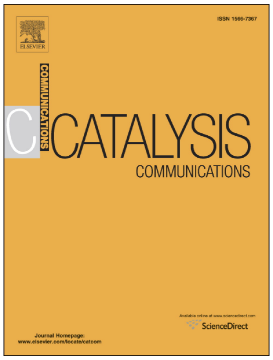

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Eco-friendly hydrogenation of aryl azides to primary amines on graphene oxide-decorated bimetallic Rh-Pt nanoparticles (RhPt@GO NPs)

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Abstract

Graphene oxide-supported rhodium/platinum (Rh-Pt) nanoparticles (Rh-Pt@GO NPs) are a promising catalyst for the reduction of aryl azides to primary amines. Rh-Pt@GO NPs have been produced by the microwave-assisted sonochemical method. This catalyst showed superior catalytic activity to afford quantitative yields of primary amines under an extremely mild condition in the presence of sodium borohydride. The synthesized novel catalyst was easily recovered by centrifugation and reused without loss of its catalytic activity. The spectroscopic analyses of the RhPt@GO NPs indicated the formation of highly crystalline, monodisperse, and colloidally stable RhPt@GO NPs.

Key words: RhPt@GO NPs, Heterogeneous catalyst, Hydrogenation, Sodium borohydride, Azides

1.Introduction

The chemistry of azides has attracted considerable interest from scientists because they are important key compounds for the production of biologically significant molecules such as nucleosides, carbohydrates, and heterocycles [1-4]. They are extensively used for the formation of peptides [5], imines [6], tetrazoles [7], triazoles [8], nitriles [9], and amines [10]. Numerous synthetic routes have been published in literature for the reduction of azides to amines, for example, $NiCl_2$-Zn [11], $FeCl_3$-Zn [12], $NaBH_4$/phase-transfer catalyst [13], Sm/I_2 [14], and tellurium metal [15]. However, these designed catalytic systems require harsh reaction conditions to employ hydrogenation of azides. During the years, scientific efforts have been undertaken on the use of heterogeneous catalysts for azide reduction process because they are accessible, reusable, and recyclable, and they are easily separable from the reaction medium [16-18]. Recently, the design of bimetallic nanocatalysts experience advanced interest for transfer hydrogenation reaction because of the cooperative interaction regarding better selectivity, activity, and stability [19-23].

In this paper, we report the production of highly efficient and monodisperse bimetallic RhPt@GO NPs for the reduction of aryl azides to primary amines for the first time. Sodium borohydride contributed to azide reduction as a potential hydrogen source in minimum amount of water. Various azide derivatives were easily converted to primary amines by an eco-friendly reaction condition where water is used as a green solvent.

2.Experimental

2.1 Catalyst Preparation

The previously published catalytic system was modified [24]. Briefly, 0.25 mmol $PtCl_4$, 0.25 mmol $RhCl_3$, and 0.25 mmol oleylamine (OA) were vigorously stirred in 25 mL of ethylene glycol (EG) solution, and the pH value of the mixture was set to 12.0 using NaOH–EG mixture. Then, the mixture was placed at the center of a microwave oven (1200 W) for consecutive heating time of 60 s. In this reaction, EG has been used for the reduction of $PtCl_4$ and $RhCl_3$. The observation of a brownish–black color indicates the formation of Rh-Pt nanoparticles. After reaction, filtration process was applied, and the crude product was washed with acetone and deionized water for several times. OA was used to stabilize metal nanoparticles against agglomeration. The prepared NPs were furnished in a 1:1 ratio with graphene oxide using an ultrasonic sonicator. Finally, the solid Rh-Pt@GO NPs were dried under vacuum at room temperature.

2.2 General procedure for the catalytic reduction of aromatic azido compounds

To a mixture of 1 ml of H_2O and 2 mg of catalyst was added 0.25 mmol of aromatic azido compound at room temperature. Next, 0.25 mmol of $NaBH_4$ was added to the reaction media, and the vessel was closed. The reaction then proceeded with unequivocal stirring and checked by TLC. Most of the reactions were completed within 3-60 min. After completion of the reaction, the catalyst was removed by centrifugation at 6000 rpm and washed several times with ethanol and water. At that point, the prepared catalyst was exposed to dry for further use. The solvent was removed under vacuum atmosphere.

