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Selective and Recyclable Rhodium Nanocatalysts for the Reductive N-Alkylation of Nitrobenzenes and Amines with Aldehydes

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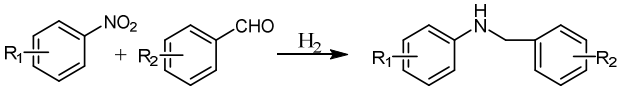
Rhodium nanocatalysts were prepared and applied for the reductive N-alkylation of nitrobenzenes and amines to the corresponding second amines with aldehydes and ketones. Functional nitrobenzenes, such as nitrobenzenes with F, Cl, Br, CH_3O and CH_3 were transformed to the corresponding secondary amines in good to excellent yields. Moreover, the Rh@CN catalyzed N-alkylation of a series of primary amines with aldehydes and ketones gave the corresponding secondary amines in high yield also. The Rh@CN was heterogeneous, and can be reusable several times (at least 4 times) for the reductive N-alkylation of nitroarenes.

Introduction

Secondary amines and their derivatives exist in many biologically active molecules, and are important intermediates for the synthesis of pharmaceuticals, dyes and fine chemicals[1], so the C-N bond formation becomes an important area in pure and applied chemistry. The nucleophilic substitution of alkyl halides with amines in the presence of stoichiometric amounts of inorganic bases is one of the most common methods of C-N bond formation[2]. However, the nucleophilic substitution process has some problems, for example, the toxic nature of alkyl halides, low selectivity of monoalkylation of primary amines. Additionally, the process produces large amounts of waste salts (stoichiometric amount of salts). The alkylation of amines with alcohols is a good way for the C-N bond formation, but the reaction conditions are harsh and the catalysts are difficult to be reused[3]. The reductive N-alkylation of amines with aldehydes (or ketones) is an attractive procedure for C-N bond formation reaction[4]. The method includes two synthetic steps: the C=N bond formation and the hydrogenation of the imines to the corresponding N-alkylated amines. Most anilines are produced by the reduction of nitrobenzenes. Therefore, the reductive N-alkylation using nitrobenzenes is considered to be an attractive idea as it does not require prior reduction of nitrobenzenes. The selectivity of the reaction is a challenging issue, so the development of effective catalysts is highly desirable. Several catalysts based on Pd[5], Pt[6], Ir[7] and Au[8] catalysts have be reported for the reductive N-alkylation of nitrobenzenes with aldehydes. However, these catalysts are not selective enough for the N-alkylation of nitrobenzenes with aldehydes, and aldehydes cannot be used efficiently in the N-alkylation. Benzyl alcohol and toluene are always found as the by-products in the reaction. Recently, Fe[9] and Co[10] complexes with N contained ligands were pyrolysed in activated carbon as heterogeneous catalysts for the hydrogenation of nitro aromatics efficiently. The 1, 10-phenanthroline (Phen) can be linked with the activated carbon to form stable N-doped carbon materials, which were used as good catalyst supports. And the Fe[11] or Co[12] catalysts can also be used for the reductive N-alkylation of nitrobenzenes with aldehydes. However, the efficiency of the catalysts was not high enough.



Scheme 1. Rh@CN catalyzed reductive alkylation of nitrobenzenes with aldehydes

We have reported the transfer hydrogenation of C=O bond and the selective hydrogenation of nitroaromatics recently, [13] and we are also interested in the direct N-alkylation of nitrobenzenes with aldehydes. Here rhodium nanoparticles were supported on N-doped carbon materials as heterogeneous catalysts, which were highly selective and efficient for the reductive N-alkylation of nitrobenzenes and amines with aldehydes and ketones (Scheme 1). Functional nitrobenzenes, such as nitrobenzenes with F, Cl, Br, CH_3O and CH_3 groups, were reductive alkylated with aldehydes efficiently to the corresponding amines in good to excellent yields. Moreover, the Rh@CN catalyzed N-alkylation of a series of

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primary amines with aldehydes and ketones gave the corresponding secondary amines in high yields also.

