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Palladium Nanoparticles on a Creatine-Modified Bentonite Support: An Efficient and Sustainable Catalyst for Nitroarene Reduction

Mohammad Gholinejad,^{*[a,b]} Zahra Rasouli,^[a] Carmen Najera^{*[c]} José M. Sansano^[c]

Dedication ((optional))

Abstract: Creatine as the nitrogen-rich, green and cheap compound is used for modification of natural bentonite and the resulting material employed for stabilization of Pd nanoparticles having an average diameter of 3 nm. This new material **bento-crt@Pd** characterized using different techniques such as X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), solid state UV-vis, scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA), and energy-dispersive X-ray spectroscopy (EDX). This green catalyst promotes the efficient reduction of aromatic nitro compounds in aqueous media. Using this catalyst, nitroarenes having electron donating as well as electron withdrawing groups were reduced efficiently to corresponding amines at room temperature. The catalyst can be recycled for seven times and reused catalyst was characterized by TEM and XPS.

Introduction

Aromatic amines are important class of molecules present in pharmaceutical drugs, natural products, and agrochemicals. In addition, anilines are important starting material for the synthesis of a wide variety of organic molecules.^[1] One of the common methods for synthesizing amines is through the reduction of corresponding nitro compounds. Traditional methods such as Bechamp reduction suffer from several drawbacks such as low efficiency, costly steam distillation and production of a large number of waste.^[2] In recent years, transition metal catalyzed reduction of nitro compounds using various reducing agents is a straightforward protocol for the production of amines.^[3] Amongst the different transition metals, palladium is very efficient for the

selective reduction of nitro compounds to amines. There are a considerable number of homogeneous and heterogeneous palladium catalysts which have been reported for performing nitroarenes reduction.^[4] However, due to high price and toxicity of palladium and probability of product contamination with Pd which has ≤ 5 ppm allowance, there is a growing demand for using high TON and recyclable catalysts.^[5] Along with this line for green chemistry standpoints, the use of naturally occurring compounds and materials are highly desirable for design and synthesis of heterogeneous catalysts.^[6] Clay minerals having different properties such as cheap price, high surface area, mechanical and thermal stability, and ion exchange ability are among the promising supports for the preparation of heterogeneous catalysts. Bentonite is one of the wide families of clay materials which is the result of the devitrification and chemical variation of glassy volcanic ash or tuff. Bentonite is of great industrial importance for different applications such as binder in tablet manufacturing and in diarrhea medications, as filler in pharmaceuticals, wastewater purification, removal of impurities in oils, animal feed supplement, suspension agent in varnishes etc.^[7] Moreover, one of the important aspects of bentonite, include its application in catalytic process. Along with this line, chemically-modified bentonite supported transition metals are employed in different organic reactions. For achieving desired properties, different ligands are used for modification of this solid support and its following application for stabilization of transition metals.^[8]

Creatine is an amino acid containing a guanidine unit, which it is not a proteinogenic amino acid. Creatine can be attained in the food we eat (typically meat and fish) or formed endogenously in the body from the amino acids glycine, arginine, and methionine.^[9] In this work, we describe the use of creatine as a ligand for the modification of bentonite as green and naturally available solid and the resulting material is employed for the stabilization of Pd nanoparticles and applied as a heterogeneous catalyst in the reduction of nitroarenes.

Results and Discussion

The catalyst preparation steps are summarized in Scheme 1. Briefly, natural bentonite was treated with (3-chloropropyl) triethoxysilane in toluene under reflux condition to afford chloro functionalized bentonite, which was allowed to react with creatine in the presence of triethylamine in xylene at 130 °C affording bentonite-creatine (bento-crt). Finally, Pd NPs supported on creatine modified bentonite were easily obtained by dissolving

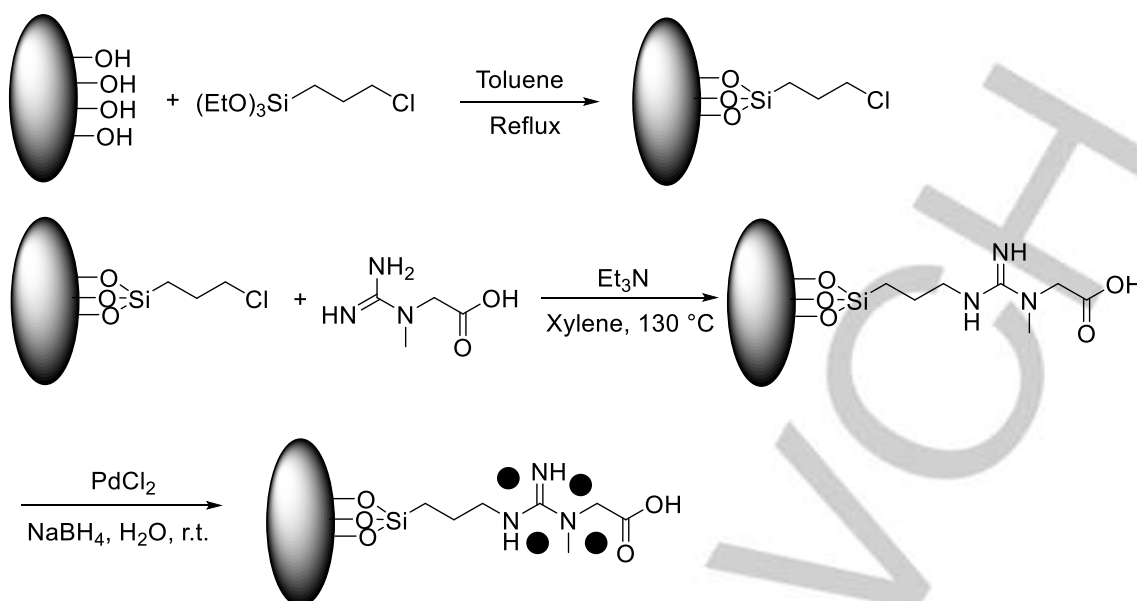
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and sonicating PdCl₂ in water followed by treating with bento-crt. Using atomic absorption spectroscopy (AAS), the loading of Pd

was found to be 0.08 mmol/g. This new material is referred to as **bento-crt@Pd** throughout the text of this article.