3. Results and discussion

The as-synthesized RhPt@GO bimetallic nanoparticles were analyzed by XRD, TEM, HRTEM, and XPS techniques. Fig. 1 indicates the comparison of XRD patterns of the monometallic Pt@GO and the bimetallic RhPt@GO nanoparticles. Four diffraction peaks have been observed for the monometallic and bimetallic nanoparticles that are related to the face-centered cubic crystalline form and assigned to the (111), (200), (220), and (311) planes. For the monometallic Pt@GO and bimetallic RhPt@GO NPs, the shift in peak positions confirmed the alloy formation of Pt and Rh. Furthermore, the average crystalline size of RhPt@GO NPs was determined from the related XRD patterns using Scherrer equation, and it was determined to be approximately 3.64 ± 0.34 nm as a crystalline particle size [25-31].

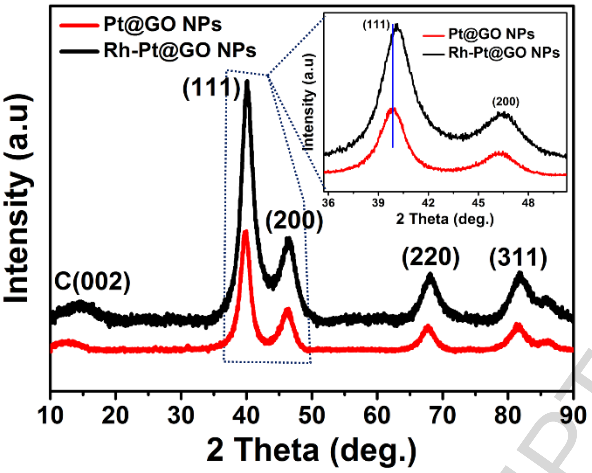


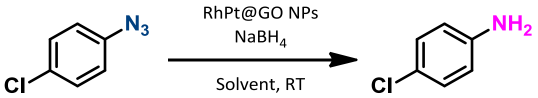
Fig. 1. XRD pattern of Rh-Pt@GO NPs

Particle size distribution has been analyzed by TEM and HR-TEM as illustrated in Fig. S4 (see ESI page S4). The TEM image of RhPt@GO indicates that fine particles are homogeneously distributed on graphene oxide. Moreover, HR-TEM measurement for monodisperse RhPt@GO has been utilized to analyze the atomic lattice fringes in Fig. S4a [32]. A particle size histogram was employed for a distribution test of 100 particles, and it was observed that the distribution is Gaussian, and the most reasonable size of the particles was approximately 4.12 ± 0.45 nm (Fig. S4c). Particle size identified by TEM results coordinates well with XRD results. Fig. S4b and d indicates the electron energy loss spectroscopy mapping image and line profile scanned on the arrow shown in HRTEM for platinum and rhodium elements of RhPt@GO NPs, and it is apparent that both rhodium and platinum exist as a whole region of the designed catalyst that verified the alloy formation of the nanocatalyst.

The Pt 4f and Rh 3d regions in XPS spectra of the RhPt@GO are illustrated in Fig. S4e-f. As shown in Fig. S4f, for the Rh-Pt@GO bimetallic nanoparticles, the Pt 4f spectrum appears as doublet that comprises a low-energy band (Pt $4f_{5/2}$) at 70.8 eV and a high-energy band (Pt $4f_{7/2}$) at 74.3 eV, and the Rh 3d spectrum appears as doublet that comprises a high-energy band (Rh $3d_{3/2}$) at 313.4 eV and a low-energy band (Rh $3d_{5/2}$) at 307.1 eV, thus demonstrating the existence of mainly metallic platinum and rhodium rather than oxygen-containing compounds. The peaks of Rh (III) at 309.3 eV, Pt (II) at around 72.3 eV, and Pt (IV) at around 74.1 eV in Fig. S4 (e) and (f) may be formed by the surface oxidation and/or chemisorption of atmospheric oxygen during the preparation process [25-33].