Experimental section

The preparation of the Rh@CN

$RhCl_3 \cdot 3H_2O$ (52.6mg) was dissolved in ethanol (100 mL) with stirring, then 1,10-phenanthroline monohydrate (108mg) was added into the solution at room temperature (Rh: Phen=1:3 molar ratio). After stirring for another 1 h, activated carbon (1 g) was added into the solution and the mixture was stirring for 10 hours at 60 °C. After the mixture cooled to room temperature, the ethanol was removed by the rotary evaporation under vacuum. The black solid was dried in a drying oven at 60 °C under vacuum for 12 hours, and then the solid (the precursor of Rh@CN) was transferred into a quartz boat and placed in the tube furnace under N_2. The tube furnace was heated to 800 °C at the rate of 10 °C per minute, and kept at 800 °C for 2 hours under N_2. After the tube furnace cooled to room temperature, the catalyst Rh@CN (containing Rh 2.01 wt %, detected by ICP) was obtained as black powders.

The preparation of the Rh@CN-5

The same procedure as that described above for the preparation of Rh@CN was followed, except $RhCl_3 \cdot 3H_2O$ increased to 131.5mg (containing Rh 4.95 wt %, detected by ICP).

The preparation of the Ru@CN

The precursor of Ru@CN was $RuCl_3$ with 1, 10-phenanthroline monohydrate (Ru: Phen=1:3 molar ratio) in activated carbon. The same procedure as that described above for the preparation of Rh@CN was followed, except Ru was used instead of Rh as the metal catalyst (containing Ru 1.98 wt %, detected by ICP).

General procedure for the reductive N-alkylation reactions

The reductive N-alkylation of nitrobenzenes (or amines) with aldehydes was carried out in an autoclave. Typically, an aldehyde (0.5mmol), a nitrobenzene (or amine) (0.55 mmol), ethanol (4.0 mL), Rh@CN 14 mg (0.5% mol Rh) were added into the autoclave with a stir bar. Then the autoclave was flushed with H_2 more than three times to remove the air, and filled with H_2 (3Mpa). The mixture was stirred under 80 ^oC for the given time. When the autoclave cooled to the room temperature, 50 µL $C_{16}H_{34}$ was added to the reaction mixture as internal standard for GC analysis. The Rh@CN catalyst was filtrated off and washed with ethanol (3×4.0 mL). The products (in the filtrate mixture) were analyzed by GC. The products were purified by column chromatography on silica gel (petroleum ether: ethyl acetate=20:1) and identified by ^1H-NMR.

The reusability of the Rh@CN

When the reaction completed and the reaction mixture was cooled, the catalyst was collected by filtration. The catalyst was washed by ethanol (3×4.0 mL) and dried under vacuum at the 25 ^oC for 12 h, and then used again for the next reaction cycle.

Results and discussions

TEM analysis

The Rh@CN catalyst was characterized by TEM and the Rh particles were highly dispersed in the CN materials (Figure 1). Although the catalyst Rh@CN was prepared through high temperature (up to 800 °C), the Rh nanoparticles were kept at about only 6 nm (Figure 1-a), which indicated that the Rh@CN was highly thermal stable, and the Phen structure was profitable for the stabilization of Rh nanoparticles in the Rh@CN catalyst.

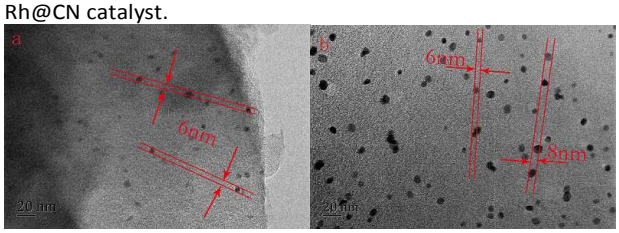


Figure 1. (a)TEM image of the fresh Rh@CN nanocatalyst; (b) TEM image of Rh@CN nanocatalyst recovered for the 4th time; scale bar=20 nm.

