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Chitosan supported bimetallic Pd/Co nanoparticles as a heterogeneous catalyst for the reduction of nitroaromatics to amines

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A R T I C L E I N F O

A B S T R A C T

A new bimetallic nanocomposite of chitosan was prepared. Pd and Co nanoparticles were deposited on chitosan to produce a new heterogeneous recyclable catalyst for use in the bimetallic catalytic reduction reaction. The catalyst was characterized with common analysis methods for nanocomposites including Energy Dispersive X-Ray Spectroscopy, X-Ray Diffraction pattern, Thermal Gravimetric Analysis, Flame Atomic Absorption Spectroscopy and Scanning Electron Microscopy, and applied in the reduction reaction of nitroaromatics using $NaBH_4$ at room temperature. The bimetallic system gave good results compared to each of the applied metals. Various aromatic amines and diamines were used in the reduction reaction. The aromatic amines were obtained as the sole product of the reduction reaction with 15 mol% Pd and 12 mol% Co during 2h. This reaction had some advantages such as mild reaction conditions, high yield, green solvent, and a recyclable catalyst. Also, the recovered catalyst was applicable in the reduction reaction without a significant decrease in the activity for up to six times.

1. Introduction

The reduction of aromatic and aliphatic nitro compounds is one of the most important reactions in the organic synthesis for the preparation of amines [1-3]. Aromatic amines are considered intermediates in the preparation of dyes, antioxidants, pharmaceuticals and agrochemicals [4-6]. Various methods have been introduced for the reduction of aromatic nitro compounds [7-9], all of which use a hydrogen source such as alcohols, hydrazine hydrates, silanes and formats [10-18]. The application of sodium borohydride ($NaBH_4$) in combination with metal nanoparticles represents an important catalytic system for the reduction of organic nitro compounds in modern preparative chemistry. The reduction of organic nitro compound into corresponding amine with $NaBH_4$ does not perform under normal conditions [19], instead $NaBH_4$ in combination with transition metal halides such as Co, Ni, Cu

is an efficient route for this reaction [20,21]. The $NaBH_4$ in protic moieties reduces transition metal ions to produce metal boride nanoparticles which allows for the rapid reduction of the nitro compound into their corresponding amine [22-24]. Recently, some of the transition metals such as Pd and Au showed good catalytic activity in the reduction of nitro compounds [25]. However, great enhancements in the reduction rate were observed for bimetallic systems such as Pd-Ni, Pd-Cu and Pd-Ag [26]. Metal nanoparticles are interesting catalysts compared to their bulk counterparts due to their high surface area, which lead to improved catalytic activities. The highly active surfaces of nanoparticles led to their aggregation and a decrease in the catalytic activity. The deposition of metal nanoparticles on the support is a convenient method for avoiding aggregation. Today the importance of heterogeneous catalysts is irrefutable for any catalyst researcher. Supported nanometals are one of the most important

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categories of heterogeneous catalysts with broad applications in the industry. Various supports such as silica, zeolite, alumina, titania and carbon nanotube were applied for the metal nanoparticles. Among various supports, biocompatible supports such as cellulose and chitosan are interesting [27-34]. In continuation of our efforts in the development of a new heterogeneous catalytic system based on natural polymers such as cellulose [29-34], herein a new bimetallic catalytic system was investigated for the reduction of nitroaromatics by Pd (0) and Co (0) nanoparticles supported on chitosan (Pd/CoNPs@chitosan) as a heterogeneous recoverable catalyst with $NaBH_4$ as a reducing agent (Scheme 1). The present work introduced a new cellulose-based heterogeneous catalytic system as an efficient catalyst for the reduction of nitroaromatic compounds. The catalyst was interesting due to the biocompatibility of cellulose.

$$Ar-NO_2 \xrightarrow[NaBH_4]{Pd/CoNPs@chitosan} Ar-NH_2$$
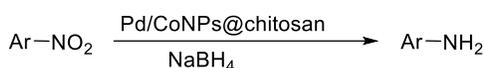
Scheme 1. Reduction reactions of nitrobenzenes

2. Material and methods

2.1. Synthesis of Pd/CoNPs@Chitosan

For the preparation of the catalyst, chitosan (1 g) was stirred with $CoCl_2.6H_2O$ (0.03 g) in H_2O (10 mL) for 24h. A solution of 5 mL of $NaBH_4$ (0.1 g) was added to the reaction vessel during 1h. The mixture was stirred for 24h and then Co@Chitosan was obtained after filtration; it was washed with H_2O (3 × 10 mL) and dried in an oven (70 °C). Co@Chitosan (1 g) was stirred with $PdCl_2$ (0.05 g) in H_2O (10 mL) for 24h, and then reduced with 5 mL of $NaBH_4$ (0.2 g) solution to Pd (0) to yield Pd/CoNPs@chitosan. The Pd/CoNPs@chitosan was obtained as a dark solid after filtration, washing with H_2O (3 × 10 mL), and drying in an oven (70 °C).

