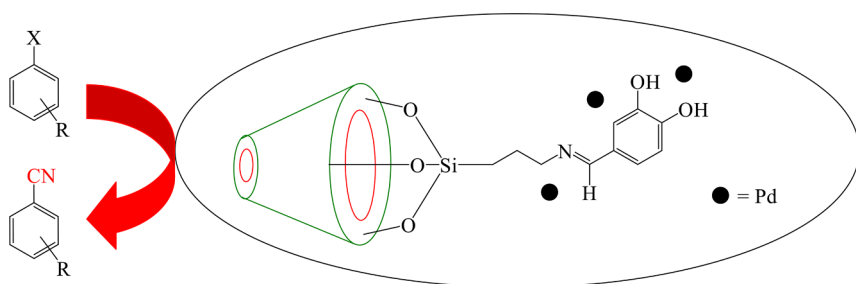
Inorganic Chemistry Communications

journal homepage: www.elsevier.com/locate/inoche

Short communication

Green synthesis of palladium nanocatalyst derived from the β -cyclodextrin used as effective heterogeneous catalyst for cyanation of aryl halidesTalat Baran^a, Mahmoud Nasrollahzadeh^{b,*}^a Department of Chemistry, Faculty of Science and Letters, Aksaray University, 68100 Aksaray, Turkey^b Department of Chemistry, Faculty of Science, University of Qom, 3716146611 Qom, Iran

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:

β -Cyclodextrin
Benzonitrile
Palladium nanoparticles
Cyanation reaction

ABSTRACT

In this study, preparation of highly stable palladium nanoparticles (Pd NPs) on Schiff base modified β -cyclodextrin (β -CD-Sch) in the absence of reducing agents has been successfully carried out. Pd NPs@ β -CD-Sch has then been applied as nanocatalyst in the synthesis of benzonitriles via cyanation reaction using $K_4Fe(CN)_6$, which is a low cost, commercially available and non-toxic cyanide source. A series of benzonitriles containing different substrates were successfully fabricated with 77–98% yields using Pd NPs@ β -CD-Sch. Moreover, Pd NPs@ β -CD-Sch catalyst was quantitatively recovered and reutilized several times, showing good reaction yields. This work revealed that i) prepared β -CD-Sch is an effective stabilizer for the fabrication of Pd NPs and ii) Pd NPs@ β -CD-Sch catalyst play an important role in the fabrication of benzonitriles.

1. Introduction

Benzonitriles are one of the most significant compounds derived from various commercial sources, which are used for the preparation of biologically active substances [1,2]. Therefore, the synthesis of these versatile compounds has recently gained importance [3]. Aryl nitriles are generally prepared via Rosenmund-von Braun reaction. However, this method generates heavy metal wastes owing to the application of stoichiometric amounts of Cu-CN [4]. Therefore, cyanation of aryl halides in the presence of cyanide agents and metal catalysts is the most

facile and powerful synthesis method for the production of aryl nitriles [3,4,5]. Different cyanide sources such as NaCN, $Zn(CN)_2$ and KCN have been employed in the fabrication of aryl nitriles using various metal catalysts [4,6]. However, these sources have some drawbacks such as high cost, long reaction times, harsh reaction conditions and low reaction yields [7]. Among cyanide sources, $K_4Fe(CN)_6$ is one of the most widely used due to its high efficiency, non-toxicity, low cost and environmental friendliness [4,8]. Different metal catalysts have recently been evaluated in the production of aryl halides in the presence of $K_4Fe(CN)_6$ [4,9,10]. Among these, Pd NPs play a major role owing to their

* Corresponding author.

E-mail addresses: mahmoudnasr81@gmail.com, m.nasrollahzadeh@qom.ac.ir (M. Nasrollahzadeh).<https://doi.org/10.1016/j.inoche.2020.108117>

Received 16 June 2020; Received in revised form 12 July 2020; Accepted 13 July 2020

Available online 17 July 2020

1387-7003/ © 2020 Elsevier B.V. All rights reserved.

high catalytic activity and wide functional group tolerance in catalytic reactions [11–15]. However, major disadvantages in the synthesis of Pd NPs are the aggregation and reusability problems. These disadvantages can be overcome by designing novel supports, which strongly interact with metals.

In recent years, natural bio-polymers have gained considerable attention due to their biodegradability, biocompatibility, and high affinity for different transition metals. Among biopolymers, β -cyclodextrin (β -CD), which is a cyclic oligosaccharide, is a natural, low cost, suitably sized, biocompatible, non-toxic and edible compound [16,17]. Additionally, β -CD has primary or secondary hydroxyl groups, pendant on the polymer chain, by which it is easily modified. Thanks to its outstanding properties and chemical structure, β -CD is an ideal stabilizer for the construction of Pd NPs [18]. Therefore, different β -CD modified supports can be prepared for the fabrication of different nanoscale palladium and their catalytic performances can then be tested in various transformations.

In continuation of our interest in the development of heterogeneous nanocatalysts on natural biopolymers, in this study, Pd NPs have been prepared on a β -CD containing Schiff base and their chemical structure has been verified by different analytical techniques. Afterwards, Pd NPs@ β -CD-Sch were evaluated as catalyst in the fabrication of benzonitriles via cyanation of aryl halides using $K_4[Fe(CN)_6]$. Pd NPs@ β -CD-Sch successfully catalyzed the conversion of various aryl halides to the desired benzonitriles in good yields within 4 h. Moreover, Pd NPs@ β -CD-Sch serve as recyclable catalysts, which could be used eight times.

2. Experimental

2.1. General remarks

β -Cyclodextrin, 3-aminopropyltriethoxysilane (APTES), 3,4-dihydroxybenzaldehyde, aryl halides (Ar-X), phenylboronic acid ($PhB(OH)_2$), NaOH, KOH, Na_2CO_3 , K_2CO_3 , $PdCl_2$, DMF, DMSO, toluene, NMP and diethyl ether were obtained from Sigma Aldrich Chemical Co. Modification of the products was confirmed by spectrophotometry (Perkin Elmer 100 FT-IR spectrophotometer). The X-ray spectra of β -CD and Pd NPs@ β -CD-Sch were obtained using a Rigaku smart lab system. The surface profiles and EDS analyses of β -CD, β -CD-NH, β -CD-Sch and NPs@ β -CD-Sch were investigated using FEI Quanta 450 FEG. The thermal behavior of the catalyst was studied by EXSTAR S11 7300.