BET&BJH analysis

Based on the nitrogen adsorption-desorption analysis, the BET (Brunauer-Emmett-Teller) surface area of the Rh@CN was 1128 $m^2\ g^{-1}$ reduced from 1706 $m^2\ g^{-1}$ (the parent AC), which implied the CN materials (from Phen) with Rh nanoparticles were formed inside the AC. And the total pore volume of the Rh@CN was reduced to 0.82cm^3/g from 1.16cm^3/g. But the average pore size increased to 2.9nm from 2.7nm (Figure 2).

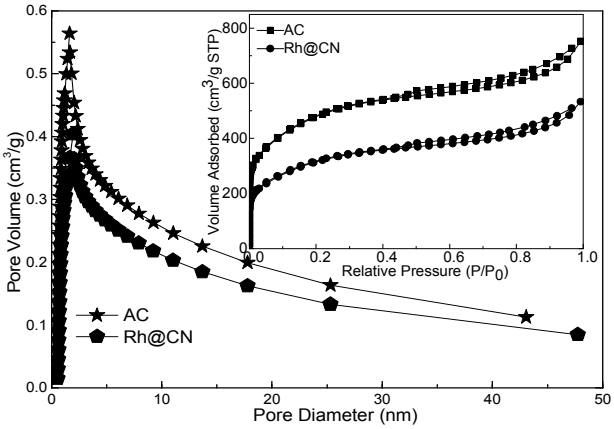


Figure 2. Nitrogen adsorption-desorption isotherms of AC and Rh@CN (shown in the inset) and BJH pore size distribution

TG analysis

The TG curve (see the Supporting Information, Figure S1) of the precursor of Rh@CN showed that small amount of water was desorbed and slight weight loss (about 1.8 %) was observed at temperature less than 200 ^oC. About 8.0% weight loss was observed at temperature between 200 to 500 °C, which was attributed to the sublimation of the excess of Phen. At temperature from 500 to 800 °C, about 2.5% of weight loss

was observed, which was attributed to the formation of Rh nanoparticles with the escape of the chlorine and the formation of N-doped graphene layers by carbonization of the remained Phen ligand [11].

XPS analysis

In order to find insights to the structures of the Rh nanocatalyst, the Rh@CN was characterized by XPS (X-ray photoelectron spectroscopy) (Figure 3). Two N1s peaks were found at 398.3 eV and 399.3 eV for the Rh@CN precursor, which were assigned to the free pyridinic nitrogen (from free Phen) and the coordinated nitrogen (coordinated phen with Rh centers) respectively (Fig. 3, the left below) [14]. The two N1s peaks at 398.3 eV and 399.5 eV for the Rh@CN catalyst were remained, and two other peaks were found at 400.4 eV and 401eV, which should be attributed to "pyrrole-type" and "graphite enclosed-type" nitrogen (Fig. 3, the left up). [9] These results suggested that the Phen structure was inserted into the activated carbon structure on the surface. The Phen structure retained and coordinated with Rh in the Rh@CN catalyst, and it was highly beneficial for the dispersion of the Rh nanoparticles and also useful for the stability of the nanocatalyst Rh@CN.

The Rh peaks of the precursor of the Rh@CN at 309.2 eV ($Rh3d_{5/2}$) and at 313.9 eV ($Rh3d_{3/2}$ Δ=4.7 eV) were from the coordinated complex $Rh(Phen)Cl_3$ (Fig. 3, the right below). As the Rh peaks of Rh@CN for $Rh3d_{5/2}$ at 307.2 eV and for $Rh3d_{3/2}$ at 311.9 eV (Δ=4.7 eV) were found, the rhodium in the catalyst Rh@CN was metallic state Rh (0) with the protection of the Phen structure after treated at 800 °C (Fig. 3, the right up)[15]. The $RhCl_3$ was decomposed into Rh metal and the Cl was released as no reducer was added.

