

Reduction of Nitroaromatics to Amines with Cellulose Supported Bimetallic Pd/Co Nanoparticles

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ABSTRACT: Pd and Co nanoparticles were deposited on cellulose for use as a heterogeneous catalyst in the bimetallic catalytic reduction reaction. The catalyst was characterized with Energy Dispersive X-Ray Spectroscopy, X-Ray Diffraction pattern, Thermal Gravimetric Analysis, Flame Atomic Absorption Spectroscopy, and Transmission Electron Microscopy, and applied in the reduction reaction of nitroaromatics using NaBH₄ at room temperature. Aromatic amines were obtained as the sole product of the reduction reaction during 2h. This reaction has some advantages such as mild reaction conditions, high yield, green solvent, and recyclable catalyst. Also, the recovered catalyst is applicable in the reduction reaction for 4 times without a significant decrease in the activity.

KEYWORDS: Reduction; Nitroaromatics; Cellulose; Heterogeneous catalyst; Bimetallic; Palladium; Cobalt.

INTRODUCTION

Reduction of aromatic and aliphatic nitro compounds is one of the most important reactions in the organic synthesis for the preparing of amines [1-3]. Aromatic amines are 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], which all of them use a hydrogen source such as alcohols, hydrazine hydrates, silanes, and formats [10-18]. The application of sodium borohydride (NaBH₄) in combination with metal nanoparticles represents an important catalytic system for the reduction of organic nitro compounds in modern preparative chemistry. Reduction of the organic nitro compound into the corresponding amine with NaBH₄

does not perform under normal conditions [19], instead, NaBH₄ in combination with transition metal halides such as Co, Ni, Cu is an efficient route for this reaction [20,21]. NaBH₄, in protic moieties, reduces transition metal ions to produce metal boride nanoparticles which allow to 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, a great enhancement in the reduction rate was observed for bimetallic systems such as Pd-Ni, Pd-Cu, and Pd-Ag [26].

Today, the importance of heterogeneous catalysts is irrefutable for any catalyst researcher. Supported

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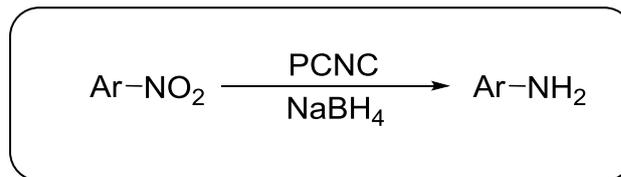
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nanometals are one of the most important categories of heterogeneous catalysts with broad applications in the industry [27-30]. Various supports such as silica, zeolite, alumina, titania, and carbon nanotube were applied for the metal nanoparticles. Among them, cellulose has been attracted great attention due to some advantages such as hydrophilicity, chirality, biodegradability, and high functionality. In recent years wide studies were performed on cellulose and its derivatives focusing on their biological, chemical, as well as mechanical properties. Cellulose and its derivatives can be used as a support since they are renewable, biodegradable and non-toxic [31]. Cellulose supported Cu(0) for Aza-Michael addition [32], Pd(0) for Heck and Sonagashira couplings [33,34], Cu(I)/Pd(0) for Click cyclization [35], Pd(0) for epoxidation of ethylbenzene [36], Co(II) for the oxidation reactions [37,38], gold for oxidation reactions [39], and Pd/graphene quantum dots for the reduction of nitroaromatics [40] are some example of cellulose supported catalysts.

Metal nanoparticles are interesting catalysts due to high surface area compared to their bulk counterparts leading to improved catalytic activities. The highly active surface of these nanoparticles could lead to aggregation of the nanoparticles which the aggregation decrease the catalytic activity. Deposition of metal nanoparticles on the support is a convenient method for avoiding of the aggregation. In continuation of our efforts to the development of a new catalytic system with cellulose as the support [34-40], herein a new efficient bimetallic catalytic system was introduced for the reduction of nitroaromatics by Pd(0) and Co(0) Nanoparticles supported on Cellulose (PCNC) as a heterogeneous recoverable catalyst with NaBH₄ as a reducing agent (Scheme 1).