2.2. Typical procedure for the reduction of nitrobenzene

Nitrobenzene (0.12 g 1.00 mmol) was added to a round-bottomed flask containing colloidal of Pd/CoNPs@chitosan (0.01 g) in H_2O (2 mL) at room temperature. 3 mL of $NaBH_4$ solution (1.1 mmol) was added dropwise to the reaction vessel during stirring for 0.5 h. The completion of the reaction was monitored by thin-layer chromatography (TLC). After 1.5 h, the Pd/CoNPs@chitosan was separated via filtration and washed with acetone (2 × 5 mL). The filtrate solvent was evaporated under a vacuum and the product was purified with column chromatography with *n*-hexane:ethylacetate (4:1). Also, the conversion was determined with Gas Chromatography (GC).

3. Results and discussion

For the study of the bimetallic system including Pd and Co on the reduction reaction new catalyst, Pd/CoNPs@chitosan was prepared, characterized, and examined in the reduction reaction. The Pd/CoNPs@chitosan preparation was performed in two steps that included depositions of Co (0) and Pd(0). Each step included the dispersion of a cation (Co (II) or Pd(II)) and its chemical reduction to the corresponding metal. The catalyst was characterized via Energy Dispersive X-Ray Spectroscopy (EDS), X-Ray Diffraction pattern (XRD), Thermal Gravimetric Analysis (TGA), Flame Atomic Absorption Spectroscopy (FAAS), and Scanning Electron Microscopy (SEM). EDS is a common method for approving the metal loading on the support. The EDS analysis showed that Pd and Co nanoparticles were loaded on the chitosan surface (Figure 1). Via Flame Atomic Absorption Spectroscopy (FAAS), the amount of Pd and Co loading on the support was determined to be 0.15 mmol and 0.12 mmol per 1g Pd/CoNPs@chitosan, respectively.
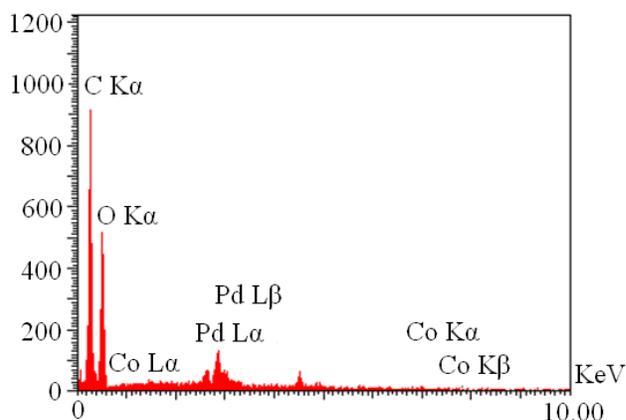
Fig. 1. The EDS analysis of Pd/CoNPs@chitosan

The structure of Pd/CoNPs@chitosan was determined by powder XRD. The characteristic diffraction peaks for chitosan Pd (111) and Co (111) indicated the deposition of Pd and Co on the catalyst.
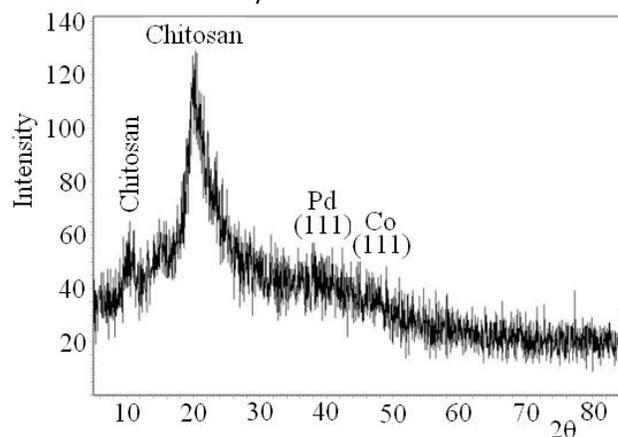
Fig. 2. The XRD pattern of Pd/CoNPs@chitosan