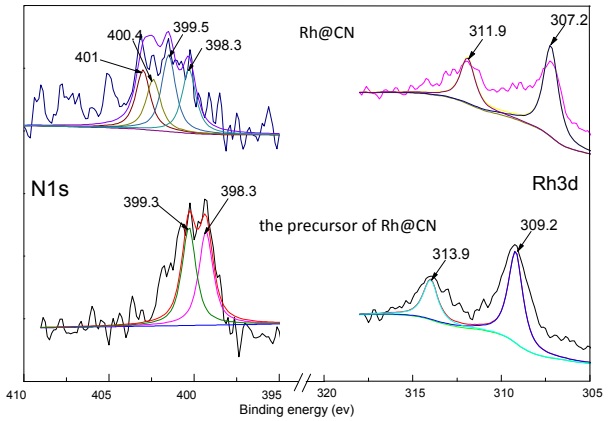


Figure 3. The XPS spectra of the precursor and Rh@CN catalyst

XRD analysis

The presence of metallic state Rh (0) was also confirmed by XRD (the X-ray diffraction) analysis. Three characteristic peaks (2ϑ=41.1, 47.8 and 69.9°) were observed for the metal rhodium particles. These peaks were assigned to Rh (111), Rh (200) and Rh (220), respectively (see the Supporting Information, Figure S2).

EDX analysis

The element contents of the Rh@CN were evaluated by EDS (Energy Dispersive X-Ray Spectroscopy), and the contents of C, N, and Rh were 98.68%, 0.67%, 0.65%, respectively (see the Supporting Information, Figure S3). The content of Rh from EDX analysis was lower than that from ICP analysis, which was due to the enrichment of Rh nanoparticles inside the pores of the CN material, and not all Rh can be detected by EDS in the Rh@CN.

Reaction condition screening for the reductive N-alkylation of nitrobenzene with benzaldehyde

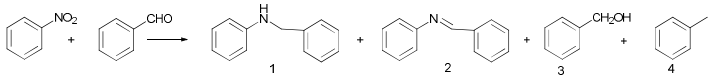
The reductive N-alkylation of nitrobenzene with benzaldehyde was used as the model reaction, and the optimization of reaction conditions was performed. The results are listed in Table 1. The Rh@CN catalyst was highly active for the reductive alkylation of nitrobenzene with benzaldehyde in ethanol (Table 1, entry 4). Ethanol was helpful for Rh@CN catalyzed hydrogenation of the nitrobenzene and beneficial for the condensation of aniline with benzaldehyde to form the corresponding imine. THF was also good solvent (Table 1, entry 3), but toluene and cyclohexane were less effective solvents for the transformation (Table 1, entry 1-2). The added nitrobenzene and benzaldhyde remained and no conversion was detected when 1, 4-dioxane was used as solvent (Table 1, entry 5). No benzyl aniline was found when H_2O was used as solvent (toluene, benzyl alcohol and aniline were detected as by-products) (Table 1, entry 6). The reductive N-alkylation of nitrobenzene afforded benzyl aniline in 75% yield without solvent (Table 1, entry 10). The Rh/C, Ru@CN were not good catalysts for the transformation (Table 1, entry 7, 9), as both the activity and selectivity were not good. No benzyl aniline was found with Pd/C catalyst under similar reaction conditions, only toluene, benzyl alcohol and aniline were detected (Table 1, entry 8). The Rh@CN-5 catalyst was similarly active to the Rh@CN for the reductive N-alkylation of nitrobenzene with benzaldehyde in ethanol (Table 1, entry 11). No reduction was detected using N_2 instead of H_2, which indicated that H_2 was the reducer and ethanol was only as solvent (Table 1, entry 12). Under milder reaction conditions, the reductive N-alkylation gave low yields (Table 1, entry 13-16). No benzyl aniline was detected using the precursor of Rh@CN as catalyst, which indicated the Rh complex was not active for the transformation (Table 1, entry 17). The gram-scale reaction was performed using the model reaction, and benzyl aniline was obtained in good yield (Table 1, entry 18).

The reusability of the Rh@CN nanocatalyst

The reusability of the Rh@CN nanocatalyst was tested for the reductive N-alkylation of nitrobenzene with benzaldehyde and the results are shown in Figure S4. The Rh@CN nanocatalyst was easily recycled by filtration and reused for the next reaction cycle. After removal of the Rh@CN nanocatalyst by filtration, the filtrate was investigated by ICP, and no Rh was detected (below the detection limitation of 7 ppb). The filtrate was inactive towards further reductive N-alkylation reactions. The Rh@CN can be reused at least 4 times without obvious deactivation, and benzyl aniline was obtained in good yield (in 92% yield at the 4th time). The 4th time recovered Rh@CN was analyzed by TEM also and the mean diameter of the

recovered Rh nanoparticles were increased a little (about 8nm, see Figure 1b).

