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Palladium-modified functionalized cyclodextrin as an efficient and recyclable catalyst for reduction of nitroarenes†

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A palladium-modified functionalized cyclodextrin (DACH-Pd-β-CD) catalytic system was synthesized and characterised. It showed high catalytic performance in the reduction of different nitroarenes to the corresponding anilines with the presence of sodium borohydride in water at room temperature. The yields of the desired products are up to 99%. Furthermore, the catalyst can be easily separated and still could maintain high catalytic activity after five cycles and no leaching of Pd into solution occurred.

Aromatic amines are a significant class of compounds which are widely used as organic intermediates in the preparation of dye polymers, pharmaceuticals, agrochemicals and natural products.[1] The most common and conventional route for preparing the aromatic amines is through the reduction of corresponding nitroarenes using the method of catalytic hydrogenation.[2] In the progress of catalytic hydrogenation, mental catalysts are very important. Common metal catalysts include noble metals (Pt, Ru, Rh and Pd) and non-noble metals (Fe, Co, Ni, Cu and Zn).[3] It shows that there are many disadvantages to using them from previous studies, such as high H_2 pressure, long reaction time, low yield, high temperature and serious environmental pollution.[4] It is well known that the traditional catalyst for reduction nitroarenes is Fe–HCl system. However, the catalytic system exerts many disadvantages, such as poor yield, larger iron dosage and Fe–FeO sludge.[5]

In recent years, the concept of "Green and Sustainable Chemistry" has been accepted by more and more researchers of modern organic synthesis.[6] More efficient and recyclable catalysts are needed for the reduction of nitroarenes. Many reports revealed that noble metals nanoparticles, such as Pt/C, Rh and Pd/C, usually have excellent activity for reduction of nitroarenes under the atmosphere of H_2.[7] In addition, the reducing agent of hydrazine, silanes and sodium borohydride play a significant role in the reduction reactions as hydrogen donors.[8]

Palladium is a great transition metal for reduction of nitroarenes, which has been successfully used in different catalytic forms, such as Pd–polymer, Pd–silicon hydride, Pd/C nanofiber and so on.[9] These Pd catalysts show a great catalytic performance for chemoselective reduction reaction of nitroarenes. On the other hand, they can be used repeatedly for many times and still maintain excellent catalytic performance. Moreover, the Pd catalysts are often used together with $NaBH_4$ in the reduction of nitroarenes.[10] $NaBH_4$ has less ability and chemical selectivity while reducing nitroarenes to corresponding amines in the absence of metals and the reactions usually stay at intermediate stage of azo, azoxy, and hydrazo.[11] Hence, lots of work had been done by our team to explore some water-soluble and recyclable Pd complexes so as to achieve their catalytic activity with $NaBH_4$ for reduction of nitroarenes in water.

Due to the special structure of lipophilic central cavity and hydrophilic outer surface of cyclodextrin (CD), the water solubility of CD is excellent which can provide a lipophilic microreactor for organic molecules in water. In addition, it was reported that cyclohexanediamine (DACH) as a perfect ligand could successfully complex with several metals, such as Pt and Pd.[12]

In this paper, a palladium-modified functionalized cyclodextrin (DACH-Pd-β-CD) was synthesized and characterized by NMR, XRD, TEM and EDS. The catalytic activity and the recyclability for the reduction of nitroarenes in the presence of $NaBH_4$ in water were researched. Moreover, the leaching experiment was carried out.