Scheme 1. The synthetic route toward the **bento-crt@Pd**.

In order to confirm the successful attachment of creatine to bentonite, structure of creatine, bentonite, and bento-crt were studied by Fourier-transform infrared spectroscopy (FT-IR). Results indicated sharp absorption peak at 1696 cm⁻¹ related to C-O stretching vibrations of carboxylic acid in creatine as well as in bento-crt. In addition, an absorption peak related to C-N stretching vibrations of guanidine at 1615 cm⁻¹ and peak related to NH stretching vibrations centered at 3339 cm⁻¹ were observable in both creatine and bento-crt, indicating successful grafting of creatine. Also, an absorption peak at 2786 cm⁻¹ is related to vibrations of the C-H bonds of the methyl group (Figure 1).^[10]

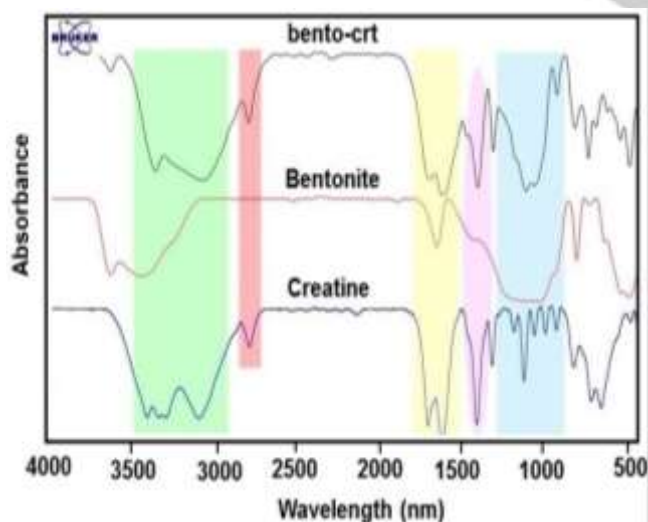


Figure 1. FT-IR spectra of creatine, bentonite and bento-crt.

Thermogravimetric analyses (TGA) of bentonite@Cl and bento-crt were studied between 25 and 800 °C. TGA measurements for **bento-crt** showed prominent increasing of weight loss between 150-800 °C due to the addition of creatine as an organic group (Figure 2).

The BET surface area decreased in bentonite@Cl (238.627 m²/g) compared with **bento-crt** (24.032 m²/g) which may be attributed to the possibility that the pores of bentonite@Cl covered by creatine.

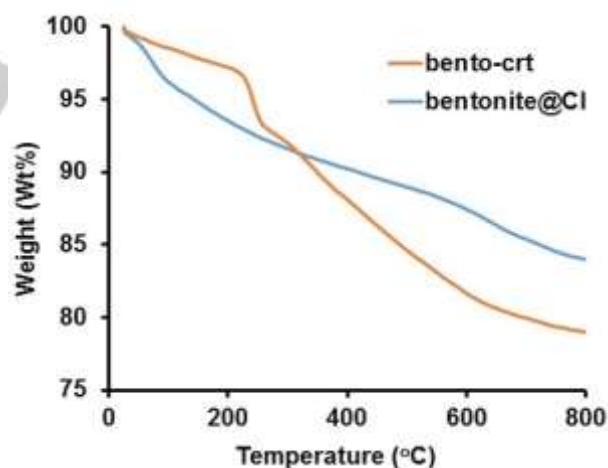


Figure 2. Thermogravimetric diagrams of bentonite@Cl, bento-crt.

Solid state UV-vis spectra of palladium chloride and **bento-crt@pd** were also studied (Fig. 1, ESI). The reduction of Pd(II) to

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Pd(0) in **bento-crt@Pd** was confirmed by the disappearance of a peak at 280 nm corresponding to Pd(II) species.^[11]

The corresponding scanning electron microscope (SEM) images of **bento-crt@Pd** at different magnifications showed the presence of Pd nanoparticles (bright dots) stabilized on clay

layers (Fig. 2, ESI). Also, transmission electron microscope (TEM) images of **bento-crt@Pd** in different magnifications indicate incorporation of uniformly dispersed Pd NPs with the calculated average size of 3.1 nm (Figure 3).