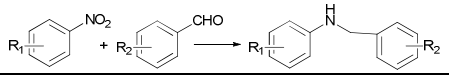
Table 1 Screening of the reductive N-alkylation of nitrobenzene with benzaldehyde [a]



Entry	Catalyst	Solvent	T/ °C	Pressure/ Mpa	Conv./%	Selsectivity/%[b]			
						1	2	3	4
1	Rh@CN	Toluene	80	3	76	89	11	0	0
2	Rh@CN	Cyclohexane	80	3	100	83	17	0	0
3	Rh@CN	THF	80	3	94	95	5	0	0
4	**Rh@CN**	**Ethanol**	80	3	**100**	**100**	**0**	**0**	**0**
5	Rh@CN	1,4-Dioxane	80	3	0	0	0	0	0
6	Rh@CN	H_2O	80	3	100	0	0	70	30
7	Rh/C	Ethanol	80	3	66	58	42	0	0
8	Pd/C	Ethanol	80	3	100	0	0	82	18
9	Ru@CN	Ethanol	80	3	100	40	60	0	0
10	Rh@CN	Solvent free	80	3	100	75	25	0	0
11	Rh@CN-5	Ethanol	80	3	99	99	1	0	0
12[c]	Rh@CN	Ethanol	80	3	0	0	0	0	0
13	Rh@CN	Ethanol	rt	3	50	72	28	0	0
14	Rh@CN	Ethanol	60	3	90	86	14	0	0
15	Rh@CN	Ethanol	80	0.1	15	26	74	0	0
16	Rh@CN	Ethanol	80	1	92	91	9	0	0
17[d]	Rh@CN	Ethanol	80	3	0	0	0	0	0
18[e]	Rh@CN	Ethanol	80	3	100	97	3	0	0

[a] Reaction conditions: benzaldehyde 0.5 mmol; nitrobenzene, 0.55 mmol; solvent 4.0 mL; Rh@CN 14 mg (0.5 mol % Rh, or other catalysts containing 0.5 mol% noble metal); in 6 hours; [b] Conversion (of benzaldehyde) and selectivity were determined by GC ($C_{16}H_{34}$ used as internal standard); [c] N_2 instead of H_2; [d] the precursor of the Rh@CN used as catalyst; [e] the reaction was scaled up to 20 times.

Table 2. Rh@CN catalyzed the reductive N-alkylation of nitrobenzenes with aldehydes.[a]



Entry	R_1	R_2	Time/h	Yield/%
1	H	H	6	99
2	4-F	H	6	94
3	2-Cl	H	8	98
4	3-Cl	H	6	94
5	4-Cl	H	6	96
6	4-Br	H	12	91
7	4-CH_3	H	10	98
8	4-OCH_3	H	12	94
9	H	4-F	6	95
10	H	4-Cl	6	94
11	H	2-CH_3	15	89
12	H	3-CH_3	10	92
13	H	4-CH_3	10	97
14	H	4-OCH_3	10	95
15	H	octanal	12	85
16	H	cyclohexanecarboxaldehyde	12	91
17	H	3-phenylpropanal	12	86
18	H	furfural	8	96

[a] Reaction conditions: aldehyde, 0.5 mmol; nitrobenzene, 0.55 mmol; Rh@CN 14 mg (0.5 mol % Rh); 80 °C; H_2 3Mpa; 4.0mL ethanol. The conversions and yields were determined by GC ($C_{16}H_{34}$ used as internal standard).