GC-MS was used for the characterization of benzonitriles using an Agilent GC-7890 A-MS 5975 instrument.

2.2. Synthesis of β -CD-Sch as stabilizer

Firstly, amine attached β -CD was easily fabricated according to a previously reported method [19,20] and entitled as β -CD-NH₂. Briefly, 2 g of β -CD and 5 mL of APTES were stirred at 100 °C in toluene solvent for 24 h. β -CD-NH₂ (1 g) and 3,4-dihydroxybenzaldehyde (1 g) were then transferred to 40 mL of ethanol solvent and the mixture was refluxed for 48 h. Finally, the support material, denoted as β -CD-Sch, was filtered, washed with ethanol and dried (Scheme 1).

2.3. Synthesis of Pd NPs@ β -CD-Sch catalyst

0.5 g of β -CD-Sch and 0.1 g of $PdCl_2$ were added to 25 mL of ethanol and the mixture obtained was stirred for 5 h at 70 °C in the absence of any reducing agent. Afterwards, the reaction color changed to black. Finally, Pd NPs@ β -CD-Sch was filtered, rinsed with water and dried for use in catalytic applications (Scheme 1).

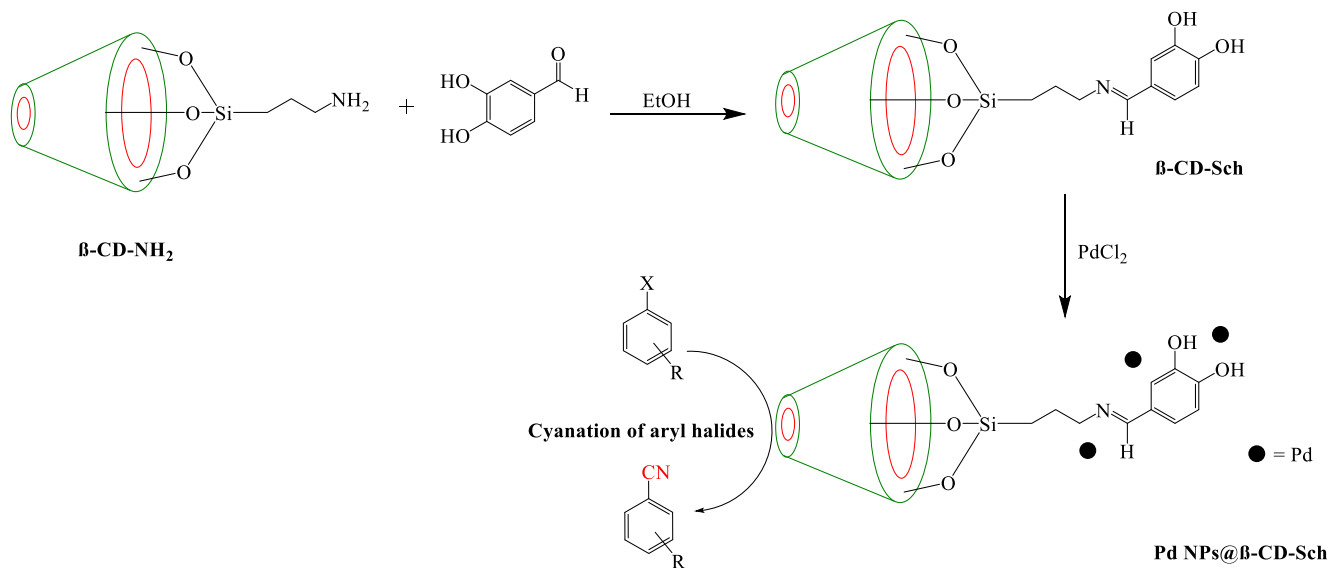
2.4. Typical synthesis method for cyanation of aryl halides

Pd NPs@ β -CD-Sch catalyst (0.05 mol. %), aryl halide (1 mmol), $K_4[Fe(CN)_6]$ (0.2 mmol) and Na_2CO_3 (1.5 mmol) were added to 6 mL of DMF and the mixture obtained was stirred at 120 °C for 4 h. The mixture was then cooled to room temperature and the product was extracted with Et_2O (10 mL) and H_2O (5 mL) three times and dried over $MgSO_4$. Afterwards, the organic solvents were evaporated to obtain benzonitriles.

3. Results and discussion

3.1. Pd NPs@ β -CD-Sch characterization

FT-IR analysis was used to confirm the chemical structures of β -CD, β -CD-NH₂, β -CD-Sch and Pd NPs@ β -CD-Sch (Fig. 1). Important peaks are observed in the FT-IR spectrum of β -CD at 3294 cm^{-1} (vibration of symmetrical and asymmetrical stretching of the -OH groups), 2924 cm^{-1} (vibration of C-H stretch), 1643 cm^{-1} (H-O-H bending), 1152 cm^{-1} and 1020 cm^{-1} (asymmetric and symmetric C-O-C



Scheme 1. Preparation of Pd NPs@ β -CD-Sch.