After completion of the catalyst system and characterization, the catalytic activity of RhPt@GO NPs for hydrogenation of aryl azides to primary amines was examined. As depicted in Table 1, optimization of the reduction reaction was attempted on the basis of the amount of catalyst/hydrogen source, solvent system, and time interval. The objective was to determine the conditions for the exact amine formation at room temperature. In literature, the yield of amine formation was successfully increased when tetrahydrofuran and methanol were utilized as the solvent system [34]. Our goal was also to accomplish the reduction of azides in a short time where water was only used as an eco-friendly solvent without any significant loss of yield. Finally, 2.0 mg of the catalyst and 1.0 mmol of hydrogen source demonstrated excellent performance for the conversion of azides into amines with only 1.0 ml of water (Table 1, entry 9).

Table 1 Optimization experiments for the reduction of 4-chloro azidobenzene to 4-chloro aniline[a]



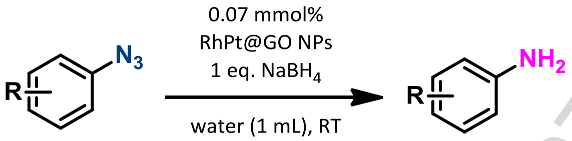
Entry	**Solvent**	**Catalyst** ***(mg)***	**NaBH$_4$** ***(eq.)***	**Time** ***(min)***	**Yield^b** ***(%)***
1	EtOH	4	3	90	15
2	CH_2Cl_2	4	3	300	No reaction
3	MeOH	4	3	40	95
4	MeOH/H_2O (1:1)	4	3	10	>99
5	H_2O	4	3	6	>99
6	H_2O	2	3	6	>99
7	H_2O	1	3	50	>99
8	H_2O	2	2	7	>99
9	**H_2O**	**2**	**1**	**8**	**>99**
10	H_2O	-	1	360	trace

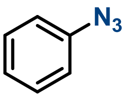
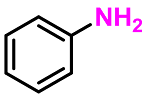
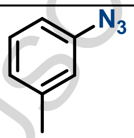
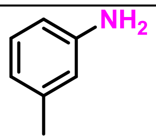
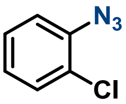
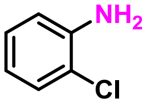
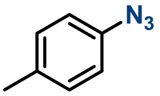
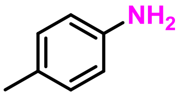
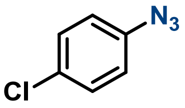
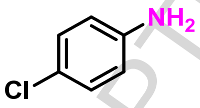
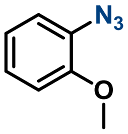
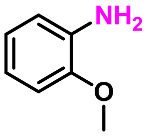
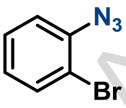
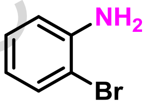
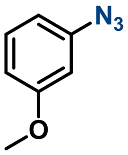
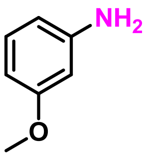
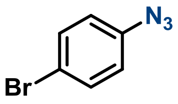
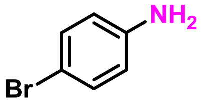
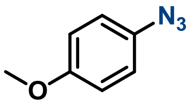
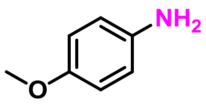
[a] Reaction conditions: 4-chloro azidobenzene (0.25 mmol), RhPt@GO NPs (10.8 wt% metal content), and room temperature. [b]GC yield.

