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Catalytic application of 1,3,5-triazine-pentaethylenehexamine polymer-supported palladium nanoparticles in the convenient reduction of nitroarenes with sodium borohydride or hydrazine

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Abstract: The catalytic activity of 1,3,5-triazine-pentaethylenehexamine (TAPEHA) polymer-supported Pd nanoparticles was investigated in the reduction of nitro arenes to the corresponding amines by $NaBH_4$ or $N_2H_4.H_2O$. Optimized reaction conditions for both systems were successfully tested on 20 nitroarenes with different characteristics. Considerably high yields (80%–98% in $NaBH_4$ and 85%–98% in N_2H_4) were obtained in a short time and at ambient temperature. In addition to these methods being selective against other reducible functionalities such as –CN, –Br, –Cl, and –I, the catalyst can be recovered easily and reused more than ten times.

Key words: Heterogeneous catalysis, nitro reduction, Pd nanoparticles, reusable catalyst

1. Introduction

Primary amine compounds are important frameworks due to their excess properties that they present as initial reactive or intermediates in some industrial branches like pigments, agrochemicals, pharmaceuticals, and polymers.[1] Hence, there are a wide variety of methods to obtain amine compounds in the literature.[2] One of the most preferred methods among them is the reduction of nitro groups to the corresponding amines.[3] However, current methods suffer from some drawbacks;[4] many of them require high temperature/pressure, long reaction time, and carcinogenic solvents; are toxic, expensive, and unstable with no reusable catalyst; and provide low yields.[5] In order to overcome these problems, researchers try to develop more economical, easily available, and environmentally friendly methods for the synthesis of primary amines with high yield and minimum waste products.[6,7] One of the most popular methods in the last decades is the reduction of nitro groups by using the combinations of a hydrogen source such as $NaBH_4$ and N_2H_4 with transition metals. Since the 1960s many catalysts working very quickly and at high efficiency under moderate conditions have been developed and considered practical in the reduction of nitro compounds.[8] Today, transition metal-containing catalysts with a hydrogen source are under development.[9,10] However, many disadvantages such as high catalytic loading, inability to reuse the catalyst, and high costs remain.[11] Thus, developing environmentally friendly alternatives is of great importance.

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Metallic nanoparticles that are used as heterogeneous catalysts offer particular advantages in terms of selectivity, activity, stability, and energy efficiency.[12] In spite of the fact that palladium-based catalysts have a wide range of applications in both synthetic and industrial chemistry,[13] the development of nanoscale palladium particles and widespread applications in organic synthesis were carried out only during the last few decades.[14] On the one hand, homogeneous palladium catalysts are generally preferred due to their high activity, but recovery and reuse of the catalyst are impossible in this case.[15] Furthermore, when it is considered palladium is a precious metal and thus currently used palladium catalysts are really expensive and also sensitive to the air,[16] it is clear that stable and easily reusable palladium catalysts are urgently needed for sustainable chemistry.[17] In recent years, lots of studies were carried out for this purpose.[18] To be able to produce heterogeneous palladium catalysts, a large number of solid materials (such as carbon structures,[19] polymers,[20] and mesoporous silica[21]), micelles, microemulsions, surfactants, and ionic liquids (ILs) have been utilized as supports for palladium.[22] Nevertheless, the number of reusable palladium catalysts capable of reducing by green solvent at room temperature is still limited.

In our previous works, we carried out hydrogenation of alkenes,[23] hydrogenation of vegetable oils,[24] and nitro reduction[25] with an automobile catalytic convertor. Here, palladium loaded 1,3,5-triazine-pentaethylenehexamine (TAPEHA) polymer nanoparticle as a novel heterogeneous catalyst was used for reduction of aromatic nitro compounds (Figure 1).

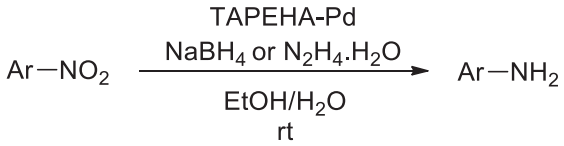


Figure 1. Reduction of aromatic nitro compounds with TAPEHA-Pd and $NaBH_4$ or $N_2H_4.H_2O$.