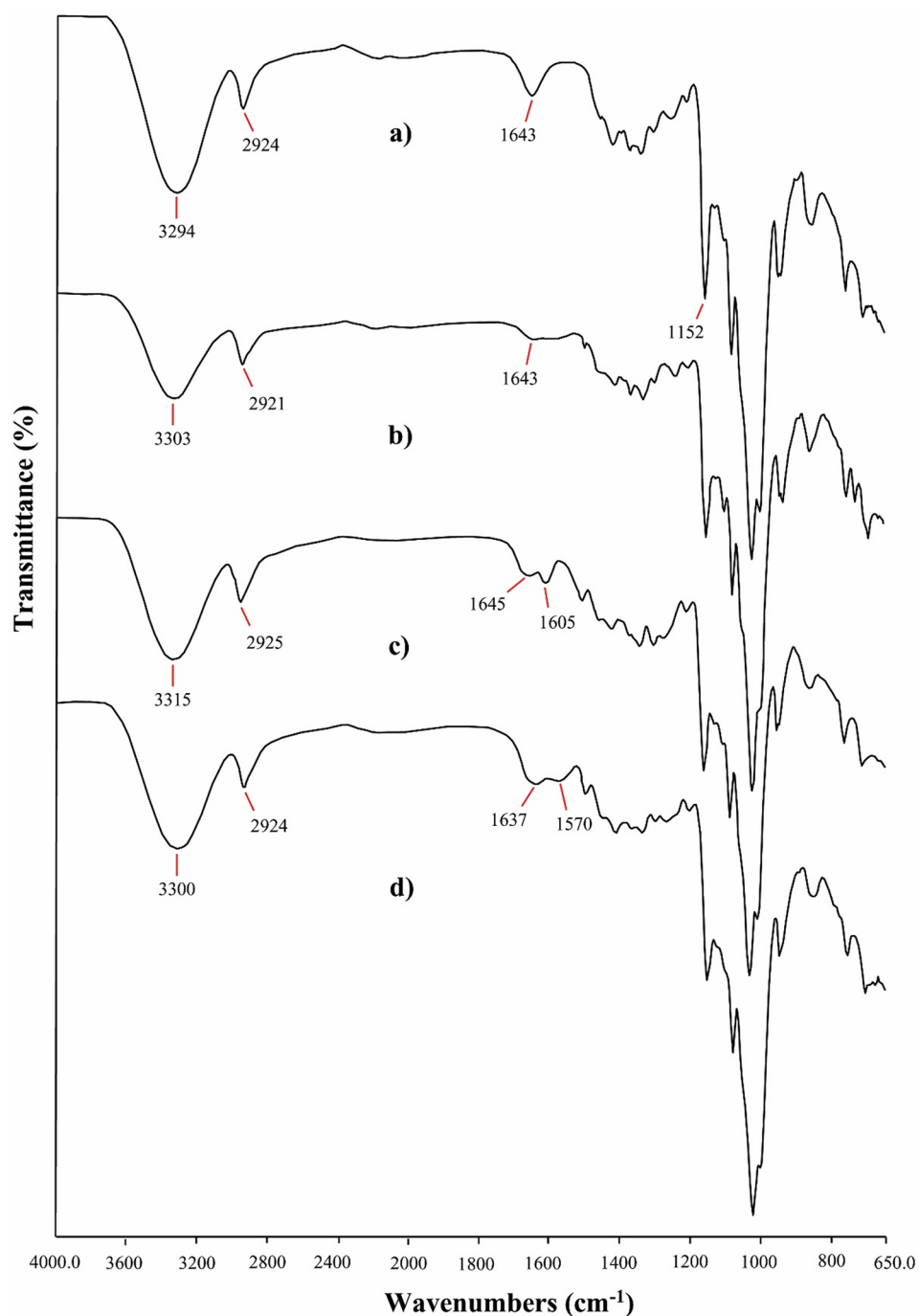


Fig. 1. FT-IR spectra of β -CD (a), β -CD-NH₂ (b), β -CD-Sch (c) and Pd NPs@ β -CD-Sch (d).

stretching) [21]. Owing to the intense stretching of C–O–C in the spectrum of β -CD-NH₂, Si-O-Si peaks were masked and thus not observed. Therefore, ninhydrin test was performed, similar to our previous works, to verify the attachment of NH₂ groups on the β -CD (Fig. 2). As observed in Fig. 2, after the ninhydrin test, the formation of a purple colored solution with an absorption band at 580 nm confirmed the presence of NH₂ groups on β -CD [19,22]. Additionally, EDS analysis of β -CD-NH₂ clearly shows the presence of Si peak. These analyses confirm that NH₂ groups have been successfully bonded on the β -CD surface. The FT-IR spectrum of β -CD-Sch shows a new peak at 1605 cm⁻¹, which corresponds to the imine band, indicating the formation of Schiff base. Although the FT-IR spectrum of β -CD-Sch was similar to that of Pd NPs@ β -CD-Sch, the peaks due to Pd NPs@ β -CD-Sch were observed to generally shift to lower wavenumbers compared

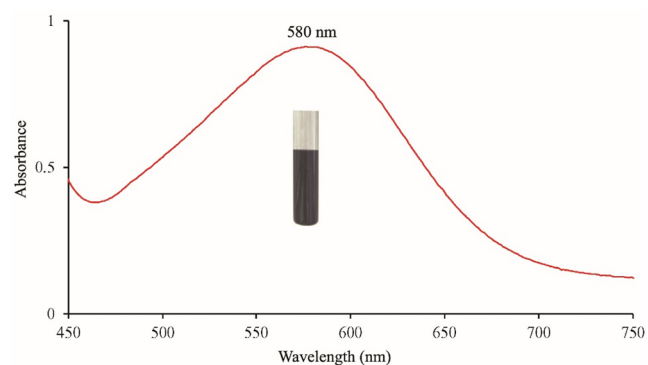


Fig. 2. Ninhydrin test of β -CD-NH₂.

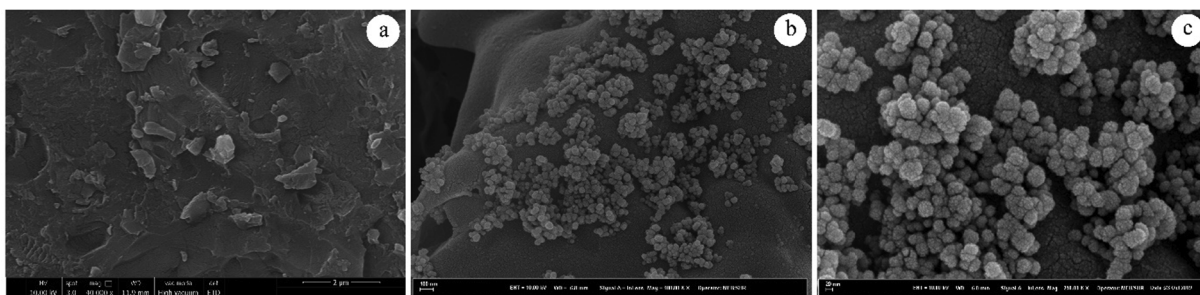


Fig. 3. FE-SEM images of β -CD (a) and Pd NPs@ β -CD-Sch (b, c).