TGA was applied to study the thermal behavior of chitosan and Pd/CoNPs@chitosan. Chitosan started to decompose above 268 °C in the air (Figure 3a). The Pd/CoNPs@chitosan had a lower decomposition temperature which showed that

Pd or Co had catalytic activity for the decomposition of chitosan (Figure 3b).
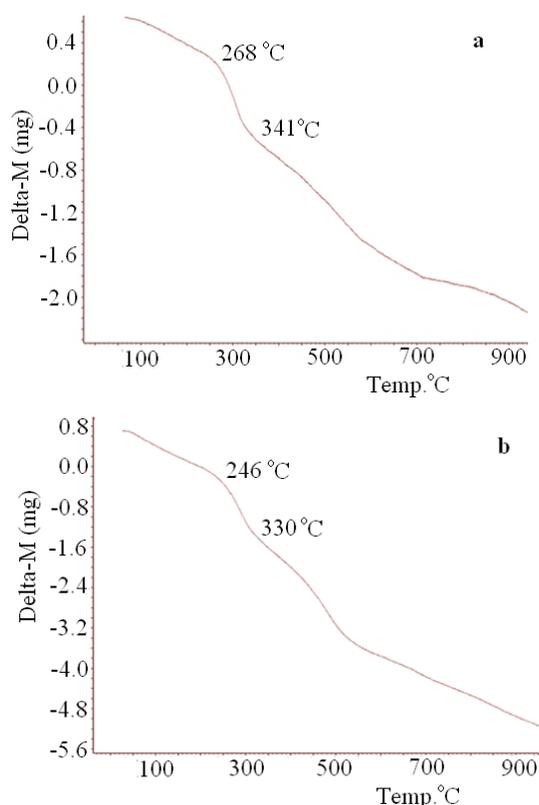
Fig. 3. TGA of chitosan (a) and Pd/CoNPs@chitosan (b)

The SEM image of the catalyst indicated the formation and distribution of nanoparticles Co and Pd on the chitosan surface (Figure 4).
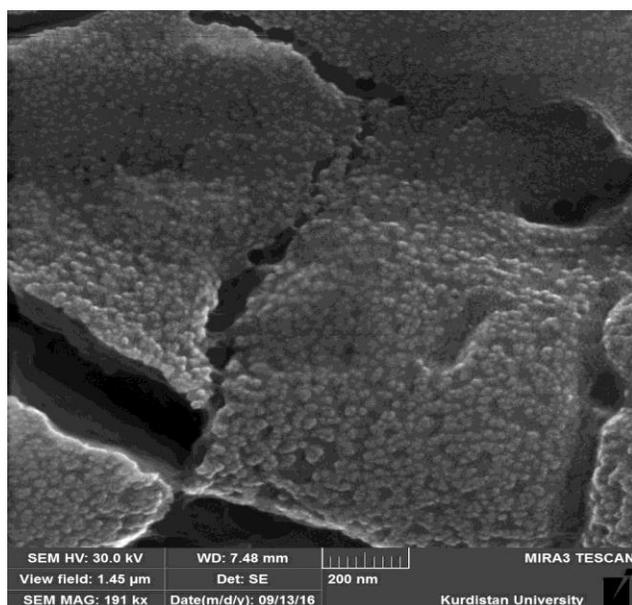
Fig. 4. SEM image of Pd/CoNPs@chitosan

