

Article

Switchable Access to Amines and Imines from Reductive Coupling of Nitroarenes with Alcohols Catalyzed by Biomass-Derived Cobalt Nanoparticles

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Abstract: Cobalt nanoparticles modified with N-doped hierarchical porous carbon derived from biomass are found to be a highly efficient, reusable heterogeneous catalyst for the coupling of nitroarenes with alcohols, selectively affording imines and amines via the borrowing hydrogen strategy for the first time. The product selectivity between imine and amine may be precisely tuned by simple alteration of the reaction conditions without changing the catalyst in one reaction system. In this study, a broad set of complex imines and amines was successfully synthesized in good to high yields with various functional groups tolerated for both nitroarenes and alcohols, highlighting the potentially practical utility of the protocol. This heterogeneous catalyst can be easily removed from the reaction medium by external magnet and can be reused at least four times without significant loss in activity and selectivity.

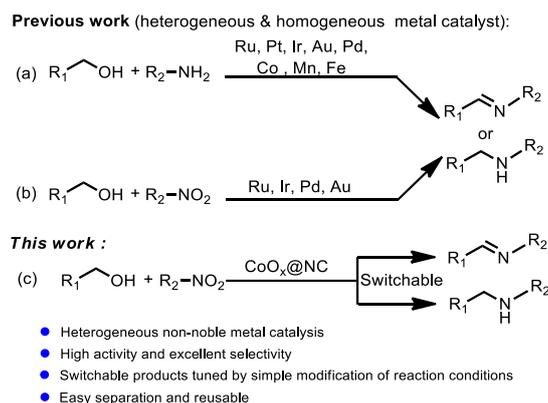
Keywords: nanostructured cobalt catalyst; borrowing hydrogen; imine synthesis; amine synthesis; nitroarenes

1. Introduction

Imines as versatile building blocks are ubiquitous in useful organic molecules such as pharmaceuticals, natural products and bioactive heterocycles [1]. The traditional method for the synthesis of imines is the condensation of highly reactive carbonyls with amines under the catalysis of a Lewis acid. They can also be prepared by the oxidative strategy of self-condensation of primary amines [2–6], dehydrogenation of secondary amines [7–10], or by the oxidative coupling of alcohols with amines [11–16]. However, the procedures mentioned above generally suffer from practical drawbacks such as poor selectivity, low catalytic activity, harsh reaction conditions, difficulty for catalyst reuse, and so on. Furthermore, these well-developed procedures of preparing imines generally use aryl amines as starting materials, which are usually produced by reduction of nitroarenes with stoichiometric metals or catalyzed by transition metals under high pressure of hydrogen. As such, from both an economic and environmental perspective, it is desirable to develop a heterogeneous base-metal catalytic approach for highly efficient and selective synthesis of imines from readily available and inexpensive nitroarenes.

The borrowing hydrogen strategy has been widely applied in organic transformations to construct various C-X (X = C, N, S) compounds in the last decade [17–19]. In this context, of particular importance is the N-alkylation of amines with alcohols to synthesize structurally complex primary and/or secondary amine compounds, which represents one of the most straightforward, efficient and eco-friendly methodologies for amine synthesis. As a consequence, a number of homogeneous and heterogeneous metal catalysts (e.g., Pt [20,21], Pd [22], Ru [23–29], Ir [30–34], Au [35], Fe [36–39], Mn [40,41], and Co [42–45]) have been developed for such a reaction (Scheme 1a). Despite great

achievements, direct synthesis of imines by the coupling of nitroarenes and alcohols with high activity and selectivity via the borrowing hydrogen strategy remains challenging. To date, only a handful of examples enabled by noble metal catalysts (e.g., Pd [46,47], Ru [48], Ir [49], and Au [50,51]) have been reported; however, their catalytic activities and selectivities are rather low and accompanied by limited substrate scopes (Scheme 1b). In addition, the high cost and limited reserve on earth of noble metal catalysts significantly impedes their large-scale industrial application. Notably, no successful direct imine formation from nitroarenes and alcohols catalyzed by heterogeneous base metal catalysts has been described, to the best of our knowledge.



Scheme 1. Synthesis of imines or amines from reductive amination via the borrowing hydrogen strategy.