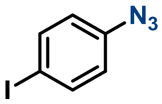
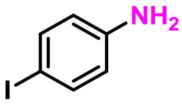
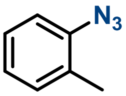
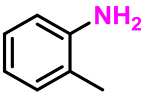
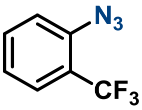
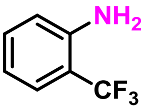
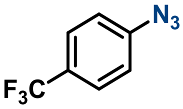
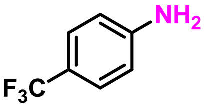
Table 2 indicates that all of azido benzenes were successfully reduced to primary amines in the presence of RhPt@GO NPs through hydrolysis of sodium borohydride. The aniline derivatives were quantitatively obtained within 3-60 min at room temperature with a minimum amount of solvent. Azidobenzene (1), 1-azido-2-chlorobenzene (3), 1-azido-4-chlorobenzene (5), 1-azido-2-bromobenzene (7), and 1-azido-4-bromobenzene (9) were successfully reduced to aniline (2), 2-chloroaniline (4), 4-chloroaniline (6), 2-bromoaniline (8), and 4-bromoaniline (10) with the yields higher than 99% within 8 min (Table 2, entries 1-5, respectively). Surprisingly, 1-azido-4-iodobenzene (11) was barely converted to 4-iodoaniline (12) after 1 h (Table 2, entry 6). ^{1}H NMR spectrum of 4-iodoaniline compound indicates the formation of side product (10%), which confirms the reduction of both iodine and azido groups. The plausible reason is a competitive reaction between dehalogenation of iodine and reduction of the azide group. As reported before, C-I bond strength is not quite strong, and it can be easily broken to afford dehalogenated product in the presence of a heterogeneous catalyst. For example, dehalogenation of iodobenzene was carried out in methanol after 1.5 h in the presence of excess ammonia borane (NH_3BH_3) and RuPd@GO NPs [35]. To approve the reasonable effect, the reaction was continued for 4 h with excess amount of hydrogen source (1 mmol $NaBH_4$). GC analyses confirmed the other side product formed by both iodine and azido group reduction. *o*-, *m*-, and *p*-Azido toluene compounds (13, 15, 17) were reduced faster than halogenated aromatic azido compounds because of the electron-donating methyl groups. The corresponding compounds were converted to aniline derivatives (14, 16, 18) with high reaction efficiency and quantitative yield (Table 2, entries 7-9). Similar results were observed for the reduction of *o*-, *m*-, and *p*-azido anisole compounds (19, 21, 23). They were easily reduced to primary amines with high yields in short time (Table 2, entries 10-12) because of the electron-releasing ability of the methoxy group. 1-Azido-2-(trifluoromethyl)benzene (25) and 1-azido-4-(trifluoromethyl)benzene (27) were also converted to 2-(trifluoromethyl)aniline (26) and 4-(trifluoro methyl)aniline (28) with high yields (Table 2, entries 13, 14). However, the completion of the reduction process was observed as longer time than expected. The possible reason is not only the electron-withdrawing effect and repulsion by the negatively charged fluorines with the surface but also the steric hindrance of the trifluoromethyl group.

Recently, bimetallic nanocatalysts have been preferred more than monometallic nanocatalysts because of the diverse electronic structure, cooperative effect, and new catalytic sites [19-23]. In the light of literature data and our previous studies, we compared the activity of bimetallic and monometallic catalytic systems for the reduction of azides. As illustrated in Table 3, the reduction process was completed in a shorter time with high yield, while RhPt@GO NPs were used as the catalyst under the same conditions.

Table 2 RhPt@GO NP-assisted hydrogenation of various R-N_3 compounds[a]



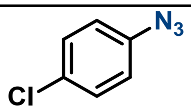
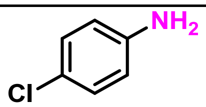
Entry	Azide	Amine	Yield[b] (%)	Time (min)	Entry	Azide	Amine	Yield[b] (%)	Time (min
1	 **1**	 **2**	>99	8	8	 **15**	 **16**	>99	6
2	 **3**	 **4**	>99	8	9	 **17**	 **18**	>99	5
3	 **5**	 **6**	>99	8	10	 **19**	 **20**	>99	3
4	 **7**	 **8**	>99	8	11	 **21**	 **22**	>99	4
5	 **9**	 **10**	>99	8	12	 **23**	 **24**	>99	3

6	 **11**	 **12**	**90**	**60**
7	 **13**	 **14**	**>99**	**5**
13	 **25**	 **26**	**>99**	**40**
14	 **27**	 **28**	**>99**	**25**

[a] Reaction conditions: azide (0.25 mmol), $NaBH_4$ (0.25 mmol), and catalyst (2 mg, 10.8 wt% metal content) were used in 1 ml of water at room temperature. [b]GC yield.