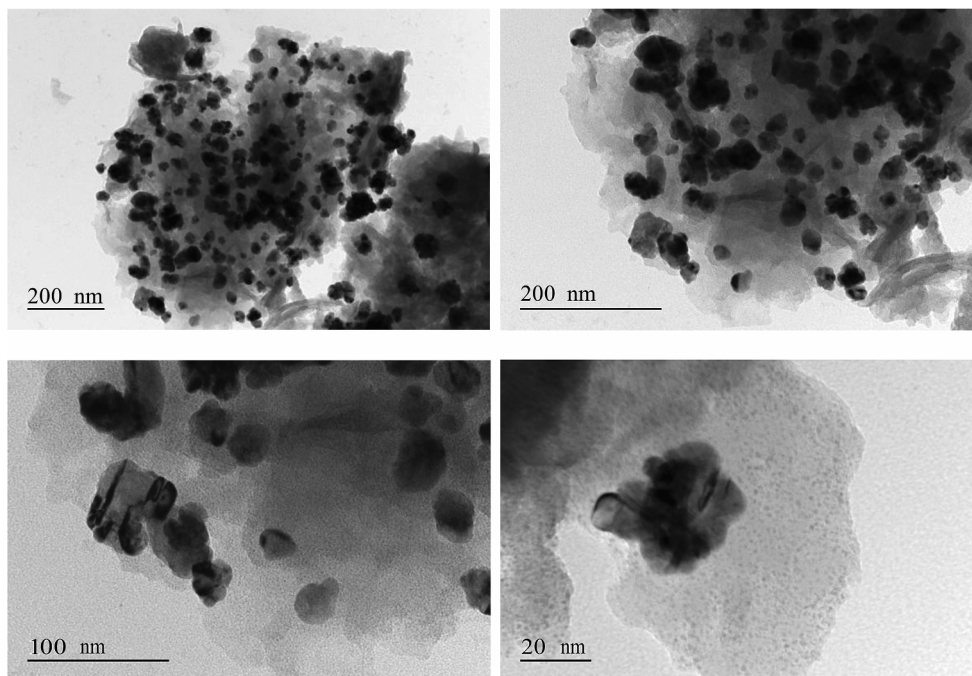


Fig. 4. TEM images of Pd NPs@ β -CD-Sch.

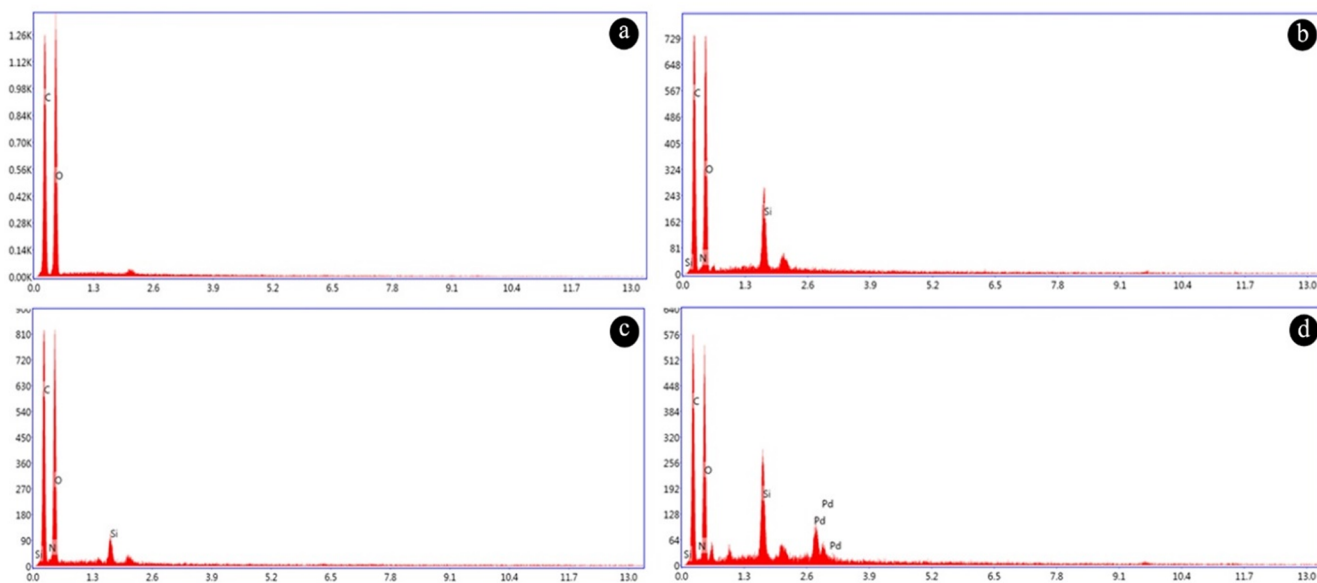


Fig. 5. EDS spectra of β -CD (a), β -CD-NH₂ (b), β -CD-Sch (c) and Pd NPs@ β -CD-Sch (d).