EXPERIMENTAL SECTION

Cellulose was purchased from Merck with a particle size $\leq 20\%$ less than 20 μm , $\leq 2\%$ greater than 160 μm , and $\geq 80\%$ between 20 and 160 μm . The chemicals were purchased from Merck and used without further purification. Energy Dispersive X-ray Spectroscopy (EDS) was performed with a Scanning Electron Microscope of TSCAN company. Transition Electron Microscopy (TEM) micrograph was obtained with LEO 912AB electron microscope. Au determination



Scheme 1: Reduction reactions of nitrobenzene.

was carried out on a Flame Atomic Absorption Spectroscopy (FAAS) (Shimadzu model AA-680 atomic absorption spectrometer) with a hollow cathode lamp.

Synthesis of PdNPs@Cellulose

Cellulose (1 g) was stirred with PdCl₂ (0.05 g) in H₂O (10 mL) for 24h. 5 mL of NaBH₄ (0.07 g) solution was added to the reaction vessel during 1h. The mixture was stirred for 24h and then, PdNPs@Cellulose was obtained after filtration, washing with H₂O (3 \times 10 mL) and drying in an oven (70 $^{\circ}\text{C}$).

Synthesis of CoNPs@Cellulose

Cellulose (1 g) was stirred with CoCl₂.6H₂O (0.03 g) in H₂O (10 mL) for 24h. 5 mL of NaBH₄ (0.07 g) solution was added to the reaction vessel during 1h. The mixture was stirred for 24h and then, CoNPs@Cellulose was obtained after filtration, washing with H₂O (3 \times 10 mL) and drying in an oven (70 $^{\circ}\text{C}$).

Synthesis of PCNC

For the preparation of the catalyst, cellulose (1 g) was stirred with CoCl₂.6H₂O (0.03 g) in H₂O (10 mL) for 24h. 5 mL of NaBH₄ (0.1 g) solution was added to the reaction vessel during 1h. The mixture was stirred for 24h and then, Co@Cellulose was obtained after filtration, washing with H₂O (3 \times 10 mL) and drying in an oven (70 $^{\circ}\text{C}$). Co@Cellulose (1 g) was stirred with PdCl₂ (0.05 g) in H₂O (10 mL) for 24h, and then, reduced with 5 mL of NaBH₄ (0.2 g) solution to Pd(0) to yield PCNC. PCNC after filtration, washing with H₂O (3 \times 10mL) and drying in an oven (70 $^{\circ}\text{C}$) was obtained as a dark solid.

A typical procedure for the reduction of nitrobenzene

Nitrobenzene (0.12 g, 1.00 mmol) was added to a round-bottomed flask containing colloidal of PCNC (0.05 g) in H₂O (5 mL) at room temperature. 5 mL of NaBH₄ solution (2 mmol) was added dropwise to the reaction vessel under stirring during 0.5 h. After 1.5 h, PCNC

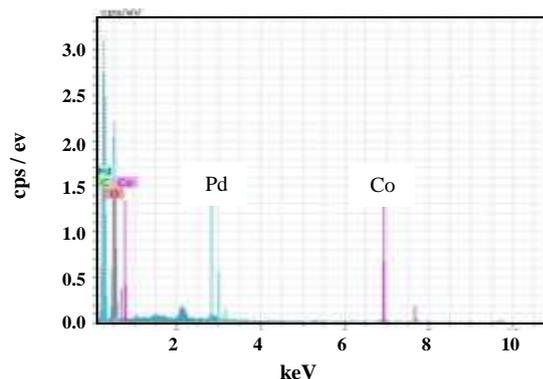


Fig. 1: The EDS analysis of PCNC.

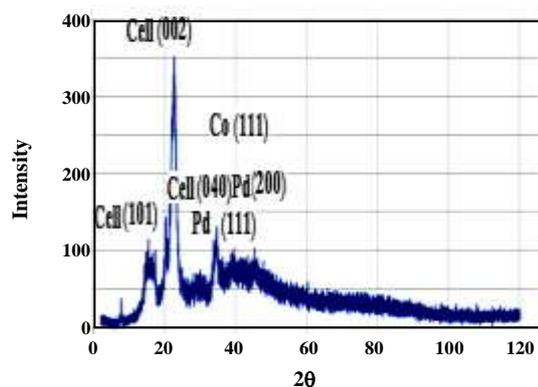


Fig. 2: The EDS analysis of PCNC.