The TEM images of DACH-β-CD (Fig. 1A, 100 nm), DACH-Pd-β-CD and its histogram for particle size distribution (Fig. 1B, 200 nm) as well as HR-TEM image of DACH-Pd-β-CD (Fig. 1C) are shown in Fig. 1. The sample was onto a piece of copper grid and dried at room temperature under vacuum. Comparing with Fig. 1A and B, many black spots appeared to be observed in

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† Electronic supplementary information (ESI) available: Experimental details, characterizations, NMR, XRD, EDS, FT-IR, HR-MS and TG spectra, and measurements. See DOI: 10.1039/c5ra23271f

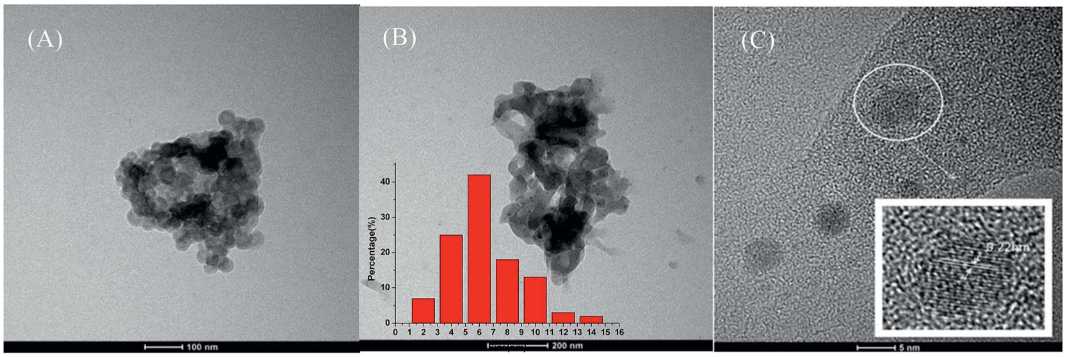
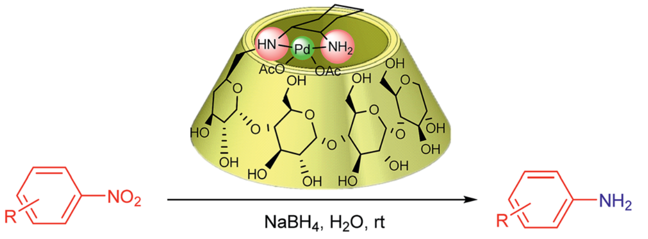


Fig. 1 TEM image: (A) DACH-β-CD at 100 nm (B) DACH-Pd-β-CD at 200 nm (C) HR-TEM image of DACH-Pd-β-CD at 5 nm.

Fig. 1B, but not in Fig. 1A. The result may indicate that the formation of the catalyst. In order to count the size of particles, we enlarged the image (Fig. S11†) and the histogram inserted in Fig. 1B. The average diameter of the particles was 6 ± 0.5 nm. In order to further demonstrate the presence of Pd, the HR-TEM image of DACH-Pd-β-CD was presented (Fig. 1C). The average interplanar distance of DACH-Pd-β-CD was measured to be ~0.22 nm, which corresponds well to the plane of Pd. Moreover, the present of Pd was also demonstrated by means of EDS (Fig. S4†) and XRD (Fig. S3†). The detailed synthetic steps and other characterization results are in ESI.†

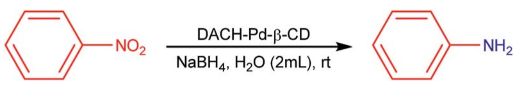
Owing to study the catalytic activity of DACH-Pd-β-CD, different nitroarenes, DACH-Pd-β-CD and $NaBH_4$ were employed in water in a sealed tube at room temperature (Scheme 1). Preliminary investigation of the reduction of nitrobenzene was carried out to optimise the reaction conditions (Table 1). At first, DACH-Pd-β-CD was absent and the usage of $NaBH_4$ ranged from 3 to 10 equiv. (entries 1–3). However, the yields were very low from 5–12%. Without $NaBH_4$, no products were detected (entries 4–6). The result indicated that $NaBH_4$ had less ability and chemical selectivity to reduce nitroarenes to the corresponding amines in the absence of DACH-Pd-β-CD. Then, the consumption of $NaBH_4$ was fixed (3 mmol) and the amount of DACH-Pd-β-CD was gradually increased from 0.1 to 5 mol% (entries 7–10). The results showed that the yields of aniline are up to 99% when DACH-Pd-β-CD is from 0.5 to 5 mol% and a dosage of more than 0.5 mol% did not cause a distinct increase yields. In addition, the usage of $NaBH_4$ is also very crucial. From entries 10–12 and 8, the optimization is 3 equiv. Considering the influence of reaction time, the yields were studied after 0.5 h, 1 h and 3 h (entries 14 and 15, 8). As a result, the reaction could complete during 3 h.