The catalytic activity of Pd/CoNPs@chitosan was evaluated in the reduction of nitroaromatics. The determination of the Pd and Co ratio on the catalyst was important for obtaining a high efficiency of the reduction reaction. Initially, the reduction reaction of nitrobenzene was examined in the presence of CoNPs@Chitosan and PdNPs@Chitosan, separately (Table 1, entries 1-6). These tests revealed optimum amounts of Pd NPs and Co NPs for the reduction of nitrobenzene. The ^{1}H NMR study showed that the reduction of nitrobenzene proceeded to give aniline (**2a**) as the sole product in the presence of each of CoNPs@Chitosan and PdNPs@Chitosan. The reduction of nitrobenzene in the presence of PdNPs@Chitosan gave aniline with 0.15 mol% of Pd in 74% yield during 2h (Table 1, entries 1-3). The reaction in the presence of CoNPs@Chitosan needed longer times in which a 60% yield was obtained with 0.12 mol% Co during 5h (Table 1, entries 4-6). Also, the results showed that the catalytic activity of Pd was higher than Co for the reduction of nitrobenzene (Table 1, entries 1-6). The optimized Pd and Co amounts were used in the preparation of Pd/CoNPs@chitosan. The reduction of nitrobenzene using Pd/CoNPs@chitosan with 15 mol% Pd and 12 mol% Co proceeded to give aniline (**2a**) as the sole product with a 93% yield in short reaction duration (2h). The reduction reaction in the presence of Pd/CoNPs@Chitosan was performed in H_2O at room temperature during 2h with a 93% isolated yield. Also, the conversion of nitrobenzene to aniline was obtained at 100%. The reaction did not proceed in the absence of the catalyst (Table 1, entry 8). In addition, the reaction did not perform in the absence of $NaBH_4$ and gave a low yield in a low amount of $NaBH_4$ (Table 1, entries 9 and 10). After screening a variety of solvents, H_2O was determined to be the best solvent (Table 1, entries 11-15). The reaction was performed in just the protic solvents, which may be attributed to the good activity of $NaBH_4$ in these solvents (Table 1, entries 5-9). Since the bimetallic system (Pd/CoNPs@chitosan) afforded a high yield in a short time, these results supported the high activity of Pd bimetallic catalysts in the nitroaromatic reduction [26].

Table 1. Optimization of the reaction conditions for reduction of nitrobenzene using PdNPs@Chitosan and CoNPs@Chitosan[a]

Entry	Pd (mol%)	Co (mol%)	Solvent	Time (h)	Yield (%)[b]
1	0.08	-	H_2O	2	59
2	0.15	-	H_2O	2	74
3	0.22	-	H_2O	2	76
4	-	0.06	H_2O	5	51
5	-	0.12	H_2O	5	60
6	-	0.18	H_2O	5	60
7	0.15	0.12	H_2O	2	93
8	-	-	H_2O	2	0
9 [c]	0.15	0.12	H_2O	2	0
10[d]	0.15	0.12	H_2O	2	89
11	0.15	0.12	EtOH	5	78
12	0.15	0.12	MeOH	5	81
13	0.15	0.12	Toluene	5	0
14	0.15	0.12	CH_2Cl_2	5	0
15	0.15	0.12	MeCN	5	0

[a]Reaction conditions nitrobenzene (1 mmol) $NaBH_4$ (1.1 mmol) solvent (5 mL) room temperature [b]Isolated yield. [c]Without $NaBH_4$. [d]$NaBH_4$ (1 mmol)

The Pd/CoNPs@chitosan catalytic activity was investigated for various electron withdrawing and electron donating substituted nitroaromatics and dinitroaromatics. The reduction reaction successfully afforded amine compounds in high yields. For the nitro carboxylic acids, the reaction gave corresponding amino carboxylic acids. This result showed that the carboxylic acid group was stable versus the reduction with $NaBH_4$ in the presence of Pd/CoNPs@chitosan (Table 2, entries 2 and 3). The reduction of dinitroaromatics also gave the corresponding diamines good yields in the presence of excess catalyst and $NaBH_4$ (Table 2, entries 4, 8 and 9).

Table 2. The reduction of various nitroaromatics using Pd/CoNPs@chitosan and $NaBH_4$

Entry	R	Yield (%)[b]
1	Ph	93
2	*p*-HOOC-Ph	85
3	*o*-HOOC-Ph	86
4[c]	*p*-O_2N-Ph	86[d]
5	*p*-H_2N-Ph	89
6	*p*-H_3C-Ph	92
7	*o*-H_3C-Ph	91
8[c]	*m*-O_2N-Ph	86[e]
9	naphtyl	86
10[c]	*o*-O_2N-Ph	87[f]

[a]Reaction conditions nitroaromatic 1 (1 mmol) $NaBH_4$ (1.1 mmol) Pd/CoNPs@chitosan (0.01 g) H_2O (5 mL) room temperature 2h. [b]Isolated yield. [c]$NaBH_4$ (2.2 mmol). [d]R○́=*p*-H_2N-Ph. [e]R○́=*m*-H_2N-Ph. [f]R○́=*o*-H_2N-Ph.