The reductive N-alkylation of nitrobenzenes with aldehydes

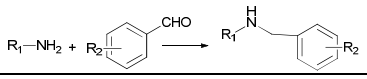
The scope of the reductive N-alkylation was then explored using a number of nitrobenzenes and aldehydes, and the results are shown in Table 2. The Rh@CN was highly active and selective for the reductive N-alkylation of nitrobenzenes with aldehydes, and halides (F, Cl and Br), CH_3, CH_3O groups were tolerated well during the transformation. The corresponding N-alkyl aniline were obtained in good to excellent yields (Table 2, entry 2-14). The steric effects related to the substituents were low, and 2-nitrochlorobenzene and 2-methylbenzaldehyde were converted to the corresponding amines in high yields also (Table 2, entry 3, 11). Moreover, the aliphatic aldehyde (such as octanal, cyclohexanecarboxaldehyde, 3-phenylpropanal) can also be converted to the N-alkyl aniline in good yield (Table 2, entry 15-17). When the heterocyclic aldehyde, furfural was used as the substrate, N-phenyl furfurylamine was obtained in exclllent yield (96%) (Table 2, entry 18).

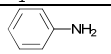
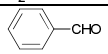
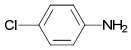
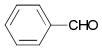
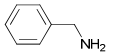
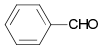
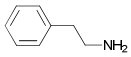
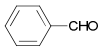
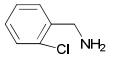
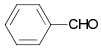
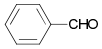
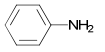
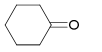
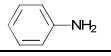
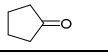
The reductive N-alkylation of amines and aldehydes

As the reductive N-alkylation of nitrobenzenes should go through the reduction of the nitrobenzenes to the corresponding anilines firstly, the reductive N-alkylation of amines with aldehydes was also studied with the Rh@CN catalyst. And the results are shown in Table 3. Indeed, the alkylation of anilines was performed rapidly with benzaldehyde, and the corresponding secondary amines were obtained in high yield (Table 3, entry 1-2). Alkylamines (e.g.,

benzyl amine, 2-chlorobenzyl amine, β-phenylethylamine, n-octyl amine) can also be used for the N-alkylation, and the corresponding secondary amines were obtained in high yields also (Table 3, entry 3-6). Moreover, the N-alkylation of aniline with cyclohexanone and cyclopentanone gave the corresponding secondary amines in good yields respectively (Table 3, entry 7, 8).

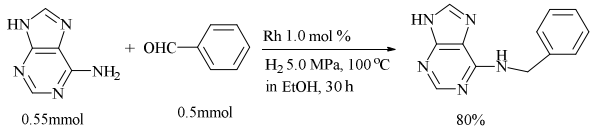
Table 3 Rh@CN catalyzed the reductive N-alkylation of amine and aldehyde [a]



Entry	R_1	R_2	Time/h	Yield/%
1			1	97
2			4	99
3			12	99
4			12	98
5			12	99
6	n-$C_8H_{17}NH_2$		12	90
7			12	96
8			12	92

[a] Reaction conditions: aldehyde, 0.5 mmol; amine, 0.55 mmol; Rh@CN 14 mg (0.5 mol % Rh); 80 °C; H_2 3Mpa; 4.0mL ethanol. The conversions and yields were determined by GC ($C_{16}H_{34}$ used as internal standard).

Encouraged by above results, 6-benzylaminopurine (a plant growth regulator) was prepared by the reductive N-alkylation of adenine with benzaldehyde using the Rh@CN catalyst. To our delight, 6-benzylaminopurine was obtained in 80% yield (Scheme 2). Since adenine and 6-benzylaminopurine are poorly soluble in ethanol, higher reaction temperature and higher H_2 pressure were required.



Scheme 2 Rh@CN catalyzed synthesis of 6-benzylaminopurine

The reaction sequence of the reductive N-alkylation of nitrobenzene with benzaldehyde

The reaction sequence of the reductive N-alkylation of nitrobenzene with benzaldehyde was investigated, and the time-concentration profile was followed (Figure 4). Aniline, the imine and benzyl aniline can be detected at the first 3 hours. Then benzyl aniline was increased smoothly, and the imine was decreased along. Finally, the imine was transformed to benzyl aniline completely. Benzaldehyde was converted to benzyl aniline in 100% yield in 6 hours, and no toluene or benzyl alcohol were detected. As nitrobenzene was excess (10% excess), aniline increased slowly to about 10% in the end.