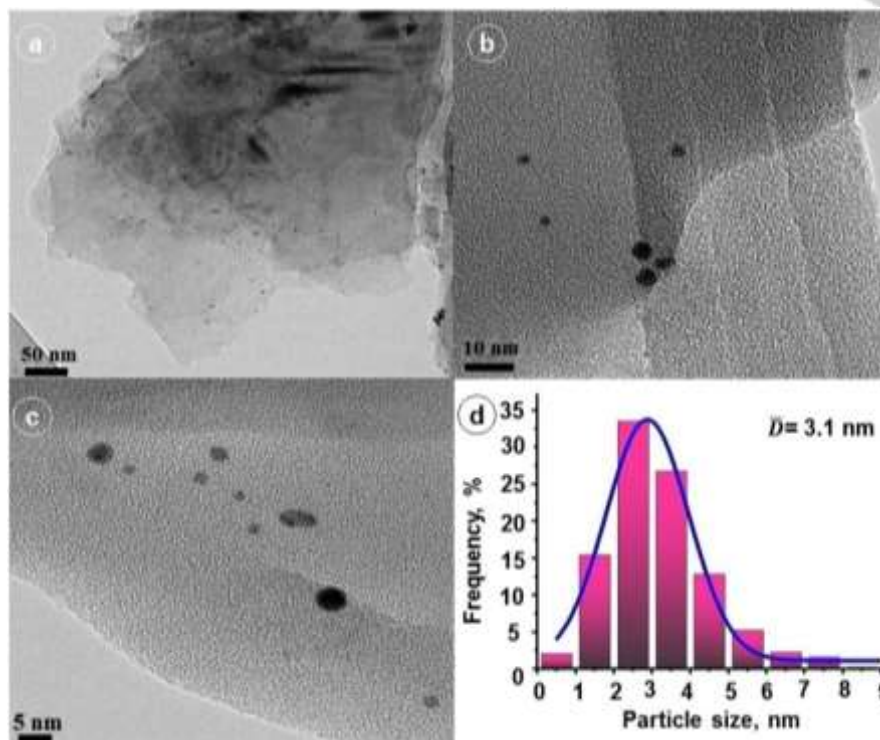


Figure 3. TEM images of **bento-crt@Pd** in different magnification (a-c). The solid curve is Gaussian fit to the data (d).

X-ray diffraction (XRD) analysis of the **bento-crt@Pd** showed the Bragg's reflections related to bentonite^[12] at $2\theta = 20, 22, 27.9, 35.4, 62$ and also the presence of Pd(0) based on the Bragg's reflections related to palladium^[13] that appeared at $2\theta = 40.2, 46.7$ and 68.2 (Figure 4).

Energy dispersive X-Ray spectroscopy (EDS) obtained from SEM analysis confirmed the presence of bentonite elements as well as N and Pd (Table 1 in ESI) in the structure of the **bento-crt@Pd** (Figure 5).

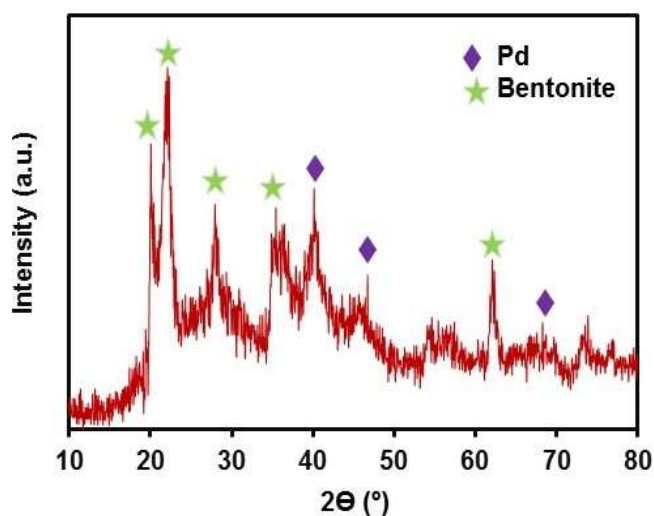


Figure 4. XRD pattern of **bento-crt@Pd**.

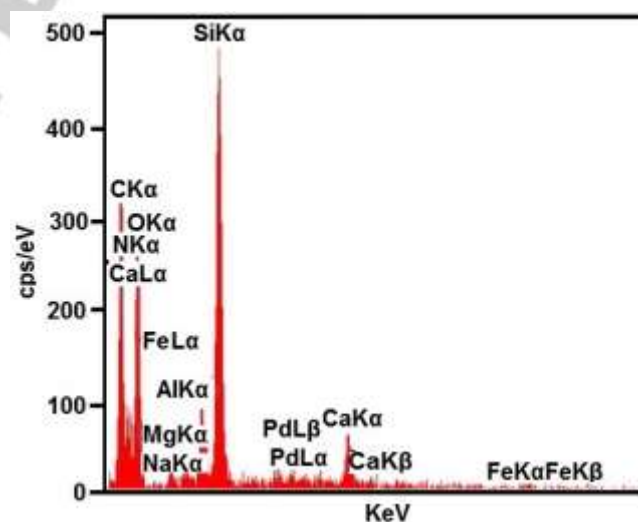


Figure 5. EDS spectrum of **bento-crt@Pd**.