In order to further explored the effect of other reduction agents, H_2 (1 atm, entry 16) and hydrazine hydrate (entry 17) was used. The results showed that the condition of H_2 was significant which could lead to an excellent yield of 95%. However, under the same conditions, the yield was only 8% by using hydrazine hydrate. Then using the open vessel instead of sealed tube and the other conditions did not change, there was only 38% aniline obtained (entry 18). So it



Scheme 1 Reduction of nitroaromatic catalyzed by DACH-Pd-β-CD.

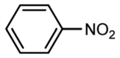
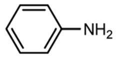
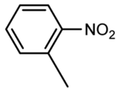
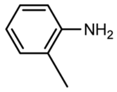
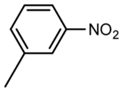
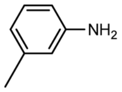
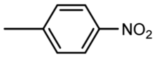
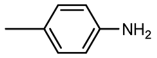
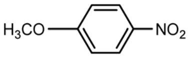
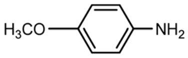
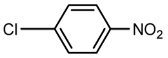
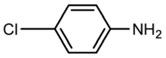
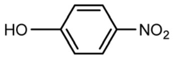
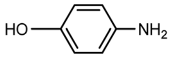
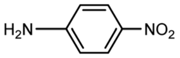
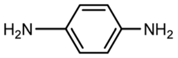
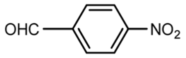
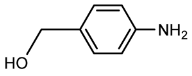
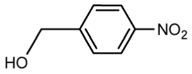
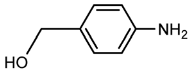
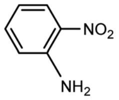
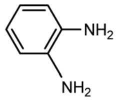
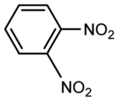
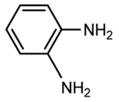
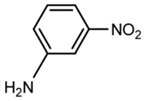
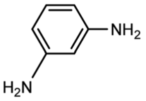
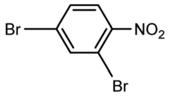
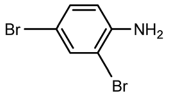
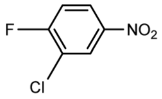
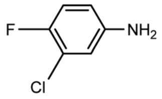
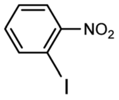
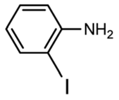
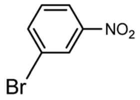
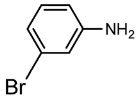
Table 1 Optimization of the reaction conditions[a]



Entry	DACH-Pd-β-CD (mol%)	$NaBH_4$ (eq.)	Time (h)	Yield[b] (%)
1	—	3	3	5
2	—	3	12	8
3	—	10	3	12
4	1	—	3	—
5	5	—	3	—
6	10	—	5	—
7	0.1	3	3	52
8	**0.5**	**3**	**3**	**99**
9	1	3	3	99
10	5	3	3	99
11	0.5	1	3	63
12	0.5	5	3	99
13	0.5	10	3	98
14	0.5	3	0.5	82
15	0.5	3	1	93
16[c]	0.5	—	8	95
17[d]	0.5	—	6	8
18[e]	0.5	3	6	38
19[f]	0.5	3	3	96

[a] Reaction conditions: 1.0 mmol of nitrobenzene (0.123 g, 0.102 mL), given amounts of DACH-Pd-β-CD and $NaBH_4$ were stirred in a sealed tube (2 mL H_2O) at room temperature for the appropriate amount of time. [b] Isolated yields. [c] Reaction carried out under H_2 (1 atm) in the absence of $NaBH_4$. [d] Hydrazine hydrate was used. [e] The open vessel conditions have been carried out. [f] 10 mmol of nitrobenzene (1.23 g, 1.02 mL), 30 mmol $NaBH_4$ (1.135 g) and 20 mL H_2O.