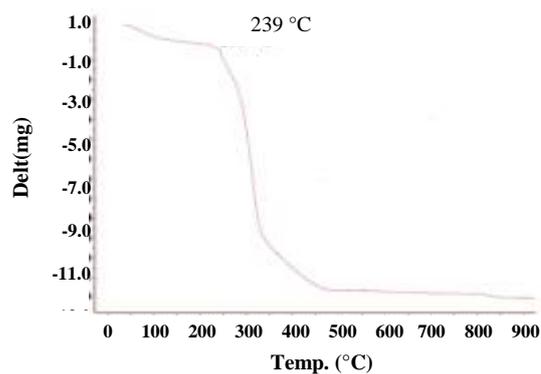


Fig. 3: The TGA of PCNC.

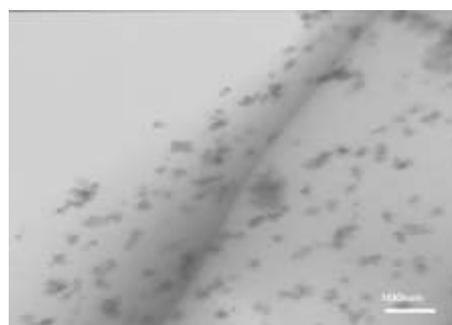


Fig. 4: TEM image of PCNC.

was separated via filtration and washed with acetone (2×5 mL). The filtrate solvent was evaporated under vacuum and the product purified with column chromatography with *n*-hexane:ethylacetate (4:1).

RESULTS AND DISCUSSION

The catalyst preparation was performed in two steps including depositions of Co(0) and Pd(0). Each step includes a dispersion of a cation (Co(II) or Pd(II)) and its chemical reduction to metal. The catalyst was characterized with Energy Dispersive x-ray Spectroscopy (EDS), X-Ray Diffraction (XRD) pattern, Thermal Gravimetric Analysis (TGA), Flame Atomic Absorption Spectroscopy (FAAS) and Transmission Electron Microscopy (TEM).

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 cellulose surface (Fig. 1). The amount of Pd and Co loading on the support was determined to be 0.096 mmol and 0.075

mmol respectively per 1g PCNC with Flame Atomic Absorption Spectroscopy (FAAS).

The structure of PCNC was determined by powder XRD. Characteristic diffraction peaks for cellulose (101), cellulose (002), cellulose (040), Pd (111), Pd (200) and Co (111) indicate deposition of Pd and Co on the cellulose.

ThermoGravimetric Analysis (TGA) which applied for the study of thermal behavior of materials evidenced PCNC starts to decomposition above 239 °C in the air which it's good thermal stability for a catalyst (Fig. 2).

The TEM image of the catalyst indicates the formation and distribution of nanoparticles on the cellulose surface which attributed to the CoNPs and Pd NPs (Fig. 4).

The catalytic activity of PCNC was evaluated in the reduction of nitroaromatics. Determination of the Pd and Co ratios on the catalyst is an important factor for obtaining the high efficiency of the reduction reaction. So at first, the reduction reaction of nitrobenzene was examined in the presence of CoNPs@Cellulose

Table 1: Optimization of the reaction conditions for reduction of nitrobenzene^a

Entry	(Pd mol%)	(Co mol%)	Solvent	Yield (%) ^b
1	0.38	-	H ₂ O	61
2	0.48	-	H ₂ O	87
3	0.58	-	H ₂ O	89
4	-	2.6	H ₂ O	46
5	-	3.2	H ₂ O	53
6	-	3.8	H ₂ O	54
7	0.38	2.6	H ₂ O	87
8	0.48	3.2	H ₂ O	95
9	0.58	3.8	H ₂ O	95
10 ^c	0.48	3.2	H ₂ O	73
11	0.48	3.2	EtOH	91
12	0.48	3.2	EtOH:H ₂ O (1:1)	95
13	0.48	3.2	MeCN	0
14	0.48	3.2	MeOH	76
15	0.48	3.2	CH ₂ Cl ₂	0
16	0	0	H ₂ O	0

a) Reaction conditions: nitrobenzene (2 mmol), NaBH₄ (1.1 mmol), solvent (5 mL), room temperature, 2h.