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X-ray photoelectron spectroscopy (XPS) of bentonite@Cl in Mg, Na, Ca, Al, Si, Cl, C, and O were studied. The XPS spectrum of Mg 1s showed a peak at 1302 eV confirming the presence of Mg(II) in the structure of bentonite (Figure 6a).^[14] The binding energy observed for Na 1s is 1071.9 eV, which is characteristic of Na(I) oxidation state (Figure 6b).^[15] Furthermore, XPS spectrum in the Ca 2p region confirm the presence of Ca(II) with showing a doublet peak located at 347 and 350.5 eV (Figure 6c).^[16] Presence of Al(III) in the structure was confirmed with appearing two peaks at 73.6 and 74.2 eV related to Al 2p (Figure 6d).^[17] The binding energy of Si 2p appears at 101.9 and 102.7 eV, which are related to the Si-O bond (Figure 6e).^[17b] XPS spectrum in Cl 2p region show two peaks center at 200.4 and 201.78 eV corresponding to Cl 2p_{3/2} and Cl 2p_{1/2} (Figure 6f).^[18] In addition, peaks located at 284.7, 287.08 and 287.7 eV were related to C 1s orbital in C–C/C–H, C–O/C–Cl and O–C–O forms, respectively (Figure 6g).^[19] XPS spectrum in O 1s region showed three peaks between 529.0–533.0 related to oxygen of metal oxides in clay structure (Figure 6h).^[20]

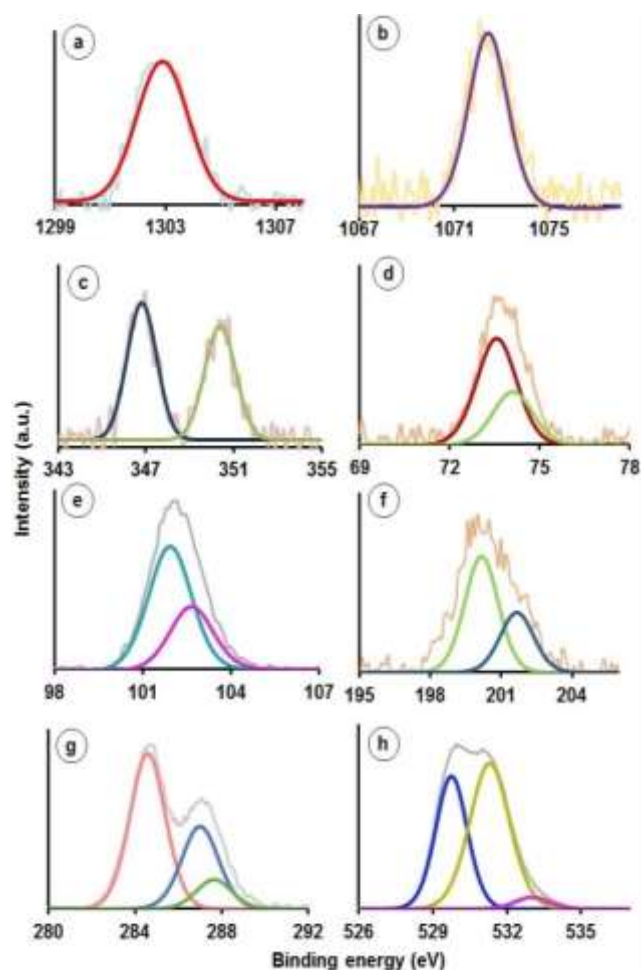


Figure 6. XPS spectrum of bentonite@Cl in a) Mg 1s, b) Na 1s, c) Ca 2p, d) Al 2p, e) Si 2p, f) Cl 2p, g) C 1s, and h) O1s regions.

In order to confirm the addition of creatine, XPS spectrum of a region of N 1s was studied, and results showed an intense peak at 400 eV related to the nitrogen of creatine (Figure 7a).^[21] The

XPS spectrum in the Pd 3d region showed the presence of two intense doublets at 335.6 and 340.9 eV related to Pd(0) and peaks at 337.7 and 342 eV related to Pd(II) corresponding to Pd 3d_{5/2} and Pd 3d_{3/2}, respectively (Figure 7b).^[22]

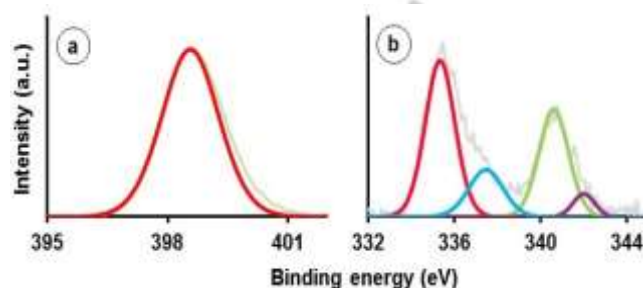
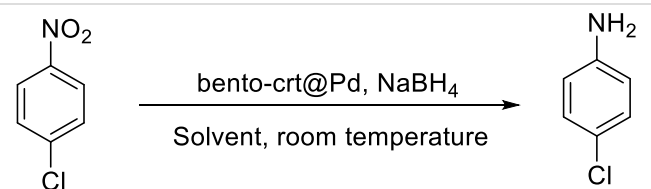


Figure 7. XPS spectrum of **bento-crt@Pd** in a) N 1s, b) Pd 3d.