In a continuation of our studies to develop green catalysis for sustainable organic synthesis, we have recently developed highly efficient and recyclable inexpensive cobalt nanocomposites on an N-doped hierarchical carbon derived from biomass for the chemoselective hydrogenation of functionalized nitroarenes [52]. Inspired by the results that we obtained, we are eager to extend the use of this catalyst to the reductive coupling of nitroarenes with alcohols through the borrowing hydrogen strategy without H_2 . Herein, we report a heterogeneous catalyst based on cobalt nanoparticles modified with N-doped hierarchical porous carbon which exhibits outstanding catalytic performance for direct imine synthesis from the reductive coupling of nitroarenes with alcohols via the borrowing hydrogen pathway under mild conditions. The hybrid nanostructured catalyst was prepared by pyrolysis of naturally renewable biomass in combination with low-cost and earth-abundant cobalt salts in a simple and eco-friendly manner. A broad set of nitroarenes were able to efficiently couple with various benzyl alcohols to deliver imines in good to high yields. Remarkably, the product selectivity between the imine and amine could be readily tuned by simple modification of reaction conditions. To the best of our knowledge, this is the first report of direct and selective synthesis of C-N compounds from readily available and inexpensive nitroarenes and alcohols catalyzed by a heterogeneous base-metal catalyst via the borrowing hydrogen strategy (Scheme 1c).

2. Results and Discussion

The hybrid nanostructured cobalt nanoparticles modified with N-doped hierarchical porous carbon were synthesized by a facile cascade process of hydrothermal-pyrolysis (see details in Supporting Information (SI)). Fresh bamboo shoots were chosen as naturally renewable biomass which contain nearly 8 wt% of N from their intrinsic proteins and amino acids. The bamboo shoots were first cut into slices, dried, and ground into powder, followed by the hydrothermal process. The resulting solids were homogeneously mixed with CoCl_2 followed by pyrolysis under a N_2 atmosphere at varying temperatures to obtain the hybrid nanostructured material, hereafter denoted as $\text{CoO}_x\text{@NC-T}$ (where T represents the pyrolysis temperature). This method of preparing catalysts has been published before. In [52] full characterization is discussed.

Inspired by the recently impressive progress of cobalt nanoparticles (NPs) supported on carbons for reduction of nitro compounds [53,54], we commenced the reductive coupling of nitrobenzene (**1a**) and benzyl alcohol (**2a**) as a model reaction to demonstrate the feasibility of the catalysts $\text{CoO}_x\text{@NC-T}$ for C-N bond construction. The representative results are summarized in Table 1. The reaction was initially performed in the presence of $\text{CoO}_x\text{@NC-800}$ and two equivalents of *t*BuOK in toluene at 120 °C for 15 h (Table 1, Entry 7). To our surprise, 63% GC conversion of **1a** with high selectivity (98%) to **3a** was observed (Table 1, Entry 6). To further optimize the reaction conditions, a set of factors was screened. The screening of several different bases showed that *t*BuOK gave the best catalytic efficiency in terms of activity and selectivity (Table 1, Entries 1–4 and 8). Among the solvents investigated, toluene showed superior catalytic performance (Table S6 (See Supplementary Materials)). A decrease in the reaction temperature led to a lower catalytic activity without influencing the selectivity to **3a** (Table S7 (See Supplementary Materials)). Subsequently, the testing of the catalysts prepared at variable pyrolysis temperatures (700, 800, and 900 °C) showed $\text{CoO}_x\text{@NC-800}$ to be the best candidate (Table S5 (See Supplementary Materials)). The catalyst $\text{CoO}_x\text{@NC-T}$ is indispensable for the success of this reductive coupling reaction. A considerably lower reactivity with poor selectivity to **3a** or even no reactivity was observed in the presence of CoCl_2 , pure Co_3O_4 , or pure nano Co_3O_4 (100 nm) as a catalyst, or in the absence of a catalyst under otherwise identical conditions (Table 1, entries 13–16).