2. Results and discussion

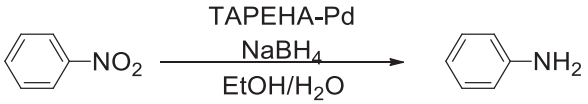
The support material used in Pd-based catalysts should undoubtedly have a high palladium-adsorption capacity, stability, and low resolution. TAPEHA demonstrated a good affinity toward palladium by virtue of having a high density of amine and triazine functional groups. The Pd-adsorption capacity of this polymer was found to be 4.18 mmol/g Pd(II) (444 mg/g) by column technique and this is one of the highest values in the literature.[26,27] TAPEHA-Pd is also stable and has very low solubility in water and many organic solvents.

It is known that Pd(II) is reduced to Pd(0) in the presence of a hydride source like $NaBH_4$ or N_2H_4.[28–30] For this reason, Pd(II)-trapped TAPEHA has been reduced to Pd(0) state during the reduction experiment. It can be clearly observed with color change in the polymer from yellow to black[31] during the first second of adding $NaBH_4$ or $N_2H_4.H_2O$. As expected, nitro reduction has been carried out with Pd(0) catalyst in our experiments. Thus, when recycled TAPEHA-PdNPs containing Pd(0) form are used in the next reaction, the catalyst shows the same catalytic activity. TAPEHA-PdNPs can be recovered by filtration and used again in another reduction reaction. It was reused ten times without any loss of activity. The amount of catalyst is taken as 0.015 g for the reduction of 1 mmol nitro compound.

2.1. Optimum reaction conditions in $NaBH_4$ mediated reductions

To determine the optimum reaction conditions in $NaBH_4$-mediated reductions, a series of experiments were performed based on nitrobenzene (Table 1).

Table 1. Reduction of nitrobenzene in the presence of $NaBH_4$ under different reaction conditions[a].



Entry	$NaBH_4$ (mmol)	EtOH/H_2O (mL)	Time[b]	Converted (%)
1	5.0	10/10	1.5 h	> 99
2	4.0	10/10	1 h	53
3	4.0	10/10	1.5 h	> 99
4	4.0	10/20	1.5 h	> 99
5	4.0	0/20	24 h	> 99
6	3.0	10/20	1.5 h	41
7	3.0	10/20	3 h	76
8	3.0	10/20	6 h	> 99
9	3.0	10/20	24 h	> 99

[a]Reaction conditions: 1 mmol nitrobenzene, 0.015 g TAPEHA-Pd or TAPEHA-PdNPs, rt.
[b]The reaction time was determined by TLC analysis.

Different ratios of EtOH/water were examined to find the best solvent mixture for the reduction. When only water was used as the solvent, the reaction conversion was completed within 24 h. However, this method was only applicable for liquid nitro compounds that are mixable in water such as nitrobenzene and 2-nitroanisole and it is not suitable for solid nitroarenes. Using only an adequate amount of EtOH to solve compounds shortened the reaction time. On the other hand, the excess of EtOH was not effective on the conversion ratio. When 3 molar equivalents of $NaBH_4$ were used the reaction was completed within 6 h. However, with 4 molar equivalents of $NaBH_4$, the conversion can be completed within 1.5 h. Consequently, the optimum reaction conditions for the reduction of nitrobenzene to aniline in $NaBH_4$-mediated reductions were 4 mmol of $NaBH_4$ and 0.015 g of TAPEHA-PdNPs for a period of 1.5 h in 20 mL of a 1:1 mixture of EtOH/water.

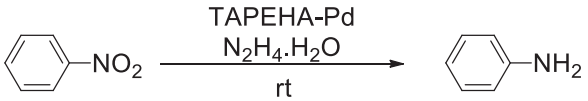
2.2. Optimum reaction conditions in N_2H_4 mediated reductions

N_2H_4-mediated reductions were also investigated to optimize the reaction conditions (Table 2). Effects of different amounts of $N_2H_4.H_2O$ in different solvent media like EtOH, EtOH/water mixture, tetrahydrofuran, or diethyl ether were examined. When EtOH was used as the solvent, conversions were completed with 4 molar equivalents of $N_2H_4.H_2O$ in 20 min, 3 molar equivalents of $N_2H_4.H_2O$ in 1 h, and 2 molar equivalents of $N_2H_4.H_2O$ in 3 h. Using 5 or more molar equivalents of $N_2H_4.H_2O$ did not accelerate the reduction (20 min) and 49% conversion ratio was detected with 1 molar equivalent of $N_2H_4.H_2O$ in 3 h.