Table 2 Reduction of various nitroarenes catalyzed by DACH-Pd-β-CD[a]

Entry	Reactant	Product	Yield[b] (%)	Select[c] (%)
1			99	99
2			99	99
3			99	99
4			99	99
5			99	99
6			96	98
7			98	96
8			95	97
9			99	96
10			96	98
11			96	93
12			93	95
13			95	96
14			94	98
15			96	96
16			98	96
17			93	97

[a] Reaction conditions: 1.0 mmol nitroarene, 3 mmol of $NaBH_4$ (0.1135 g), 0.5 mol% DACH-Pd-β-CD (11.9 mg, containing 4.5%$_w$ Pd), 2 mL water, 3 h at room temperature. [b] Isolated yields. [c] Selectivity were determined by GC.

was necessary to complete the reduction reaction with the sealed condition. To test the practical application of the catalyst, a higher scale was very necessary. Then we enlarged each quality of the reactants to ten times and the yield was up to 96% (entry 19).

As a consequence, the optimum reaction conditions are nitrobenzene (1 mmol), DACH-Pd-β-CD (0.5 mol%), $NaBH_4$ (3 mmol), 3 h reaction time and H_2O (2 mL) in the sealed tube at room temperature.

A series of nitroarenes were used to further explore the generality of catalytic performance of DACH-Pd-β-CD in Table 2. To ensure the high yields and chemical selectivity of substances, the reactions were performed in the optimum conditions (Table 1, entry 8).

The general experimental procedure is that 1.0 mmol of nitroarenes, 3 mmol of $NaBH_4$ (0.1135 g) and 0.5 mol% DACH-Pd-β-CD (11.9 mg, containing $4.5\%_w$ Pd) were added in a sealed tube with 2.0 mL H_2O. The mixture was stirred at room temperature for 3 h and monitored by TLC. After the reaction completion, the aqueous phase was extracted with ethyl acetate for 3 times (3 × 5 mL). Then the combined organic layers were dried by anhydrous $MgSO_4$ and the crude product was further purified by column chromatography.

At first, the influence of the position of substituents on the benzene ring had been explored. From entries 2–4, regardless of the methyl at *ortho*-, *meta*- or *para*-positions of nitroarenes, the catalytic system was found to be very efficient. The yields and chemical selectivity of corresponding products are about to 99%. Then the influence of electron-donating groups and electron-withdrawing groups was studied (entries 4–10). The consequence indicated that no matter the substrates were bearing electron-donating groups or electron-withdrawing groups, the yields were very high. While the other nitroarenes with functional groups (entries 11–17), DACH-Pd-β-CD still showed strong activity. All the results reveal that the catalytic system DACH-Pd-β-CD/$NaBH_4$ possesses strong catalytic activity to reduce nitroarenes.

Besides reusability is also an important factor in heterogeneous catalytic systems. The recycling experiment was conducted with the optimization reaction conditions in Table 1 (entry 8). After every cycle, 3 × 5 mL ethyl acetate was added to separate the organic phase and the aqueous phase was used in the next run with adding 3 mmol $NaBH_4$. The recycling results are shown at Fig. 2. In the first cycle, the yield was 99% and the catalytic system DACH-Pd-β-CD/$NaBH_4$ still behaved high catalytic activity with a yield of 93% after five cycles. The detailed progress of separation and reusing of catalyst was mentioned in the ESI.† Furthermore, the content of Pd in the product was determined by ICP-OES and no leaching of Pd was detected.