Table 1. Optimization of the reaction conditions ^a.

c1ccc(cc1)[N+](=O)[O-].c1ccc(cc1)CO>>c1ccc(cc1)/N=C/c2ccccc2.c1ccc(cc1)Nc2ccccc2

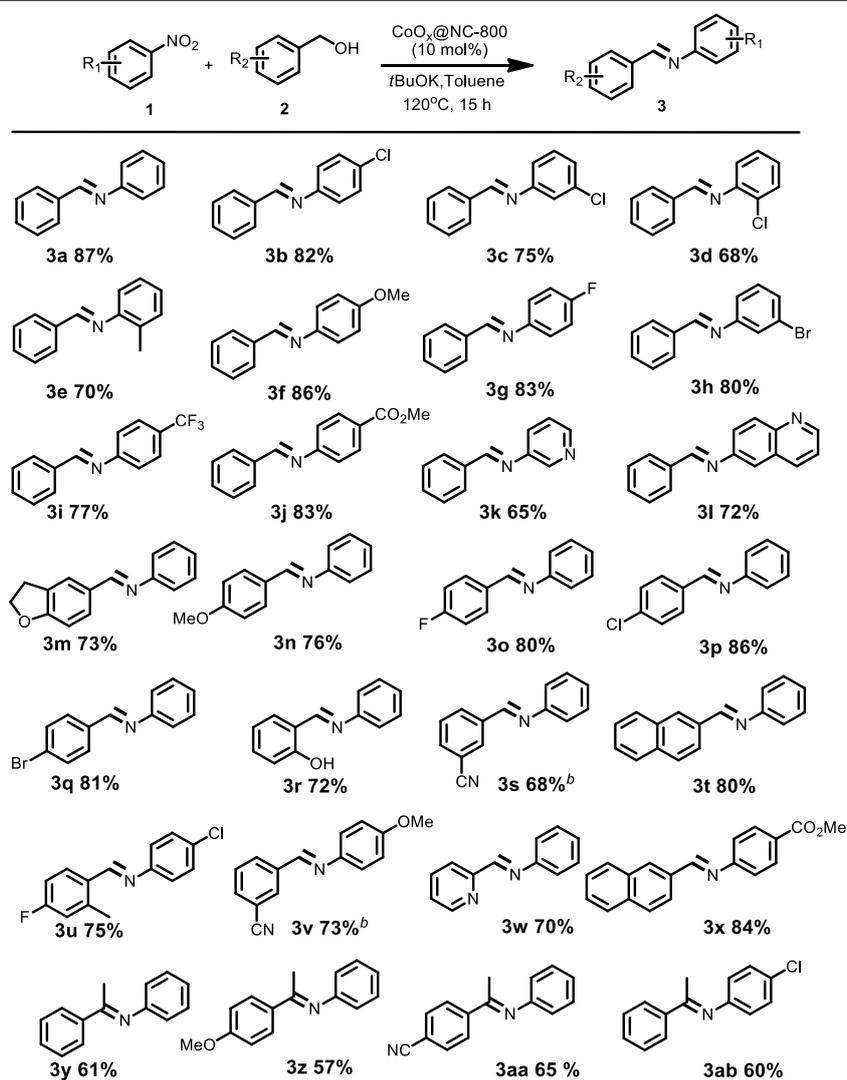
Entry	Catalyst	Base (equiv.)	Conv. (%) ^b	Selectivity (%) ^b		TON ^h
				3a	4a	
1	$\text{CoO}_x\text{@NC-800}$	Na_2CO_3 (3.0)	0	0	0	0
2	$\text{CoO}_x\text{@NC-800}$	NaOH (3.0)	21	81	19	2.1
3	$\text{CoO}_x\text{@NC-800}$	KHMDS (3.0)	100	57	43	10
4	$\text{CoO}_x\text{@NC-800}$	KOH (3.0)	27	78	22	2.7
5	$\text{CoO}_x\text{@NC-800}$	-	0	0	0	0
6	$\text{CoO}_x\text{@NC-800}$	<i>t</i> BuOK (1.0)	34	100	0	3.4
7	$\text{CoO}_x\text{@NC-800}$	<i>t</i> BuOK (2.0)	63	98 ^e	2	6.3
8	$\text{CoO}_x\text{@NC-800}$	<i>t</i> BuOK (3.0)	100	98(87) ^e	2	10
9 ^c	$\text{CoO}_x\text{@NC-800}$	<i>t</i> BuOK (4.0)	100	20	80(72) ^e	10
10 ^d	$\text{CoO}_x\text{@NC-800}$	<i>t</i> BuOK (3.0)	100	95(86) ^e	5	10
11 ^d	$\text{CoO}_x\text{@NC-800}$	<i>t</i> BuOK (4.0)	100	4	96(84) ^e	10
12	$\text{CoO}_x\text{@NC-800}$	<i>t</i> BuOK (4.0)	100	2	98	10
13	$\text{CoO}_x\text{@C-800}$ ^f	<i>t</i> BuOK (3.0)	98	35	63	9.8
14		<i>t</i> BuOK (3.0)	47	45	40	4.7
15	CoCl_2	<i>t</i> BuOK (3.0)	25	73	27	2.5
16	Co_3O_4	<i>t</i> BuOK (3.0)	57	63	37	5.7
17	Nano Co_3O_4 ^g	<i>t</i> BuOK (3.0)	64	58	42	6.4