When THF was used, the reaction was completed in 45 min with 4 molar equivalents of $N_2H_4.H_2O$ and 30 min with 5 molar equivalents of $N_2H_4.H_2O$. On the other hand, 8 molar equivalents of N_2H_4 and diethyl ether gave 75% yield in 30 min and 10 molar equivalents of $N_2H_4.H_2O$ and diethyl ether gave quantitative yield in 1 h. Hereby, the best reaction conditions for the reduction of nitrobenzene to aniline in $N_2H_4.H_2O$ mediated reductions were 4 mmol of $N_2H_4.H_2O$ and 0.015 g of TAPEHA-PdNPs for a period of 20 min in 20 mL of EtOH or a 1:1 mixture of EtOH/water.

As shown in Table 3, optimized conditions were examined with 20 other aromatic nitro compounds with both systems to make comparisons and determine the applicability of these methods. Isolated yields were found to vary between 80% and 98% with $NaBH_4$ and 85% and 98% with $N_2H_4.H_2O$. The highest yield of

Table 2. Reduction of nitrobenzene in the presence of $N_2H_4.H_2O$ under different reaction conditions[a].



Entry	$N_2H_4.H_2O$ (mmol)	Solvent(s)	Time[b]	Converted (%)
	1.0	EtOH	3 h	49
	2.0	EtOH	3 h	99
	3.0	EtOH	1 h	99
	4.0	EtOH	20 min	> 99
	5.0	EtOH	20 min	> 99
	7.0	EtOH	20 min	> 99
	4.0	EtOH/H_2O	20 min	> 99
	4.0	THF	45 min	> 99
	5.0	THF	30 min	> 99
	4.0	Et_2O	30 min	75
	5.0	Et_2O	1 h	> 99

[a]Reaction conditions: 1 mmol nitrobenzene, 0.015 g TAPEHA-Pd or TAPEHA-PdNPs, rt.
[b]The reaction time was determined by TLC analysis.

98% was obtained by reducing of 2-chloro-6-nitropyridine with $NaBH_4$ (entry 17) and 4-nitrobenzonitrile and 6-chloro-3-nitropyridin-2-amine (entries 16 and 18) with $N_2H_4.H_2O$, while relatively low yields were obtained by reducing of 4-nitrophenol (entry 6) with $NaBH_4$ (80%) and 2-nitroaniline (entry 7) with $N_2H_4.H_2O$ (85%).

It is understood that nitroarenes with an electron-withdrawing group were reduced in higher yields than for those containing an electron-donating group. At the same time, the presence of a group such as hydroxyl or amine caused a lower yield because of slight dissolution of nitroarenes in water during the extraction process.

2.3. Pd leaching from TAPEHA after use as a catalyst

The Pd content of the TAPEHA before and after use was determined in order to investigate the leaching of palladium from TAPEHA after use in the reduction reactions. The same level of Pd was found in the used and nonused TAPEHA polymer. In summary Pd was not leached from TAPEHA and our process presents a leach-free heterogeneous Pd system.

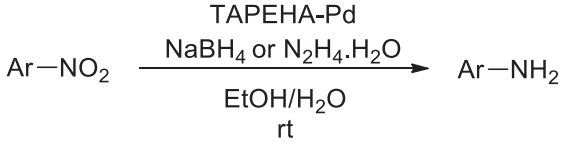
3. Conclusion

The results mentioned above demonstrate that aromatic nitro compounds are able to be reduced to corresponding amine compounds by TAPEHA-PdNPs with a hydrogen source like $NaBH_4$ or N_2H_4 in high yields within a short time and in mild conditions. Pd metal compounds that are normally air sensitive were made stable by TAPEHA support polymer and additionally TAPEHA-PdNPs catalyst did not lose the property with reuse and Pd was not leached. This system exhibited a selective catalyzed reduction with $NaBH_4$ or N_2H_4 in compounds containing other reducible functionalities such as –CN, –Cl, –Br, and –I. Green solvents like EtOH and water were used and nontoxic matters $NaBO_2$ and N_2 were obtained as byproducts. Consequently, selective, effective, easy to use, environmentally friendly, and new catalyst systems have been developed.

4. Experimental

All the chemical substances used for reduction reactions were provided commercially (Merck, Sigma-Aldrich, and Fluka).