b) Isolated yield.

c) NaBH₄ (1 mmol).

and PdNPs@Cellulose, separately (Table 1, entries 1-6). These tests revealed optimum amounts of Pd NPs and Co NPs for the reduction of nitrobenzene 0.48 mol% and 3.2 mol% Co, respectively. Interestingly, the reduction reaction was performed with both catalysts. Aniline was obtained with 87% yield in 3h using PdNPs@Cellulose and with 53% yield in 5h using CoNPs@Cellulose. The optimized Pd and Co amounts were used in the preparation of Pd/CoNPs@chitosan. So, the reduction of nitrobenzene (**1a**) (1 mmol) with PCNC and NaBH₄ was investigated for the optimization of reaction conditions. It was found that 0.48 mol% Pd/3.2 mol%Co (Table 1, entries 7-9) with 2 mmol of NaBH₄ in H₂O (Table 1, entries 11-15) at room temperature is the best reaction conditions for the reduction of nitrobenzene. The ¹H NMR study shows that the reduction of nitrobenzene proceeded to give aniline (**2a**) as the sole product with 95% yield in short reaction duration (2h). The reaction yield was decreased in the low amounts of catalyst. The reaction did not perform in the absence of NaBH₄,

and gave low yield in a low amount of NaBH₄ (Table 1, entry 10). After screening a variety of solvents, H₂O was determined to be the best solvent. The reaction was performed just in the protic solvents which may be attributed to the good activity of NaBH₄ in these solvents (Table 1, entries 11-15). Also, the reaction did not proceed in the absence of the catalyst (Table 1, entry 16). These results confirm a high activity of bimetallic systems in the reduction of nitroaromatics.

For more investigation of the PCNC activity, the reaction was examined for various electron withdrawing and electron donating substituted nitroaromatics and nitroaromatics. The reduction reaction successfully afforded aniline derivatives in good yields. For nitro carboxylic acids the reaction gave corresponding amino carboxylic acids. This result shows that the carboxylic acid group is stable versus reduction with NaBH₄ in the presence of PCNC (Table 2, entries 2 and 3). The reduction of nitroaromatics also gave the corresponding diamines with good yields in the presence of excess

Table 2: The reduction of various nitroaromatics using PCNC and NaBH₄.

$\text{R}-\text{NO}_2 \xrightarrow[\text{H}_2\text{O or H}_2\text{O:EtOH}]{\text{PCNC, NaBH}_4} \text{R}'-\text{NH}_2$			
Entry	R	solvent	Yield (%) ^b
1	Ph	H ₂ O	95
2 ^c	<i>p</i> -HOOC-Ph	H ₂ O	86
3 ^c	<i>o</i> -HOOC-Ph	H ₂ O	86
4 ^c	<i>p</i> -O ₂ N-Ph	H ₂ O/EtOH	88 ^d
5	<i>p</i> -H ₂ N-Ph	H ₂ O	89
6	<i>p</i> -H ₃ C-Ph	H ₂ O/EtOH	94
7	<i>o</i> -H ₃ C-Ph	H ₂ O/EtOH	92
8 ^c	<i>m</i> -O ₂ N-Ph	H ₂ O/EtOH	86 ^e
9	naphthyl	H ₂ O/EtOH	89
10 ^c	<i>o</i> -O ₂ N-Ph	H ₂ O/EtOH	89 ^f

a) Reaction conditions: nitroaromatic 1 (1 mmol), NaBH₄ (2 mmol), PCNC (0.05 g), solvent (5 mL), room temperature, 2h.

b) Isolated yield. c) NaBH₄ (4 mmol), d) R=*p*-H₂N-Ph. e) R=*m*-H₂N-Ph. f) R=*o*-H₂N-Ph.