^a Reaction conditions: nitrobenzene (0.2 mmol), benzyl alcohol (0.6 mmol), catalyst (10 mol%), solvent (5 mL), 120 °C, 15 h. ^b Determined by GC using dodecane as an internal standard and conversion based on the conversion of nitrobenzene. ^c 0.6 mmol benzyl alcohol was used. ^d 0.8 mmol benzyl alcohol was used. ^e Isolated yields are in parentheses. ^f The catalyst was prepared by pyrolysis of the mixture of CoCl_2 and activated carbon without any N-doping. ^g Nano Co_3O_4 particle size is equal to 100 nm. ^h TON was calculated as the mole of nitrobenzene converted to desired product normalized per Co.

Further investigations disclosed that the base *t*BuOK played a key role not only in boosting the reaction but also in affecting the product selectivity between imine (**3a**) and amine (**4a**). In the absence of base, the reaction did not proceed at all with recovery of the starting materials under standard reaction conditions (Table 1, Entry 5). However, the reductive coupling reaction was evoked upon addition of one equivalent of *t*BuOK and the reaction efficiency was gradually improved with increasing molar

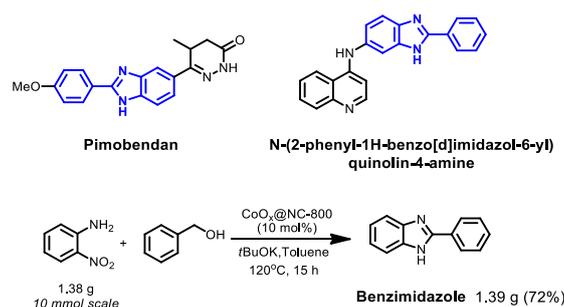
equivalents of base (Table 1, Entries 6–9). Surprisingly, the amount of tBuOK was found to significantly alter the product selectivity as shown in Scheme S2 (See Supplementary Materials) and Table 1. More specifically, 87% isolated yield to **3a** was achieved in the presence of three equivalents of base and benzyl alcohol (Table 1, Entry 8), while 84% isolated yield to **4a** was afforded with four equivalents of base and benzyl alcohol (Table 1, Entry 11) under otherwise identical conditions. These results clearly evidence the crucial effect of tBuOK on reaction efficiency and the tunability of product selectivity from imine to amine. To the best of our knowledge, this is first report of a heterogeneous non-noble metal catalyzed reductive coupling of nitroarenes with benzyl alcohols with switchable selectivity for imines or amines by simple modification of reaction conditions in one reaction system.

To explore the general applicability of this protocol, a variety of benzyl alcohols and nitroarenes were subjected to optimized reaction conditions for selective synthesis of imines, and the results are summarized in Table 2. Nitroarenes bearing different functional groups could efficiently couple with benzyl alcohol to form their corresponding imines in good to excellent yields. Nitroarenes containing electron-donating substituents (e.g., -Me, -OMe) gave relatively higher yields than those with electron-withdrawing substituents (e.g., -F, -Cl, -Br, -CF₃) (Table 2, **1b–1i**). Importantly, the pharmaceutically relevant trifluoromethyl- and F-substituted nitroarenes gave the corresponding products with satisfactory isolated yields. The ortho-substituted nitroarenes (Table 2, **1d** and **1e**) generally provided moderate yields due to steric effects. It should be noted that the heterocyclic nitro-compounds (Table 2, **1k** and **1l**) were also compatible with the present conditions and gave the corresponding imines in 65% and 72% yields, respectively. Likewise, a set of benzyl alcohols containing ether (**1m** and **1n**), halogen (Table 2, **1o–1q**), hydroxyl (Table 2, **1r**), and cyano (Table 2, **1s**) were also successful for the reductive coupling with nitrobenzene giving the desired products in 68–86% yields under standard reaction conditions. Furthermore, the combination of both various substituted benzyl alcohols with nitroarenes could also undergo the reductive coupling reaction smoothly to afford structurally more complex imines in 70–84% yields (Table 2, **3u–3x**), highlighting the generally synthetic utility of the present catalysis system. In addition, the secondary alcohols, such as 1-phenylethanol, 1-(4-methoxyphenyl) ethanol, and 4-(1-hydroxyethyl)benzotrile were also subjected to the optimized conditions for the synthesis of imines. Pleasantly, the secondary alcohols also worked with the present catalysis conditions to give their corresponding imines, albeit with relatively lower isolated yields. This is mainly because of the more difficult condensation of aniline with acetophenone than benzaldehyde. (Table 2, **3y–3ab**).