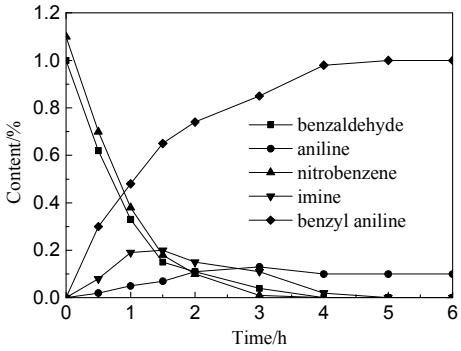
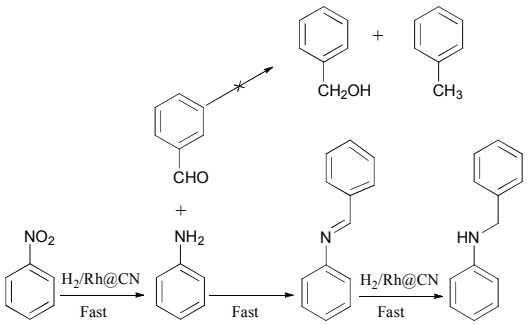


Figure 4. The reaction sequence of the reductive N-alkylation of nitrobenzene with benzaldehyde. Reaction conditions: benzaldehyde, 0.5 mmol; nitrobenzene, 0.55 mmol; Rh@CN 14 mg (0.5 mol % Rh); at 80 °C; H_2 3Mpa; 4.0 mL ethanol.

The reaction pathway discussion

Nitrobenzene should be reduced to aniline firstly, and the aniline can be detected as the reduced intermediate. Moreover, the imine from the condensation of aniline with benzaldehyde was detected also at the beginning of the reductive N-alkylation of the nitrobenzene with benzaldehyde. But no benzyl alcohol was found, which implied that the reduction of nitrobenzene is faster than the reduction of benzaldehyde. Afterwards, the imine was formed by the condensation of benzaldehyde with aniline, and then the imine was further reduced to the corresponding amine. The reduction of imine was faster than the reduction of benzaldehyde also since no benzyl alcohol or toluene was detected in the whole reduction process. In addition, we found that the reductive N-alkylation of aniline was faster than the reductive alkylation nitrobenzene (The reductive alkylation of aniline with benzaldehyde was finished in about 1 h, which is less than that (4 h) using nitrobenzene) (Table 1, entry 4 and Table 3, entry 1).



Scheme 3. A possible pathway for the reductive N-alkylation of nitrobenzene with benzaldehyde.

Based on these experimental results, we proposed the possible pathway of the Rh@CN catalyzed reductive N-alkylation of

nitrobenzene with benzaldehyde to the corresponding secondary amine (Scheme 3). Nitrobenzene was reduced to aniline firstly, and the aniline was condensed with benzaldehyde to the imine, and then the imine was reduced to benzyl aniline. During the reaction, the reaction rate was the control factor for the reductive alkylation of nitrobenzene with benzaldehyde, and the reaction rate determined the catalytic selectivity. No benzyl alcohol or toluene were found from the hydrogenation of benzaldehyde, which indicated that the added benzaldehyde fully participated into the reductive N-alkylation of the nitrobenzene.

Conclusions

In summary, Rh nanocatalysts were prepared and applied for the reductive N-alkylation of nitrobenzenes with aldehydes. The Rh@CN catalyst was found to be highly selective and efficient for the reductive N-alkylation of nitrobenzenes, and functional groups, such as F, Cl, Br, CH_3O and CH_3 were well tolerated during the transformation, and the corresponding secondary amines were obtained in good to excellent yields. Furthermore, the Rh@CN catalyst was highly active and selective for the reductive N-alkylation of primary amines with aldehydes and ketones, and the corresponding secondary amines were obtained rapidly in high yields. Moreover, the Rh@CN was heterogeneous, and can be reused several times for the reductive N-alkylation of nitrobenzene.

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Heterogeneous Rh@CN nanocatalysts were prepared and applied for the reductive N-alkylation of nitrobenzenes with aldehydes selectively.