Catalytic activity of **bento-crt@Pd** was evaluated in reduction of nitroarenes. In order to find optimized reaction conditions, reduction of 1-chloro-4-nitrobenzene as a model reaction was selected and effect of different factors such as catalyst amount, solvent, time and reducing agent were studied (Table 1). Using 0.04 mol% of Pd in different solvents such as H₂O, EtOH, THF, DMF, DMSO, 1,4-dioxane, PEG200, isopropanol, and acetone gave poor to low yields in 30 min (Table 1, entries 1-9). However, using an equal mixture of EtOH-H₂O afford 25% GC yield for the desired 4-chloroaniline product (Table 1, entry 10). By increasing reaction time to 45 and 60 min, 33 and 71% yields were obtained, respectively (Table 1, entries 11-12). Then, the catalyst amount was increased to 0.06 and 0.1 mol% and the progress of the reaction at different times were studied (Table 1, entries 13-15). Results indicated that using 0.1 mol% catalyst in 30 min afforded quantitative yield for the reaction (Table 1, entry 15). With decreasing reaction time to 20 and 15 min, yields dropped to 69 and 50% respectively (Table 1, entries 16-17). Therefore, we selected 0.1 mol% of Pd loading, EtOH-H₂O (1:1) as solvent, NaBH₄ as a reducing agent at room temperature during 30 min as the best-optimized reaction conditions (Table 1, entry 15). It is worth mentioning that in the absence of catalyst or NaBH₄ the reaction did not proceed (Table 1, entries 18 and 19). Also, it should be noted that using other reducing agents such as formic acid, ammonium formate, hydrazine, glycerol, and isopropyl alcohol gave lower yields than NaBH₄ (Table 2 in ESI).

Table 1. Optimization of the reaction conditions for the reduction of 1-chloro-4-nitrobenzene^[a].



Entry	Solvent	Pd (mol%)	Time (min)	Yield (%) ^[b]
1	H ₂ O	0.04	30	10
2	Ethanol	0.04	30	5

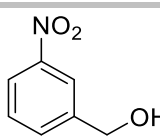
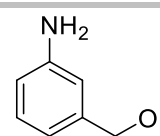
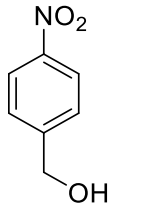
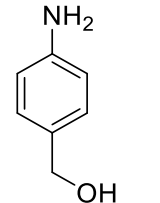
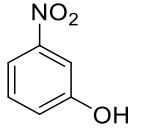
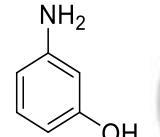
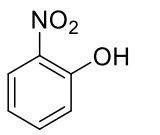
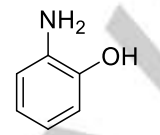
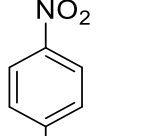
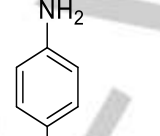
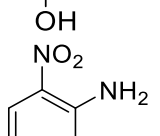
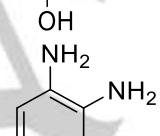
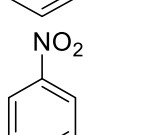
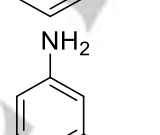
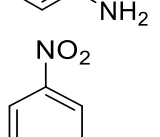
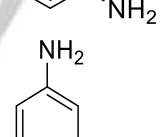
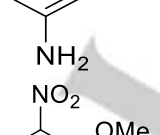
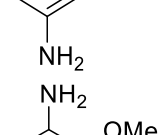
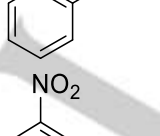
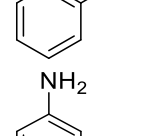
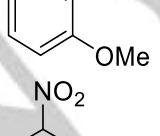
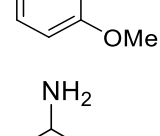
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3	THF	0.04	30	<1	18	H ₂ O:EtOH	-	30	<1
4	DMF	0.04	30	<1	19	H ₂ O:EtOH	0.1	30	5 ^[c]
5	DMSO	0.04	30	<1	[a] 1-Chloro-4-nitrobenzene (0.5 mmol), NaBH ₄ (2 mmol), solvent (1.5 mL), at room temperature. [b] Yields determined by GC. [c] Reaction run in the absence of NaBH ₄ .				
6	1,4-Dioxane	0.04	30	<1					
7	PEG200	0.04	30	4					
8	Isopropyl alcohol	0.04	30	<1	Having the optimized reaction conditions in hand, reduction of structurally different nitroarenes having electron-donating groups such as -OH, -Me, -CH ₂ OH, -NH ₂ , -OMe, as well as nitrobenzene and 1-nitronaphthalene were performed efficiently giving the corresponding anilines in high to excellent yields (Table 2, entries 1-17). In addition, reduction of nitroarenes having electron-withdrawing groups afforded the corresponding anilines in excellent yields (Table 2, entries 18-28). In the case of nitroarenes having a formyl function, both nitro and aldehyde groups were reduced to amine and alcohol groups, respectively (Table 2, entries 25-27). The scale-up of this reaction was carried out with 1-chloro-4-nitrobenzene up to 15 mmol, NaBH ₄ (60 mmol) and catalyst (210 mg) under optimized reaction conditions. This process took place in 90% isolated yield.				
9	Acetone	0.04	30	<1					
10	H ₂ O:EtOH	0.04	30	25					
11	H ₂ O:EtOH	0.04	45	33					
12	H ₂ O:EtOH	0.04	60	71					
13	H ₂ O:EtOH	0.06	30	83					
14	H ₂ O:EtOH	0.06	45	92					
15	H ₂ O:EtOH	0.1	30	>99					
16	H ₂ O:EtOH	0.1	20	69					
17	H ₂ O:EtOH	0.1	15	50					