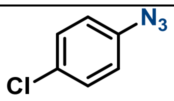
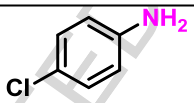
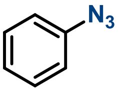
Table 3 Comparison test of monometallic and bimetallic systems for the reduction of 4-chloro azidobenzene to 4-chloro aniline[a]

Entry	**Substrate**	**Product**	**RhPt@GO**		**Pt@GO**	
			Time (*min*)	**Yield (%)**	**Time (*min*)**	**Yield (%)**

1	 **5**	 **6**	**8**	**>99**	**20**	**90**

[a] Reaction conditions: 0.25 mmol substrate, 0.25 mmol $NaBH_4$, 0.07 mmol % catalyst, 1.0 mL of water at room temperature.

Table 4 Reusability test of RhPt@GO NPs[a]

Entry	**Substrate**	**Product**	**1st**		**5th**	
			Yield[b] (%)	**Time (min)**	**Yield[b] (%)**	**Time (min)**
1			**>99**	**8**	**97**	**13**
2			**>99**	**8**	**98**	**12**

[a] Reaction conditions: substrate (0.25 mmol), $NaBH_4$ (0.25 mmol), RhPt@GO NPs (2 mg, 10.8 wt% metal content). [b] GC yield.

The reusability test of the RhPt@GO NPs was attempted. The catalyst was used five times and was able to be reused without loss of activity as illustrated in Table 4. There was no significant loss of rhodium and platinum (0.2 and 0.7 ppm leaching to a solution, respectively) after five cycles of reusability experiment analyzed by ICP-OES. The designed catalyst maintained high activity with only a slight increase in reaction time.

4. Conclusion

In this paper, a novel, eco-friendly, and recoverable synthetic process has been described for the reduction of aryl azides by the assistance of highly monodisperse RhPt@GO NPs. This catalytic system exhibited better catalytic activity than that reported in previously published articles (see ESI Table S1, page S7) for the reduction of corresponding aryl azides because of low particle size, high chemical surface area (67.58 m^2/g), and % metal (0) contents of the catalytic system. It is concluded that it will gain a new perspective in literature in both areas of application of heterogeneous catalysts and reduction of aryl azides.

Acknowledgments

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Appendix A. Supplementary data

Supplementary material (full experimental protocols, equipment, characterization of GO, EDX/SEM images, NMR spectra, and spectral data for the primary amines) is available in the online version of this article at http://

References

[1] S. C. Smith, C. H. A. Heathcock, Convenient procedure for the synthesis of bis-steroidal pyrazines: models for the cephalostatins. J. Org. Chem. 57 (1992) 6379-6380.

[2] F. E. McDonald, S. J. Danishefsky, A stereoselective route from glycols to asparagine-linked N-protected glycopeptides. J. Org. Chem. 57 (1992) 7001-7002.

[3] A. Kamal, K. V. Ramana, H. B. Ankati, A. V. Ramana, Mild and efficient reduction of azides to amines: synthesis of fused [2,1-b] quinazolinones. Tetrahedron Lett. 43 (2002) 6861-6863.

[4] H. Goksu, Recyclable aluminium oxy-hydroxide supported Pd nanoparticles for selective hydrogenation of nitro compounds via sodium borohydride hydrolysis. New J. Chem. 39 (2015) 8498-8504.

[5] B. L. Nilson, L. L. Kiessling, R. T. Raines, Staudinger ligation: A peptide from a thioester and azide. Org. Lett. 2 (2000) 1939-1941.

[6] F. Palacios, A. M. O. Retana, E. M. Marigorta, J. Pagalday, Aza-Wittig reaction of n-phosphorylalkyl phosphazenes with carbonyl compounds and phenylisocyanate. Synthesis of 4-amino-3- phosphoryl-2-azadienes and pyrazine-phosphonates. Tetrahedron 59 (2003) 2617-2623.

[7] P. Z. Demko, K. B. Sharpless, An intramolecular [2+3] cycloaddition route to fused 5-heterosubstituted tetrazoles. Org. Lett. 3 (2001) 4091-4094.