Table 3. Catalytic reduction of various nitroarenes using TAPEHA-Pd NPs.[a,b]



Entry	Reactant	Product	Yield[c] (%)	Yield[d] (%)
	nitrobenzene	Aniline[9]	92	94
	4-nitrotoluene	4-toluidine[9]	90	93
	4-nitroanisole	4-methoxyaniline[9]	86	90
	2-nitroanisole	2-methoxyaniline[9]	88	87
	3-nitrophenol	3-aminophenol[9]	81	88
	4-nitrophenol	4-aminophenol[9]	80	86
	2-nitroaniline	2-phenylenediamine[9]	84	85
	4-nitroaniline	4-phenylenediamine[9]	85	87
	3-nitroaniline	3-phenylenediamine[9]	81	88
	1,3-dinitrobenzene	3-phenylenediamine[9]	83	88
	1-bromo-3-nitrobenzene	3-bromoaniline[32]	92	90
	1-iodo-3-nitrobenzene	3-iodoaniline[33]	93	90
	4-methoxy-2-nitrophenol	2-amino-4-methoxyphenol[34]	84	89
	2-nitrobenzonitrile	2-aminobenzonitrile[9]	93	96
	3-nitrobenzonitrile	3-aminobenzonitrile[35]	93	96
	4-nitrobenzonitrile	4-aminobenzonitrile[36]	96	98
	2-chloro-6-nitropyridine	6-chloropyridin-2-amine[37]	98	97
	6-chloro-5-nitropyridin-2-amine	6-chloropyridine-2,5-diamine[38]	91	98
	5-nitroisoquinoline	5-aminoisoquinoline[39]	93	95
	2-nitro-9*h*-fluorene	9*h*-fluoren-2-amine[9]	96	94

[a]Reaction conditions: 1 mmol nitroarene, 0.015 g TAPEHA-Pd or TAPEHA-Pd NPs, 4 mmol $NaBH_4$, 20 mL $EtOH/H_2O$ (1:1), at room temperature or 1 mmol nitroarene, 0.015 g TAPEHA-Pd or TAPEHA-Pd NPs, 4 mmol $N_2H_4.H_2O$, 20 mL EtOH, at room temperature.
[b]All products were characterized by ^1H NMR and ^{13}C NMR spectra and compared with authentic samples.
[c]Isolated yield for $NaBH_4$
[d]Isolated yield for $N_2H_4.H_2O$

4.1. Synthesis of 1,3,5-triazine-pentaethylenehexamine (TAPEHA) polymer

TAPEHA polymer was synthesized according to our earlier publication.[26] In a three-necked round-bottom flask, K_2CO_3 (10 g, 72.36 mmol) was added to a solution of pentaethylenehexamine (35 g, 150.62 mmol) in THF (50 mL) and the mixture was cooled with an ice bath. Cyanuric chloride (7.5 g, 40.76 mmol) and pentaethylenehexamine (35 g, 150.62 mmol) in THF (50 mL) were slowly added from two separate dropping funnels in two idle necks, while the mixture was constantly stirred. After being stirred for 24 h in an ice bath, the THF was evaporated and the obtained cream color product was washed with deionized water and acetone three times, consecutively, and then dried in a vacuum oven for 24 h at 60 °C (Figure 2).

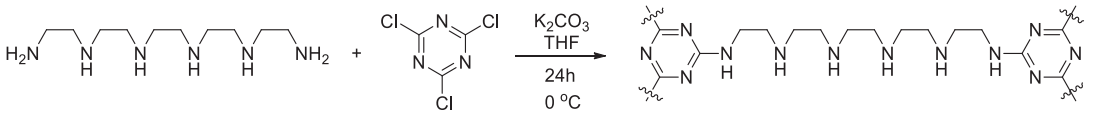


Figure 2. Synthesis of TAPEHA.

4.2. Preparation of Pd(II)-TAPEHA complex

In order to prepare Pd(II)-TAPEHA complex, 50 mg/L Pd(II) solution in 0.1 M HCl was passed through the column (10 mm i.d., 150 mm length) loaded with TAPEHA particles (1 g) using a flow rate of 5 mL/min until the Pd(II) concentration in the effluent reached 90% of its initial concentration. After this process, Pd(II)-loaded TAPEHA was retrieved from the column and used for the reduction of nitro compounds. The amount of Pd(II) loaded on TAPEHA was calculated to be 4.18 mmol/g (444 mg/g). Pd(II) ions can be uptaken by TAPEHA via electrostatic attraction (Figure 3a) and/or complex formation (Figure 3b) mechanism.[40,41]

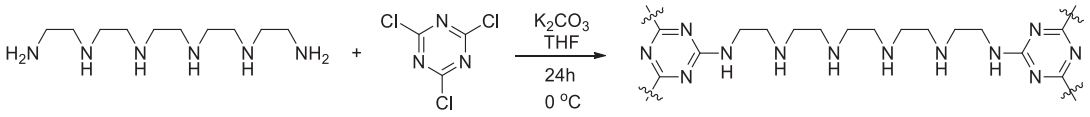


Figure 3. Proposed mechanism between Pd(II) ions and TAPEHA a) ion pair formation, b) complex formation.