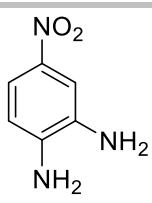
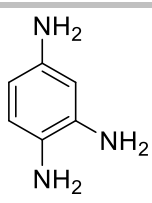
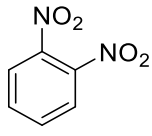
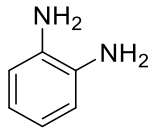
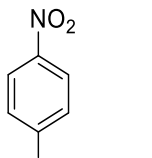
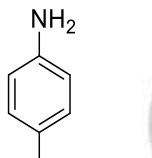
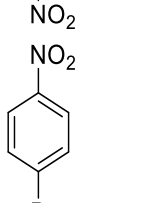
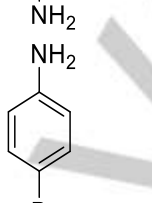
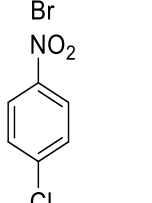
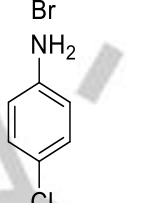
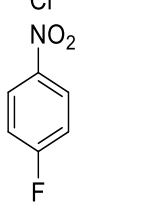
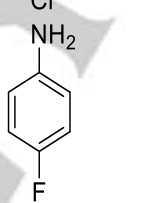
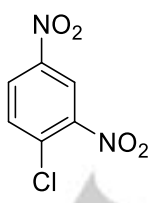
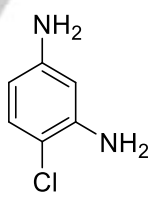
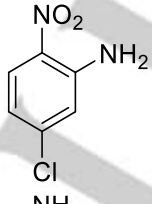
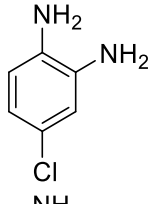
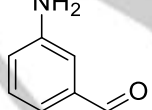
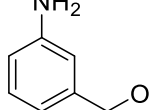
Table 2. Reduction of structurally different nitroarenes using **bento-crt@Pd**^[a].

Entry	Reactant	Time (min)	Product	Yield (%) ^[b]
1		30		99 ^[c]
2		60		90
3		30		93
4		30		85
5		30		90

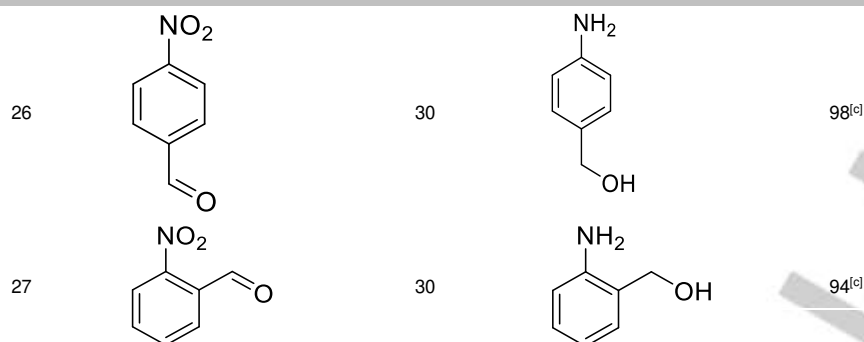
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6		30		93
7		30		95
8		30		88
9		45		84
10		30		90
11		60		99 ^[c]
12		30		96 ^[c]
13		30		92 ^[c]
14		60		88 ^[c]
15		60		95 ^[c]
16		30		99 ^[c]

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17		30		90
18		180		95
19		60		86
20		30		95 ^[c]
21		30		>99 ^[c]
22		30		90 ^[c]
23		60		92
24		30		93
25		30		96 ^[c]

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[a] Nitroarene (0.5 mmol), **bento-crt@Pd** (7 mg, 0.1 mol%), NaBH₄ (2 mmol), H₂O: EtOH (1:1, 1.5 mL), at room temperature.

[b] Isolated yield.

[c] Yield determined by GC.

In order to assess the recycling ability of this novel bentonite supported palladium catalyst, reduction of 1-chloro-4-nitrobenzene under the optimized reaction conditions was studied. For this purpose, in each cycle the heterogeneous catalyst was easily separated using centrifugation, washed with ethanol and used directly for a subsequent round of the reaction. The catalyst was recyclable for at least seven consecutive times with small drops in its catalytic activity (Figure 8). Leaching study of Pd from the catalyst during three recycling steps indicated that very small amount of Pd (0.4-1.5%) was leached conforming important role of creatine in the stability of the catalyst (Table 3).

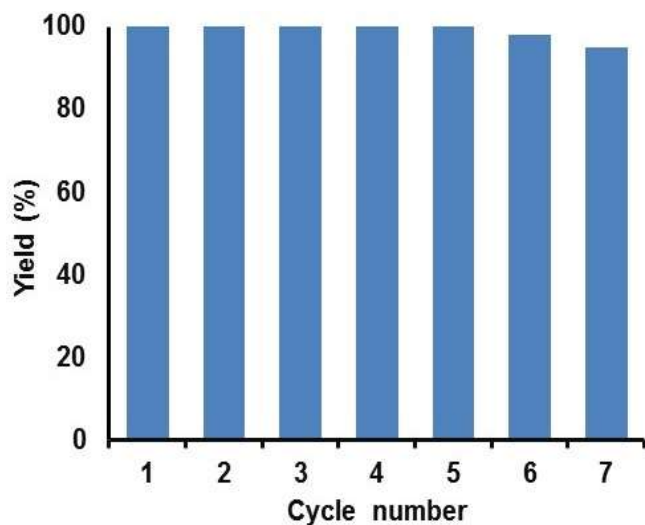
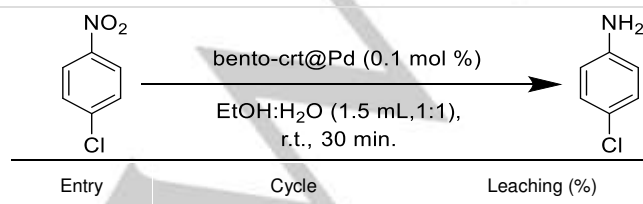


Figure 8. Recycling of the catalyst, **bento-crt@Pd**, for the reduction of 1-chloro-4-nitrobenzene.