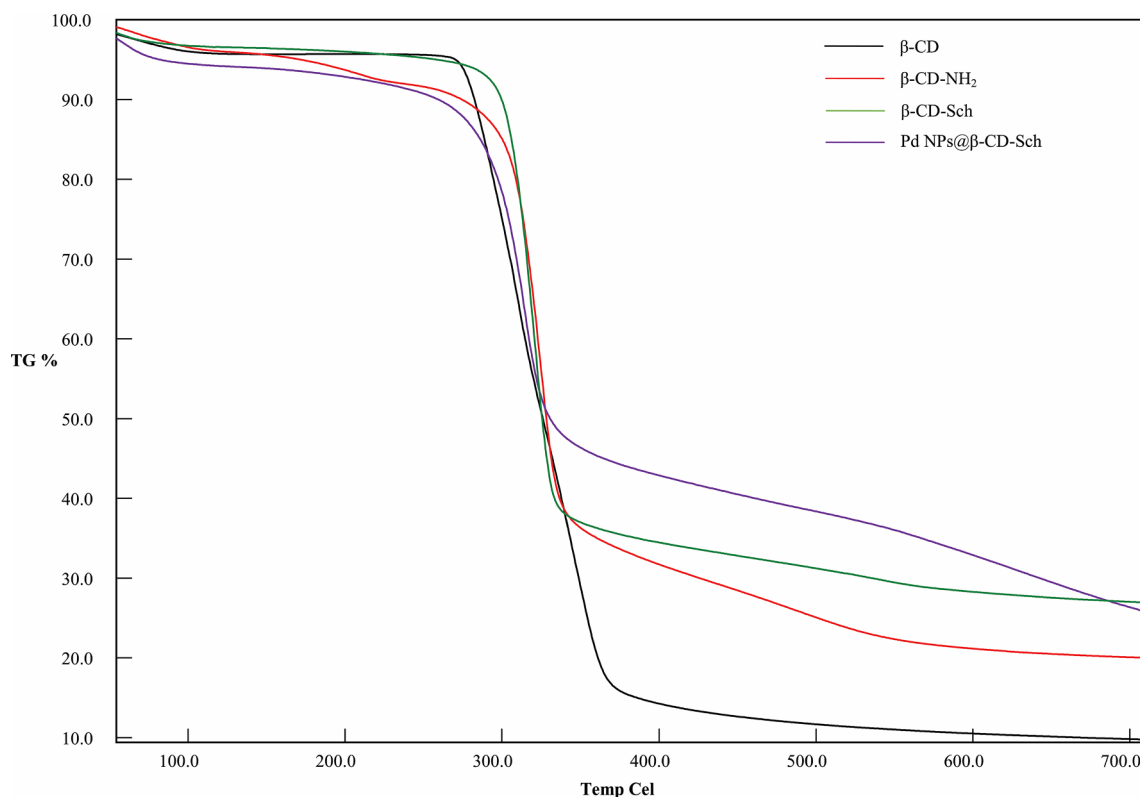


Fig. 6. TGA spectra of β -CD (a), β -CD-NH₂ (b), β -CD-Sch (c) and Pd NPs@ β -CD-Sch (d).

to β -CD-Sch. This can be explained by interaction of Pd ions with the functional groups of β -CD-Sch [23].

Fig. 3 shows the FE-SEM micrograms of β -CD and Pd NPs@ β -CD-Sch. It is clearly observed that while the β -CD has a partially flat surface, surface of Pd NPs@ β -CD is coated with Pd NPs. In addition, TEM analysis of Pd NPs@ β -CD-Sch was performed to show fabrication of Pd NPs (Fig. 4) and the size of Pd NPs was determined about 20 nm. On the other hand, the EDS analysis for each modification was performed and the corresponding spectra are shown in Fig. 5. As observed in Fig. 5, while β -CD is composed of C and N, β -CD-NH₂ and β -CD-Sch consists of C, N, O and Si elements. In the case of Pd NPs@ β -CD, the presence of Pd is clearly observed in the spectrum, confirming the formation of Pd NPs. Additionally, the amount of Pd on the catalyst was detected as 6.15% by ICP.

The thermal characteristics of β -CD, β -CD-NH₂, β -CD-Sch and Pd NPs@ β -CD-Sch were examined by TGA analysis and the corresponding spectra are shown in Fig. 6. TGA analysis showed that the temperature

(T_{\max}) at which the greatest degradation was recorded was 318 °C for β -CD. T_{\max} values of β -CD-NH₂ and β -CD-Sch were 323 and 319 °C, respectively. T_{\max} of Pd NPs@ β -CD-Sch was found to be 312 °C. These results indicate that Pd NPs@ β -CD-Sch have slightly lower thermal durability than their support. This decrease can be explained by the catalytic influence of Pd ions on the decomposition of the polymer backbone of β -CD [24]. However, the thermal durability of the catalyst is considerably high and is a suitable for different high temperature catalytic reactions.

The crystalline nature of β -CD and Pd NPs@ β -CD-Sch was studied by XRD (Fig. 7). The XRD diagram of β -CD displays typical β -CD peaks [25] (Fig. 7a). In addition to the typical peaks of β -CD, the XRD pattern of Pd NPs@ β -CD-Sch shows new diffraction peaks at 39.15°, 45.67° and 66.42° (Fig. 7b), which are indexed to (111), (200), (220) and (311) planes of face centered cubic of Pd NPs, indicating the formation of Pd NPs on the β -CD-Sch [26].

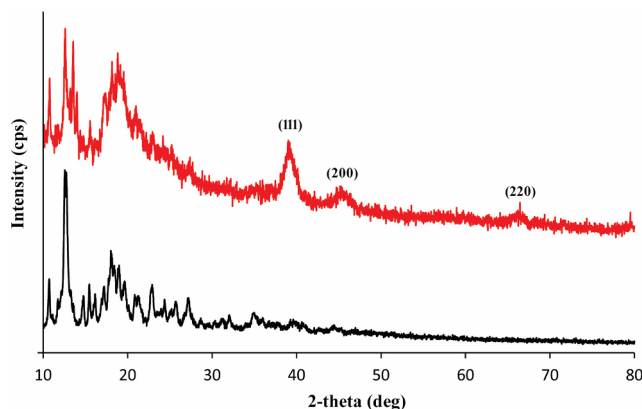


Fig. 7. XRD patterns of β -CD (a) and Pd NPs@ β -CD-Sch (b).

Table 1

Determination of optimization conditions in the cyanation of 1-iodo-3-nitrobenzene using Pd NPs@ β -CD-Sch and K₄[Fe(CN)₆].

Entry	Pd (mol%)	Solvent	Base system	Temp (°C)	Time (h)	Yield (%)
1	0.05	Toluene	K ₂ CO ₃	120	10	60
2	0.05	DMSO	K ₂ CO ₃	120	10	65
3	0.05	NMP	K ₂ CO ₃	120	12	55
4	0.05	DMF	K ₂ CO ₃	120	6	80
5	0.05	DMF	KOH	120	6	50
6	0.05	DMF	NaOH	120	6	35
7	0.05	DMF	Na ₂ CO ₃	120	4	97
8	0.05	DMF	Na ₂ CO ₃	25	4	30
9	0.05	DMF	Na ₂ CO ₃	50	4	45
10	0.05	DMF	Na ₂ CO ₃	100	4	75
11	0.05	DMF	Na ₂ CO ₃	120	4	97
12	0.02	DMF	Na ₂ CO ₃	120	8	65
13	0.1	DMF	Na ₂ CO ₃	120	4	97
14	0	DMF	Na ₂ CO ₃	120	24	0

Table 2
Catalytic behavior of Pd NPs@ β -CD-Sch against production of benzonitriles.