4.3. General procedure for $NaBH_4$-mediated reduction of nitro compounds catalyzed by TAPEHA-Pd

TAPEHA-Pd (0.015 g) was added to a solution of nitroarenes (1.0 mmol) in EtOH/water (1/1) (20 mL). After $NaBH_4$ (4.0 mmol) was slowly added to the mixture, the color of the reaction mixture turned gradually black in a few minutes, resulting in the formation of palladium nanoparticles (TAPEHA-PdNPs).[42] After being stirred for 1.5 h at room temperature and atmospheric pressure, the catalyst was removed by filtering and the filtrate was extracted with 3 $\times$ 30 mL of EtOAc. The combined organic layers were dried over $MgSO_4$ and concentrated in a vacuum.

4.4. General procedure for N_2H_4-mediated reduction of nitro compounds catalyzed by TAPEHA-Pd

TAPEHA-Pd (0.015 g) was added to a solution of nitroarenes (1.0 mmol) in EtOH (20 mL). After $N_2H_4.H_2O$ (4.0 mmol) was added the color of the catalyst was turned to black rapidly in the same way as reducing with $NaBH_4$. This color change means formation of palladium nanoparticles[43] TAPEHA-PdNPs as mentioned above. After being stirred for 20 min at room temperature and atmospheric pressure, the catalyst was removed by filtering and EtOH was removed under a vacuum.

4.5. The morphology and microstructure of TAPEHA-PdNPs

The morphology and microstructure of TAPEHA-PdNPs were examined by means of scanning electron microscopy, energy dispersive spectroscopy (SEM-EDS) (JEOL JSM-6060 LV Model), and high-resolution transmission electron microscopy (HRTEM) (JEOL 2100 JEM Model). Phase analysis of dried and calcinated powders alumina samples was performed via a Rigaku XRD instrument by using Cu Kα-radiation with a wavelength of 1.5418 Å over a 2θ range of $10 \leq 20 \leq 90$. The average crystallite sizes of powders are calculated using Scherrer's formula.[44,45] The crystallite size calculated from the characteristic peak of Pd (about $2\theta = 39.673^\circ$ for and about $2\theta = 40.341^\circ$, hkl values at 111) for Figures 4a and 4c is about 20 nm. The powders contain mainly su-micrometer sized particles and close to spherical form (Figure 4b and 4d). Moreover, powders have some particles size greater than 1 μm. These microparticles are aggregation of nano-sized primary particles. High resolution transmission electron microscopy (HRTEM) observation also verified these results (Figure 5).