Table 3. Leaching of Pd from the catalyst in the reduction of 1-chloro-4-nitrobenzene.^[a]



1	First cycle	0.4
2	Second cycle	0.9
3	Third cycle	1.5

[a] 1-Chloro-4-nitrobenzene (0.5 mmol), **bento-crt@Pd** (7 mg, 0.1 mol%), NaBH₄ (2 mmol), solvent (1.5 mL), at room temperature.

SEM images of the reused catalyst after the 7th run exhibited the morphology and structure of the catalyst have been preserved during the reaction (Fig. 3, ESI). In addition, TEM images of reused catalyst showed preservation of structure and the presence of Pd NPs in very slightly aggregate form and bigger size than fresh catalyst (Figure 9). XPS study in N 1s region showed also structure preservation and a very similar pattern to fresh catalyst. However, in the case of Pd 3d region showed that during the recycling of Pd(II) species all of them were reduced to Pd(0) (Figure 10).

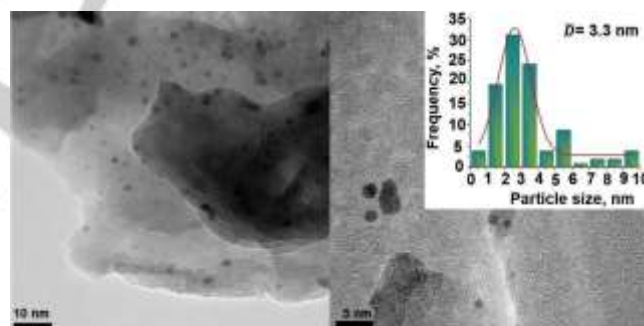


Figure 9. TEM images of reused catalyst **bento-crt@Pd** after 7 runs.

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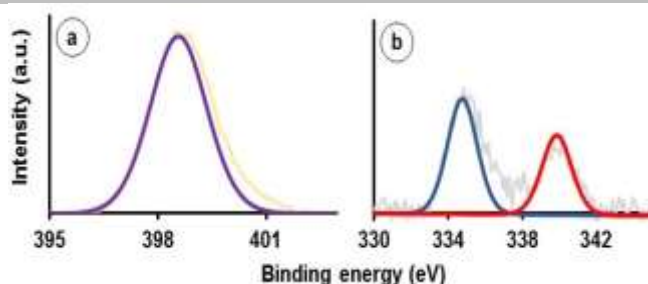


Figure 10. XPS images of reused catalyst **bento-crt@Pd** in N and Pd regions.

In order to show the effect of creatine in the stabilization of Pd NPs in the catalyst, we prepared bentonite supported Pd NPs in the absence of creatine via direct treating of bentonite with PdCl₂ and NaBH₄. TEM images of bentonite supported Pd indicated formation of uninform and almost aggregate Pd NPs (Fig. 4, ESI). Catalytic and recycling abilities of this material were examined in the reduction of 1-chloro-4-nitrobenzene. Results indicated using 0.1 mol% of this catalyst, corresponding amine product was obtained in 90%. However, in runs 2 and 3, yields decreased dramatically to 14 and 7% indicating leaching and deactivation of Pd during the recycling process (Figure 11).

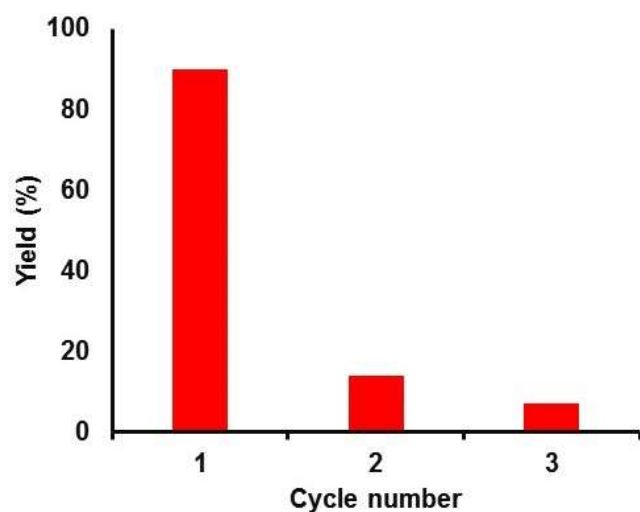


Figure 11. Recycling of the bentonite supported Pd for the reduction of 1-chloro-4-nitrobenzene.

Conclusions

In conclusion, we have prepared creatine modified bentonite supported Pd NPs, **bento-crt@Pd**. This new material has been applied as a sustainable catalyst in the reduction of aromatic nitro compounds. Using this Pd catalyst structurally different nitroarenes were selectively reduced in aqueous media, and corresponding amines were achieved in high to excellent yield at room temperature. This catalyst can be easily recovered by separation with a centrifuge and reused for at least seven cycles without noticeable detriment to its catalytic activity. The fresh and reused catalyst was characterized using different techniques.