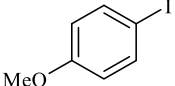
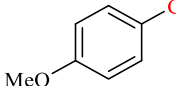
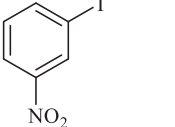
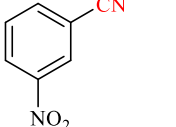
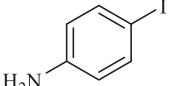
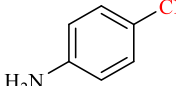
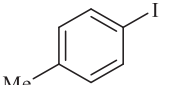
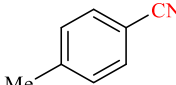
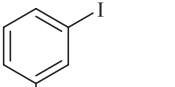
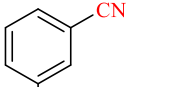
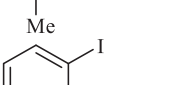
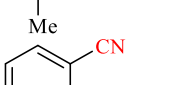
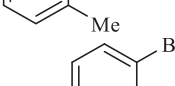
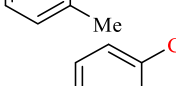
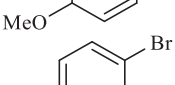
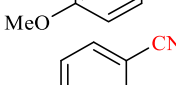
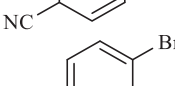
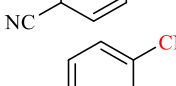
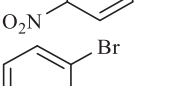
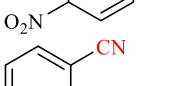
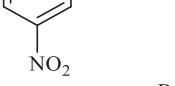
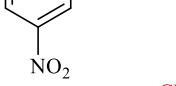
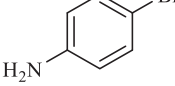
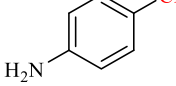
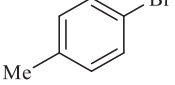
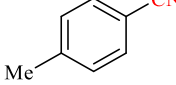
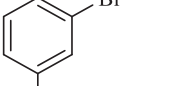
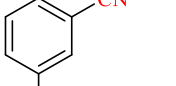
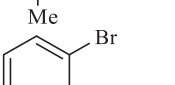
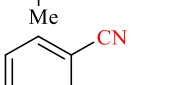
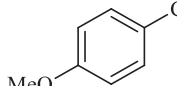
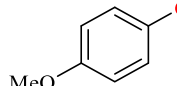
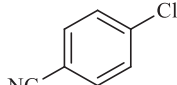
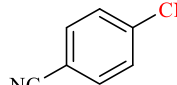
Entry	Aryl halide	Product	Yield (%)
1			95
2			97
3			89
4			94
5			92
6			88
7			92
8			98
9			96
10			93
11			85
12			90
13			88
14			86
15			83

Table 2 (continued)

Entry	Aryl halide	Product	Yield (%)
16			77
17			81

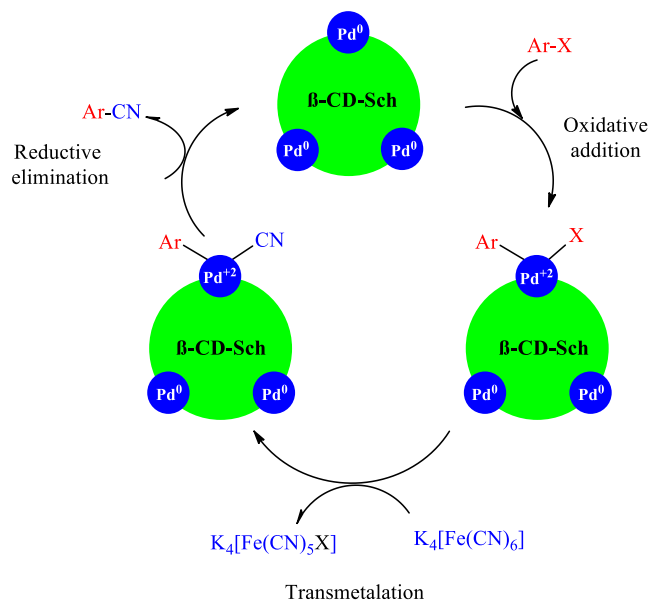
Reaction conditions: 1.5 mmol Ar-X, 0.2 mmol $K_4[Fe(CN)_6]$, 1.8 mmol Na_2CO_3 and 0.05 mol % Pd NPs@ β -CD-Sch, 6 mL of DMF, 120 °C and 4 h.

3.2. Catalytic performance of Pd NPs@ β -CD-Sch in the preparation of benzonitriles via cyanation reaction

Before investigation of the catalytic role of Pd NPs@ β -CD-Sch in the preparation of benzonitriles via cyanation of phenyl halides in the presence of $K_4[Fe(CN)_6]$, some reaction parameters were studied to find the optimal reaction conditions. Cyanation reaction of 1-iodo-3-nitrobenzene was chosen as the model reaction and the control experiments were then conducted. The results are presented in Table 1. Following the determination of the optimal values for the reaction parameters, the substrate scope of Pd NPs@ β -CD-Sch in the cyanation of structurally diverse aryl halides was studied (Table 2). Firstly, the catalytic prowess of Pd NPs@ β -CD-Sch was tested in the cyanation reaction of different aryl iodides, which afforded high reaction yields.

Table 3
Data for the cyanation reaction of *p*-iodotoluene by different catalysts.

Entry	Catalyst	Time (h)	Yield (%)	Ref
1	Pd/CuO NPs	15	89	[7]
2	Pd@CuFe ₂ O ₄	10	95	[27]
3	PS-Pd(II)-anthra	18	91	[28]
4	Pd/coral reef nanocomposite	2	88	[29]
5	Pd(TMHD) ₂	5	91	[30]
6	Pd NPs@ β -CD-Sch	4	94	Present study



Scheme 2. Possible mechanism for the cyanation of aryl halides using Pd NPs@ β -CD-Sch catalyst.

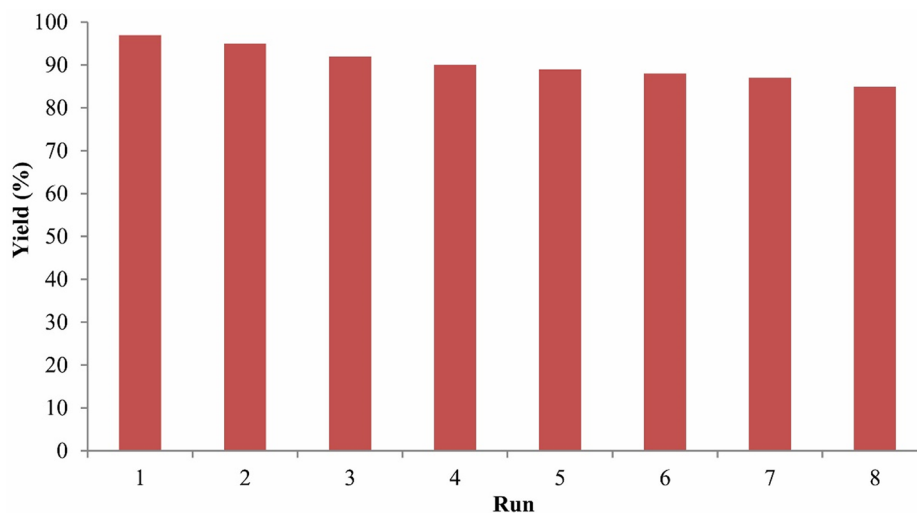


Fig. 8. Recycling experiments of the Pd NPs@ β -CD-Sch in the cyanation of 1-iodo-3-nitrobenzene.