[8] S. Kamijo, T. Jin, Z. Huo, Y. Yamamoto, Synthesis of triazoles from nonactivated terminal alkynes via the three-component coupling reaction using a Pd(0)−Cu(I) bimetallic catalyst. J. Am. Chem. Soc. 125 (2003) 7786-7787.

[9] R. Sasson, S. Rozen, From Azides to Nitriles. A Novel Fast Transformation Made Possible by BrF3. Org.Lett. 7 (2007) 2177-2179.

[10] B. Kilbas, Y. E. Yilmaz and S. Ergen, A practical and highly efficient transfer hydrogenation of aryl azides using a [Ru(p-cymene)Cl_2]$_2$ catalyst and sodium borohydride. C. R. Chimie. 21 (2018) 880-883.

[11] B. Anima, B. Mukulesh, P. Dipak, S. S. Jagir, The efficient chemoselective reduction of azides to primary amines. Synlett (11) 1997 1253-1254.

[12] P. Diganta, L. Dhrubojyoti, D. Prapajati, S. Jagir, A novel and chemoselective protocol for the reduction of azides using FeCl3-Zn system. Chem Lett. 7 (2000) 816-817.

[13] F. Rolla, Sodium Borohydride reactions under phase-transfer conditions: Reduction of azides to amines. J. Org. Chem. 47 (1982) 4327-4329.

[14] H. You, Z. Yongmin, W. Yulu, Facile reduction of azides to the corresponding amines with metallic samarium and catalytic amount of iodine. Tetrahedron Lett. 38 (1997) 1065-1066.

[15] W. Lei, L. Pinhua, C. Jianhui, Y. Jincan, A novel reduction of azides to amines with tellurium metal in near-critical water. Phosphorus, Sulfur and Silicon 178 (2003) 1807-1813.

[16] P. Sreenivasarao, S. Subham, C. Ajay, P. Bibudha, D. Jyotirmayee, Reduction of organic azides to amines using reusable Fe_3O_4 nanoparticles in aqueous medium. Catal. Sci. Technol. 3 (2013) 584-588.

[17] B. Abhijit, P. Subir, B. Arindam, Carbon nanodots, Ru nanodots and hybrid nanodots: preparation and catalytic properties. J. Mater. Chem. A. 3 (2015) 15074-15081.

[18] V. Udumula, S. H. Nazari, S. R. Burt, M. N. Alfindee, D. J. Michaelis, Chemo- and site-selective alkyl and aryl azide reductions with heterogeneous nanoparticle catalysts. ACS Catal. 6 (2016) 4423-4427.

[19] F. Tao, M. E. Grass, Y. Zhang, D. R. Butcher, F. Aksoy, S. Aloni, V. Altoe, S. Alayoglu, J. R. Renzas, C. –K. Tsung, Z. Zhu, Z. Liu, M. Salmeron, G. A. Somorjai, Evolution of structure and chemistry of bimetallic nanoparticle catalysts under reaction conditions. J. Am. Chem. Soc. 132 (2010) 8697-8703.

[20] M. Sankar, N. Dimitratos, P. J. Miedziak, P. P. Wells, C. J. Kiely, G. J. Hutchings, Designing bimetallic catalysts for a green and sustainable future. Chem. Soc. Rev. 41 (2012) 8099-8139.

[21] Y. Nangia, B. Kumar, J. Kaushal, C. R. Suri, Palladium@gold bimetallic nanostructures as peroxidase mimic for development of sensitive fluoroimmunoassay. Anal. Chim. Acta 751 (2012) 140-145.

[22] Z. Wei, J. Sun, Y. Li, A. K. Datye, Y. Wang, Bimetallic catalysts for hydrogen generation. Chem. Soc. Rev. 41 (2012) 7994-8008.

[23] J. Xiang, P. Li, H. Chong, L. Feng, F. Fu, Z. Wang, S. Zhang, M. Zhu, Bimetallic Pd-Ni core-shell nanoparticles as effective catalysts for Suzuki reaction. Nano Res. 7 (2014) 1337-1343.