Experimental Section

General remarks

All materials were purchased from Sigma-Aldrich, Across and Merck Millipore. Reactions were monitored by gas chromatography in a Varian CP-3800 apparatus. ¹H NMR spectra were recorded at 400 MHz on a Bruker Avance HD apparatus in DMSO-d₆. Chemical shifts are given on the δ-scale in ppm, and residual solvent peaks were used as internal standards. X-ray photoelectron spectroscopy (XPS) analyses were performed using a K-Alpha spectrometer. XRD patterns were recorded using a Philips X'Pert Pro instrument. Fourier transform-infrared (FT-IR) studies of samples were performed using a FT-IR spectrophotometer Bruker vector 22, by preparing their KBr pellets from 400 to 4000 cm⁻¹. The transmission electron microscopy (TEM) and scanning electron microscopy (SEM) mapping images were captured with EOL JEM-2010 and Hitachi S3000 N. The weight loss of samples was measured using a thermogravimeter NETZSCH STA 409 under an O₂ flow rate of 20 ml min⁻¹ with a heating rate of 10°C min⁻¹ from 30 to 800 °C. Digital images of the samples were acquired with Hitachi S4160 FE-SEM apparatus operating at 20 kV. Energy dispersive X-ray analysis (EDX) results were obtained using Carl Zeiss Sigma instrument. BET surface area of samples were measured using QUANTACHROME Poremaster 60 GT instrument.

Procedure for the preparation of bento-crt

In 50 mL flask, bentonite (2.6 g) was sonicated in dry toluene (30 mL) for 15 min. Then, (3-chloropropyl)triethoxysilane (10 mmol, 2.4 mL) was added and the mixture was refluxed at 110 °C for 24 h under argon atmosphere. Afterward, the solid was separated by centrifugation, washed with ethyl acetate (3×10 mL) and dried in an oven at 60 °C affording bentonite@Cl. In the next step, in a 25 mL flask, bentonite@Cl (2.5 g) was sonicated in xylene (30 mL) for 15 minutes, and creatine (10 mmol, 1.3 g) and Et₃N (20 mmol, 2.8 mL) were added. The reaction mixture was stirred at 130 °C for 24 h. Then, the reaction mixture was subjected to centrifugation and for ensuring removing of unreacted creatine, resulting solid (bento-crt) was washed with H₂O (10×20 mL) and EtOH (3×10 mL) and dried in an oven at 80 °C.

Procedure for the preparation of creatine modified bentonite Pd NPs (bento-crt@Pd)

Bento-crt (1 g) was sonicated in THF (10 mL), and sonically assistance PdCl₂ (0.1 mmol, 18 mg) in H₂O (5 mL) was added. Then, NaBH₄ (1 mmol, 37 mg) in H₂O (1 mL) was added slowly, and the resulting mixture was stirred for 24 h at room temperature. Then, the reaction mixture was subjected to centrifugation and resulting solid was washed with H₂O (2×10 mL) and ethyl acetate (3×5 mL) to remove unreacted materials and dried in an oven at 70 °C.

Procedure for the preparation of Bentonite supported Pd

Sonically assisted PdCl₂ (0.1 mmol, 18 mg) in H₂O (5 mL) was added to a stirring flask containing bentonite (1 g) and THF (10 mL). Then, NaBH₄ (1 mmol, 37 mg) in H₂O (1 mL) was added slowly, and the resulting mixture was stirred for 24 h at room temperature. Afterward, the reaction mixture was subjected to centrifugation and resulting solid was washed with H₂O (10 mL) and ethyl acetate (3×5 mL) to remove by-products and unreacted materials and dried in an oven at 70 °C.

General procedure for the reduction of nitroaromatic using bento-crt@Pd

To a 5 mL flask containing **bento-crt@Pd** (7 mg containing 0.1 mol% Pd), nitroarene (0.5 mmol), NaBH₄ (2 mmol, 75 mg) and 1:1 mixture of H₂O:

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EtOH (1.5 mL) were added. The reaction mixture was stirred at room temperature for the appropriate reaction times, and the progress of the reactions was monitored by GC, TLC and or ¹H NMR. After completion of the reaction, the crude product was extracted with ethyl acetate (3×5 mL) and further purified using column or plate chromatography.

Acknowledgements

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Keywords: Amino acids • clays • heterogeneous catalysis • palladium • nitro reduction

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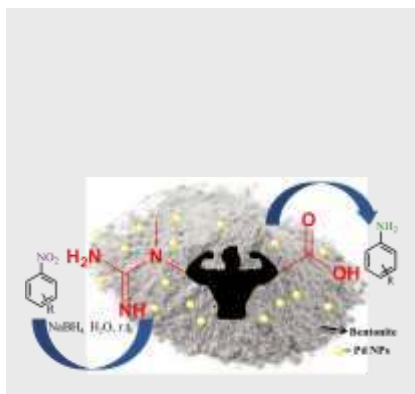
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Entry for the Table of Contents

Layout 1:

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A new sustainable Pd catalyst comprising Pd NPs supported on creatine modified bentonite has been developed for the reduction of nitroarenes.



Mohammad Gholinejad, Zahra Rasouli, Carmen Nájera, and José M. Sansano

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Palladium Nanoparticles on a Creatine-Modified Bentonite Support: An Efficient and Sustainable Catalyst for Nitroarene Reduction