For example, cyanation of 1-iodo-3-nitrobenzene yielded the desired nitrile with 97% yield. 4-Iodoanisole turned into 4-methoxy benzonitrile with 95% yield. Pd NPs@ β -CD-Sch was successfully used for the cyanation of *para*, *meta* and *ortho*-substituted iodotoluene with yields of 94, 92 and 88%, respectively. The catalytic performance of Pd NPs@ β -CD-Sch was also investigated in the conversion of various aryl bromides to the corresponding benzonitriles and the reactions were observed to proceed effectively. Cyanation of 1-bromo-4-nitrobenzene and 1-bromo-3-nitrobenzene gave 96 and 93% yields, respectively. Cyanation of 4-bromobenzonitrile was successful, giving a 98% yield. Additionally, it was found that Pd NPs@ β -CD-Sch was successfully catalyzed cyanation of aryl chlorides with good reaction yields (Table 2, entry 16–17). On the other hand, a model cyanation reaction was conducted without Pd NPs@ β -CD-Sch and no desired nitrile compound was obtained. This finding shows that Pd NPs@ β -CD-Sch plays an important role in cyanation reactions. Additionally, the catalytic ability of Pd NPs@ β -CD-Sch in the cyanation reaction of *para*-substituted iodotoluene was compared with those of the other reported catalysts and the results are displayed in Table 3. As clearly observed in Table 3, Pd NPs@ β -CD-Sch are superior with respect to the reaction time or reaction yield compared with other catalysts. Additionally, a possible mechanism for the Pd NPs@ β -CD-Sch catalyzed cyanation reaction is given in Scheme 2. As seen in Scheme 2, the reaction started with the oxidative addition of aryl halide over catalyst. Then, the reaction proceeds by transferring cyanide anion from $K_4[Fe(CN)_6]$. Finally, aryl cyanide product was produced with reductive removal step.

3.3. Reusability of Pd NPs@ β -CD-Sch

To check the recoverability/reusability of Pd NPs@ β -CD-Sch, the reaction of 1-iodo-3-nitrobenzene and $K_4[Fe(CN)_6]$ was studied. After each cyanation reaction, Pd NPs@ β -CD-Sch were separated from the reaction mixture via filtration, washed with EtOH and directly used in the next cyanation. This test revealed that Pd NPs@ β -CD-Sch is a long life catalyst, which gives 85% yield after eight cycles (Fig. 8). On the other hand, one of the most important problems in the catalytic reactions is metal leaching. Leaching test was carried out after the eighth recycling test and very low levels Pd leaching (0.2%) were recorded. This test showed that palladium leaching from β -CD-Sch is negligible during the cyanation reactions.

4. Conclusion

In conclusion, heterogeneous Pd NPs derived from β -cyclodextrin have been developed and their catalytic performance was checked in

the cyanation of phenyl iodides, bromides and chlorides. Catalytic results showed that Pd NPs@ β -CD-Sch provided good reaction yields in the synthesis of different benzonitriles by providing good functional tolerance against different substrates. Moreover, Pd NPs@ β -CD-Sch was found to be a recyclable catalyst, which can be used in eight consecutive cycles in the cyanation reactions. This study revealed that the developed Pd NPs@ β -CD-Sch were attractive/effective catalysts in the production of benzonitriles.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

We gratefully acknowledge Aksaray University and the University of Qom for the support of this work.

References

- [1] H. Zhao, X. Sun, D. Xu, Q. Zhu, Y. Zhu, Z. Dong, Fe-based N-doped dendritic catalysts for catalytic ammoxidation of aromatic aldehydes to aromatic nitriles, *J. Colloid Interface Sci.* 565 (2020) 177–185.
- [2] K. Uchida, H. Togo, Transformation of aromatic bromides into aromatic nitriles with *n*-BuLi, pivalonitrile, and iodine under metal cyanide-free conditions, *Tetrahedron* 75 (39) (2019) 130550.
- [3] G. Evano, A. Nitelet, P. Thilmann, D.F. Dewez, Metal-mediated halogen exchange in aryl and vinyl halides: A review, *Front. Chem.* 6 (2018) Article 114.
- [4] G. Yan, Y. Zhang, J. Wang, Recent advances in the synthesis of aryl nitrile compounds, *Adv. Synth. Catal.* 359 (23) (2017) 4068–4105.
- [5] M. Shee, S. Sheriff Shah, N.D. Pradeep Singh, Organophotoredox assisted cyanation of bromoarenes via silyl-radical-mediated bromine abstraction, *Chem. Commun.* 56 (2020) 4240–4243.
- [6] K.M. Marcantonio, L.F. Frey, Y. Liu, Y. Chen, J. Strine, B. Phenix, D.J. Wallace, C.-Y. Chen, An investigation into causes and effects of high cyanide levels in the palladium-catalyzed cyanation reaction, *Org. Lett.* 6 (2004) 3723–3725.
- [7] M. Nasrollahzadeh, Pd/CuO nanoparticles as a highly effective catalyst for the cyanation of aryl halides under ligand-free conditions, *Tetrahedron Lett.* 57 (2016) 337–339.
- [8] M. Nasrollahzadeh, S.M. Sajadi, Green, synthesis of Pd nanoparticles mediated by *Euphorbia thymifolia* L. leaf extract: Catalytic activity for cyanation of aryl iodides under ligand-free conditions, *J. Colloid Interface Sci.* 469 (2016) 191–195.
- [9] O.M. Nikitin, O.V. Polyakova, P.K. Sazonov, A.V. Yakimansky, M.Y. Goikhman, I.V. Podeshvo, T.V. Magdesieva, Polymer biquinolyl-containing complexes of Pd(II) as efficient catalysts for cyanation of aryl and vinyl halides with $K_4[Fe(CN)_6]$, *New J. Chem.* 40 (2016) 10465–10473.
- [10] T. Baran, Pd NPs@Fe₃O₄/chitosan/pumice hybrid beads: A highly active, magnetically retrievable, and reusable nanocatalyst for cyanation of aryl halides, *Carbohydr. Polym.* 237 (2020) 116105.