Potential Pd and Co leaching into the reaction mixture was also analyzed with FAAS analysis. For this purpose, the sample was taken through a syringe filter during the heterogeneous reduction reaction of nitrobenzene; the solvent was evaporated, and the residue was dissolved in HNO_3. The analysis of the sample via FAAS showed that the Pd and Co concentrations in the reaction solution were less than the detection limit. This result indicated that virtually no Pd and Co leached from the catalyst into the solution. The recyclability of the Pd/CoNPs@chitosan was examined in the reduction of nitrobenzene. After carrying out the reaction, the catalyst was separated via filtration as a dark solid washed with EtOH (2 × 5 mL) and reused. Only a minor decrease in the reaction yield was observed after six repetitive cycles for the reaction (Table 3).

Table 3. Successive trials by using recoverablePd/CoNPs@chitosan for the reduction reaction of nitrobenzene[a]

Trial	Catalyst amount (g)	Yield (%)[b]
1	0.010	93
2	0.009	93
3	0.009	93
4	0.009	91
5	0.008	91
6	0.008	91

[a]Reaction conditions nitrobenzene (1 mmol) $NaBH_4$ (1.1 mmol) H_2O (5 mL) r.t 2h. [b]Isolated yield.

The detailed study on the mechanism of the reduction reaction was not performed, but the presented mechanism in Scheme 2 was conceivable for the reduction reaction. The reaction was performed in two steps including the reduction of nitro aromatic compound 1 to nitroso compound 2 and the final reduction of nitroso compound 2 to amine 3. The first step involved the reduction of the nitro compound with H+ and Co. In this step, Co was oxidized to Co(II) and Pd reduced Co(II) to Co. The Pd(II) produced from the reduction reaction of Co(II) was reduced with the hydride ions of $NaBH_4$. In the second step, the reduction reaction of compound 2 was performed using the hydride ions of $NaBH_4$ [35]. The results of our catalyst were compared with some reports about the reduction of

nitrobenzene with respect to their solvent, reaction duration, temperature, yield and selectivity (Table 4).
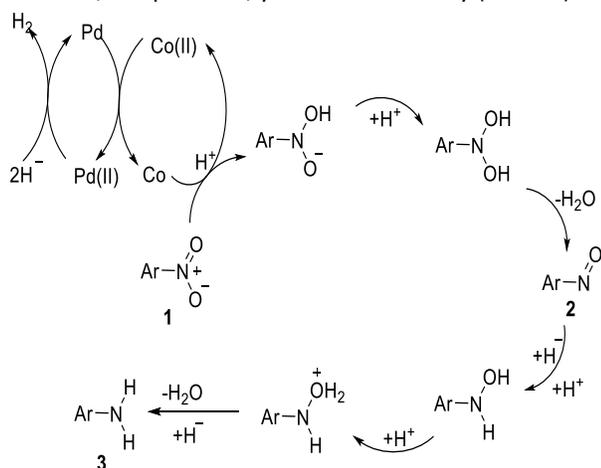
Scheme 2. The proposed mechanism for reduction of nitroaromatics using $NaBH_4$ and Pd/CoNPs@chitosan

Performing the reaction in short reaction times was advantageous for some of the previous reports. The reduction reaction of nitrobenzene with Pd/CoNPs@chitosanhad some advantages such as greener solvent compared to entries 1-3 and higher yields compared to entry 1. Also, Pd/CoNPs@chitosan was a recyclable catalyst unlike entries 2 and 3. However, the method wasa good reduction reaction regarding the recyclability of the catalyst, high yield and green solvent which were very important factors for a reduction reaction.

Table 4. Comparison of the results obtained for the reduction of nitrobenzene to aniline.

Entry	Catalyst	Solvent	Time	Temp. (°C)	Isolated Yield (%)
1	Co_3S_4 [36]	EtOH	1 h	r.t.	73
2	Raney Nickel [37]	MeOH	5 min	30-40	95
3	$Ni(OAc)_2.4H_2O$ [38]	MeCN	20 min	r.t.	92
4	Pd/CoNPs@chitosan	H_2O	2 h	r.t.	93

4. Conclusions

In conclusion, we deposited Pd and Co nanoparticles on chitosan for the preparation of a biocompatible catalyst for the reduction of nitrocompounds. After the successful synthesis and characterization of the catalyst, the catalytic reduction of nitrobenzenes to the corresponding amines was performed selectively in high yields. The reduction reaction was carried out with $NaBH_4$ in H_2O as the solvent at room temperature for 2h. Various nitrobenzenes and dinitrobenzenes were reduced to the corresponding amine in good yields. The mild reaction conditions of this reaction in combination with the recyclability of the catalyst make the presented method an interesting approach compared to most of the reports.

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