[24] Y. Yildiz, T. O. Okyay, B. Sen, B. Gezer, S. Kuzu, A. Savk, E. Demir, Z. Dasdelen, H. Sert, F. Sen, Highly monodisperse Pt/Rh Nanoparticles confined in the graphene oxide for highly and reusable sorbents for methylene blue removal from aqueous solutions. Chemistryselect. 2 (2017) 697–701.

[25] E. Erken, Y. Yildiz, B. Kilbas, F. Sen, Synthesis and characterization of nearly monodisperse Pt nanoparticles for C1 to C3 alcohol oxidation and dehydrogenetaion of dimethylamine-borane (DMAB). J. Nanosci. Nanotechnol. 16 (2016) 1685-1692.

[26] B. Çelik, E. Erken, S. Eris, Y. Yıldız, B. Sahin, H. Pamuk, F. Sen, Highly monodisperse Pt(0)@AS NPs as highly efficient and reusable catalyst: the effect of the surfactant on their catalytic activities in room temperature dehydrocoupling of DMAB. Catal. Sci. Technol. 6 (2016) 1685-1692.

[27] H. Goksu, Y. Yıldız, B. Çelik, M. Yazıcı, B. Kilbas, F. Sen, Eco-friendly hydrogenation of aromatic aldehyde compounds by tandem dehydrogenation of dimethylamine-borane in the presence of reduced graphene oxide furnished platinum nanocatalyst. Catal. Sci. Technol. 6 (2016) 2318-2324.

[28] Y. Yıldız, E. Erken, H. Pamuk, H. Sert, F. Sen, Monodisperse Pt nanoparticles assembled on reduced graphene oxide: highly efficient and reusable catalyst for methanol oxidation and

dehydrocoupling of dimethylamine-borane (DMAB). J. Nanosci. Nanotechnol. 16 (2016) 5951-5958.

[29] E. Erken, İ. Esirden, M. Kaya, F. Sen, Monodisperse Pt NPs@rGO highly efficient and reusable heterogeneous catalyst for the synthesis of 5-substituted 1H-tetrazole derivatives. Catal. Sci. Technol. 5 (2015) 4452.

[30] E. Erken, İ. Esirden, M. Kaya, F. Sen, A rapid and novel method for the synthesis of 5-substituted 1H-tetrazole catalysed by exceptional reusable monodisperse Pt NPs@AC under the Microwave Irradition. RSC Adv. 5 (2015) 68558-68564.

[31] Y. Yıldız, İ. Esirden, E. Erken, E. Demir, M. Kaya, F. Sen, Microwave (Mw)-assisted synthesis of 5-substituted 1H-tetrazoles via [3+2] cycloaddition catalysed by Mw-Pd/Co nanoparticles decorated on multi-walled carbon nanotubes. Chemistry Select, 1 (2016) 1695-1701.

[32] B. Çelik, S. Kuzu, E. Erken, H. Sert, Y. Koskun, F. Sen, Nearly Monodisperse carbon nanotube furnished nanocatalysts as highly efficient and reusable catalyst for dehydrocoupling of DMAB and C1 to C3 alcohol oxidation. Int. J. Hydrog. Energy 41 (2016) 3093-3101.

[33] B. Aday, H. Pamuk, M. Kaya, F. Sen, Graphene oxide as highly effective and readily recyclable catalyst using for the one-pot synthesis of 1,8-dioxacridine derivatives. J. Nanosci. Nanotechnology, 16 (2016) 6498-6504.

[34] K. Soai, S. Yokoyama, A. Ookawa, Reduction of azides to amines with sodium borohydride in tetrahydrofuran with dropwise addition of methanol. Synthesis 1 (1987) 48-49.

[35] H. Goksu, Y. Yıldız, B. Çelik, M. Yazici, B. Kilbas, F. Sen, Highly efficient and monodisperse graphene oxide furnished Ru/Pd nanoparticles for the dehalogenation of aryl halides via ammonia borane. Chemistryselect 5 (2016) 953-958.

Highlights

- RhPt@GO NPs catalyzed hydrogenation of aryl azides has been well established.
- RhPt@GO NPs are recoverable, reusable and stable.
- Water was only used as an eco-friendly solvent.
- Reducing reagent ($NaBH_4$) is stable, cheap and water-soluble.
- The novel process is safe, practical and economic.