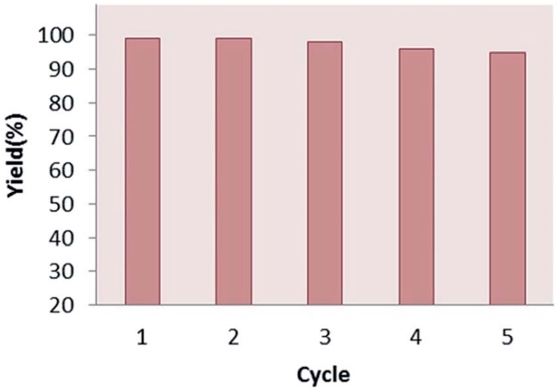


Fig. 2 Recyclability of DACH-Pd-β-CD in the reduction of nitrobenzene in H_2O.

During the reaction, $NaBH_4$ was excess and there was quantitative H_2. Therefore, the state of palladium metal in the reaction was easily reduced from Pd(II) to Pd(0). It is possible that Pd(0) played an important role in the reduction reaction.

It is reported that the possible mechanism for the reduction of nitrobenzene may go through the formation of intermediate III (hydroxylamine) and then the aniline (route A) as well as the formation of intermediates IV, V and VI (route B) (Fig. 3).[10] The major route (route A) through intermediates II and III is the preferred pathway for the reduction of nitroarenes promoted by Pd-based catalysts.[13] Another route (route B) is the unwished pathway which usually generates some azobenzene by-products which directly reduce the chemical selectivity of catalysts. During whole progress of the reduction of nitrobenzene by DACH-Pd-β-CD/$NaBH_4$ system, arylhydroxylamine (III) was the major intermediate (>99%) detected by TLC and the diazo-intermediate (V) was only in trace amounts. The concentration of intermediate III gradually decreased with time to yield the pure aniline and there were no by-products in the final product. Most importantly, the reaction probably happened in the cavity of DACH-Pd-β-CD in neat water. In order to prove the present of arylhydroxylamine (III), we tried best to isolate the pure intermediate III. However, the intermediate was close to aniline (product) on the TLC and it was difficult to be separated. On the other hand, the arylhydroxylamine (III) was easily to turn to aniline during the progress of isolation. Hence, the mixture of the intermediate and aniline were researched by ^1H NMR (Fig. S12†). In spite of the peaks of aniline, the other peaks of the intermediate were studied and it was true that the intermediate was compound III. The result suggested that the possible mechanistic pathway of nitroarene reduction is mainly through route A in the cavity of DACH-Pd-β-CD.

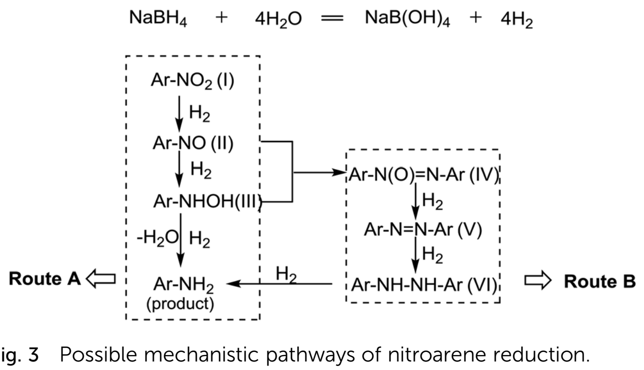


Fig. 3 Possible mechanistic pathways of nitroarene reduction.

Conclusions

In conclusion, the palladium-modified functionalized cyclodextrin catalytic system DACH-Pd-β-CD can efficiently promoted the reduction of nitroarenes in water at room temperature in the presence of $NaBH_4$. The yields of the desired products are excellent. What's more, the catalyst can be easily separated from the reaction media and still maintain high catalytic activity after five cycles. Furthermore, the Pd did not leach out in the solution during reaction. TEM analyses showed that the average diameter of the particles was 6 ± 0.5 nm. All the results indicate that DACH-Pd-β-CD/$NaBH_4$ is found to be an environmentally-friendly, efficient and recyclable catalytic system for the reduction of nitroarenes.

Acknowledgements

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