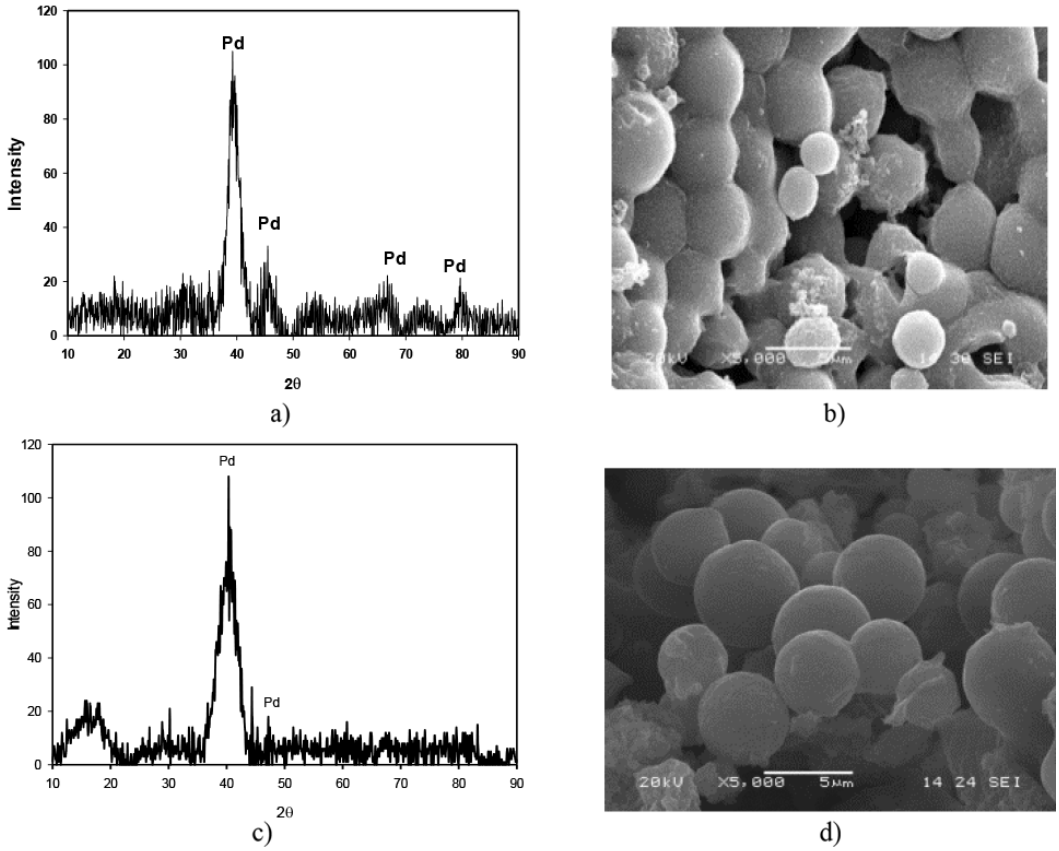


Figure 4. a) XRD pattern of powders from $NaBH_4$-mediated reduction; b) SEM micrograph of powders from $NaBH_4$-mediated reduction; c) XRD pattern of powders from N_2H_4-mediated reduction; d) SEM micrograph of powders from N_2H_4-mediated reduction.

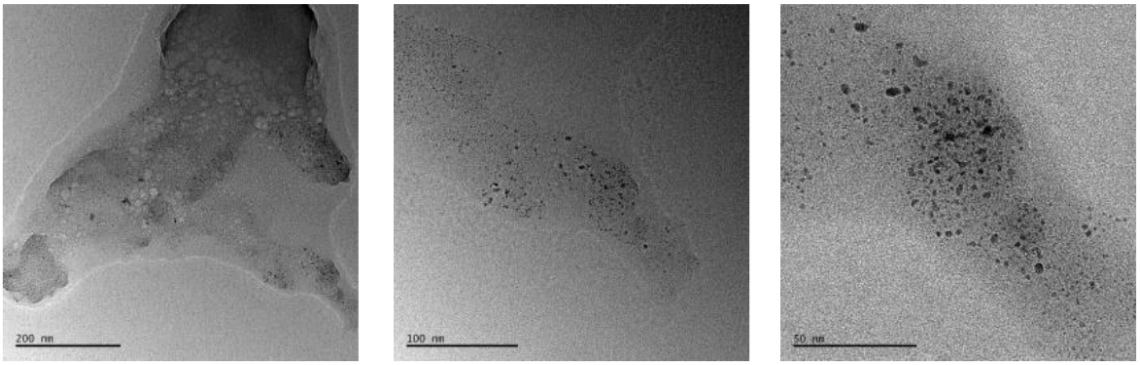


Figure 5. HRTEM images of TAPEHA-Pd NPs.

4.6. Leaching of Pd from TAPEHA by use as a catalyst

First 4 mL of of aqua regia was added to the polymer for dissolution of the TAPEHA-PdNPs and then the volatiles were evaporated to dryness. After this process was performed once more, the residue was dissolved by 10 mL of 1 M HCl solution. The palladium level in the final solution was determined using flame atomic absorption spectrometry.

4.7. Reuse of the catalyst

After the reactions, the catalyst (TAPEHA-PdNPs) was filtered off and washed thoroughly with acetone, and then dried in air for use in another reduction. The catalyst was able to be reused more than ten times without any decrease in catalytic activity (Figure 6).

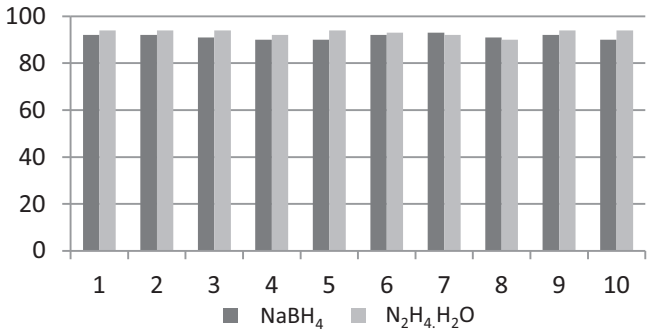


Figure 6. Reusability of TAPEHA-PdNPs for the reduction of nitrobenzene.

Acknowledgment

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