- [11] T. Baran, I. Sargin, Green synthesis of a palladium nanocatalyst anchored on magnetic lignin-chitosan beads for synthesis of biaryls and aryl halide cyanation, *Int. J. Biol. Macromol.* 155 (2020) 814–822.
- [12] S. Rostamnia, E. Doustkhah, B. Zeynizadeh, Cationic modification of SBA-15 pore walls for Pd supporting: Pd@SBA-15/ILDABCO as a catalyst for Suzuki coupling in water medium, *Micropor. Mesopor. Mater.* 222 (2016) 87–93.
- [13] S. Rostamnia, T. Rahmani, Ordered mesoporous SBA-15/PrSO₃Pd and SBA-15/PrSO₃PdNP as active, reusable and selective phosphine-free catalysts in C-X activation Heck coupling process, *Appl. Organomet. Chem.* 29 (7) (2015) 471–474.
- [14] S. Rostamnia, T. Rahmani, H. Xin, Pd(PrSO₃)₂@SBA-15 and Pd-NPs(PrSO₃)@SBA-15 hybrid materials: A highly active, reusable, and selective interface catalyst for C-X activations in air and water, *J. Ind. Eng. Chem.* 32 (2015) 218–224.
- [15] M. Heidarizadeh, E. Doustkhah, F. Saberi, S. Rostamnia, A. Hassankhani, P. Fathi Rezaei, Y. Ide, Silica nanostructures, a heterogeneous surface for dendrimer functionalization, *ChemistrySelect* 3 (25) (2018) 7137–7151.
- [16] S. Rostamnia, E. Doustkhah, Synthesis of water-dispersed magnetic nanoparticles (H₂O-DMNPs) of β -cyclodextrin modified Fe₃O₄ and its catalytic application in Kabachnik-Fields multicomponent reaction, *J. Magn. Magn. Mater.* 386 (2015) 111–116.
- [17] S. Rostamnia, E. Doustkhah, A. Hassankhani, Application of the β -cyclodextrin supramolecules as a green accelerator hosts in one-step preparation of highly functionalised rhodanine scaffolds, *Supramol. Chem.* 27 (1–2) (2015) 1–3.
- [18] X. Zhao, X. Liu, M. Lu, β -cyclodextrin-capped palladium nanoparticle-catalyzed ligand-free Suzuki and Heck couplings in low-melting β -cyclodextrin/NMU mixtures, *Appl. Organomet. Chem.* 28 (2014) 635–640.
- [19] T. Baran, N. Yilmaz Baran, A. Menteş, Highly active and recyclable heterogeneous palladium catalyst derived from guar gum for fabrication of biaryl compounds, *Int. J. Biol. Macromol.* 132 (2019) 1147–1154.
- [20] T. Baran, Highly recoverable, reusable, cost-effective, and Schiff base functionalized pectin supported Pd(II) catalyst for microwave-accelerated Suzuki cross-coupling reactions, *Int. J. Biol. Macromol.* 127 (2019) 232–239.
- [21] X. Wang, Z. Luo, Z. Xiao, Preparation, characterization, and thermal stability of β -cyclodextrin/soybean lecithin inclusion complex, *Carbohydr. Polym.* 101 (2014) 1027–1032.
- [22] N. Yilmaz Baran, T. Baran, A. Menteş, Fabrication and application of cellulose Schiff base supported Pd(II) catalyst for fast and simple synthesis of biaryls via Suzuki coupling reaction, *Appl. Catal. A* 531 (2017) 36–44.
- [23] T. Baran, N. Yilmaz Baran, A. Menteş, Sustainable chitosan/starch composite material for stabilization of palladium nanoparticles: synthesis, characterization and investigation of catalytic behaviour of Pd@chitosan/starch nanocomposite in Suzuki-Miyaura reaction, *Appl. Organomet. Chem.* 32 (2018) e4075.
- [24] T. Baran, I. Sargin, M. Kaya, A. Menteş, Green heterogeneous Pd(II) catalyst produced from chitosan-cellulose micro beads for green synthesis of biaryls, *Carbohydr. Polym.* 152 (2016) 181–188.
- [25] Y. Yao, X. Liu, T. Liu, J. Zhou, J. Zhu, G. Sun, D. He, Preparation of inclusion complex of perfluorocarbon compound with β -cyclodextrin for ultrasound contrast agent, *RSC Adv.* 5 (2015) 6305–6310.
- [26] M. Atarod, M. Nasrollahzadeh, S.M. Sajadi, Green synthesis of Pd/RGO/Fe₃O₄ nanocomposite using *Withania coagulans* leaf extract and its application as magnetically separable and reusable catalyst for the reduction of 4-nitrophenol, *J. Colloid Interface Sci.* 465 (2016) 249–258.
- [27] M. Gholinejad, A. Aminianfar, Palladium nanoparticles supported on magnetic copper ferrite nanoparticles: The synergistic effect of palladium and copper for cyanation of aryl halides with K₄[Fe(CN)₆], *J. Mol. Catal. A: Chem.* 397 (2015) 106–113.
- [28] M. Islam, P. Mondal, K. Tuhina, A.S. Roy, S. Mondal, D. Hossain, Highly efficient recyclable heterogeneous palladium catalyst for C-C coupling, amination and cyanation reactions, *J. Organomet. Chem.* 695 (2010) 2284–2295.
- [29] M. Nasrollahzadeh, F. Ghorbannezhad, S.M. Sajadi, R.S. Varma, Pd Nanocatalyst adorning coral reef nanocomposite for the synthesis of nitriles: Utility of *Cucurbita pepo* leaf extract as a stabilizing and reducing agent, *Nanomaterials* 9 (2019) 565.
- [30] N.S. Nandurkar, B.M. Bhanage, Palladium bis(2,2,6,6-tetramethyl-3,5-heptanedionate) catalyzed Suzuki, Heck, Sonogashira, and cyanation reactions, *Tetrahedron* 64 (2008) 3655–3660.