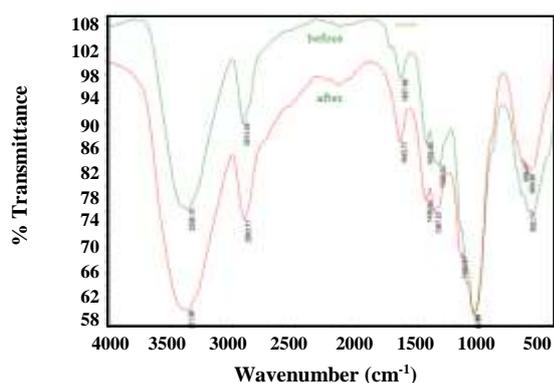


Fig. 5: FT-IR spectra for PCNC before and after recovery.

catalyst and NaBH₄ (Table 2, entries 4, 8 and 9). For some of the nitroaromatics, the reaction in H₂O did not afford good yields and H₂O:EtOH (1:1) was used as the solvent.

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 HNO₃. The analysis of the sample with FAAS showed that the Pd and Co concentrations in the reaction solution were less than the detection limit. This result indicates that virtually no Pd and Co leach from the catalyst into the solution. Also, did not observe any changes in the

FT-IR spectrum of the catalyst recovered from the reaction (Fig. 5).

Recyclability of the PCNC 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. An only minor decrease in the reaction yield was observed after four repetitive cycles for the reaction (Table 3).

Finally, a comparison study was performed for the obtained results with some recent reports about the reduction of nitrobenzene as a sample. Most important factors for this reaction are yield, solvent, temperature and reaction duration. As can be seen from Table 4, various catalysts were used for the reduction of nitrobenzene which in all of the high yields obtained. So, the challenge of this reaction is the gentling of the reaction conditions not increase the yield. A comparison of PCNC with other catalysts of Table 4 for the reduction of nitrobenzene shows that very good conditions resulted in PCNC. H₂O as the solvent at room temperature in 2h is a convenient reaction condition for the reduction of nitrobenzene with PCNC. Also, the catalyst has other advantages similar to most of the heterogeneous catalysts including easy separation and recyclability. PCNC has another advantage compared to some heterogeneous catalysts including easy preparation of the catalyst.

Table 3: Successive trials by using recoverable PCNC for the reduction reaction of nitrobenzene^a.

Trial	Catalyst amount (g)	Yield (%) ^b
1	0.05	95
2	0.05	95
3	0.04	95
4	0.04	94

a) Reaction conditions: nitrobenzene (1 mmol), NaBH₄ (2 mmol), H₂O (5 mL), r.t., 2h.

b) Isolated yield.

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

Entry	Catalyst	Ref.	Solvent	Time (h)	Temp. (°C)	Yield (%)
1	Pd-gCN	[41]	EtOH	4	70	99 (G)
2	zinc powder/chelating ethers	[42]	Ether/H ₂ O	9	70	90 (I)
3	Co-Mo ₂ C/AC	[43]	EtOH	2	80	100
4	Ni-B	[44]	H ₂ O/EtOH	8	room	99.6
5	Zinc phthalocyaninein PEG-400	[13]	EtOH	8	100	99 (G)
6	Fe ₃ O ₄ / β-alanine-acrylamide-Ni	[45]	H ₂ O	5	room	98 (I)
7	PCNC	-	H ₂ O	2	room	95

CONCLUSIONS

In conclusion, we deposited Pd and Co nanoparticles on cellulose for the preparation of a compatible catalyst for the reduction of nitro compounds. After successful synthesis and characterization of the catalyst, catalytic reduction of nitrobenzenes to the corresponding amines was performed selectively in high yields. The reduction reaction was carried out with NaBH₄ in H₂O or H₂O:EtOH (1:1) as the solvents at room temperature in 2h. Various nitrobenzenes and dinitrobenzenes were reduced to the corresponding amine in good yields. Also, the bimetallic system reduced nitrobenzenes efficiently compared to each of the metals. Mild reaction conditions of this reaction in combination with recyclability of the catalyst make the presented method an interesting approach compared to most of the reports.

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