Table 2. Synthesis of imines from various alcohols and nitroarenes ^a.

^a Reaction conditions: nitroarene (0.2 mmol), benzyl alcohol (0.6 mmol), $\text{CoO}_x\text{@NC-800}$ (10 mol%), *t*BuOK (0.6 mmol), 120 °C, toluene (5 mL), 15 h. Isolated yields of products are reported. ^b 0.8 mmol *t*BuOK was used instead.

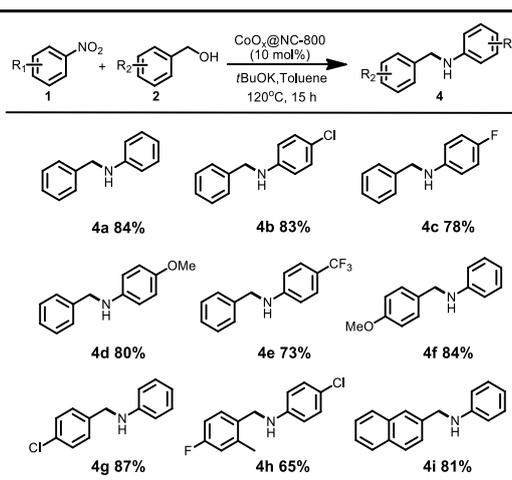
To demonstrate practical applicability, we performed a gram-scale reaction of 2-nitroaniline as substrate to undergo the coupling reaction with benzyl alcohol (Scheme 2). To our satisfaction, a one-pot cascade reaction of reductive coupling and cyclization took place smoothly under optimized conditions. Benzimidazole was successfully isolated in 72% yield, which is ubiquitous in pharmaceuticals and biologically active compounds such as Pimobendan [55] and N-(2-phenyl-1H-benzo[d]imidazol-6-yl)quinolin-4-amine [56]. This one-pot cascade procedure provides an expedient synthesis for benzimidazole.



Scheme 2. Gram-scale synthesis of benzimidazoles under standard conditions.

In addition to the reductive coupling of nitroarenes with alcohols to form imines and imidazole, we subsequently performed the reaction for direct synthesis of amines from benzyl alcohols and nitroarenes by following the developed conditions in Table 1 (Entry 11) and Scheme S2d (See Supplementary Materials). As illustrated in Table 3, various nitroarenes and benzyl alcohols could be employed for the reductive coupling reaction, affording their corresponding amines in moderate to high yields irrespective of the nature of substituents on the phenyl ring, which demonstrates the high activity and good functional group tolerance of the present protocol for the synthesis of amines under optimal reaction conditions.

Table 3. Synthesis of amines from various alcohols and nitroarenes ^a.



^a Reaction conditions: nitroarene (0.2 mmol), benzyl alcohol (0.8 mmol), CoO_x@NC-800 (10 mol%), tBuOK (0.8 mmol), toluene (5 mL), 120 °C, 15 h. Yields of isolated product are reported.

Durability and recyclability of a catalyst is critical for practical applications. Upon completion of the coupling of nitrobenzene with benzyl alcohol, the CoO_x@NC-800 catalyst was recollected by external magnet, washed, and dried after completion of a reductive coupling experiment for subsequent cycles. As shown in Figure 1, the activity and selectivity remained, with negligible changes after four recycling experiments, demonstrating the high durability of the catalyst.

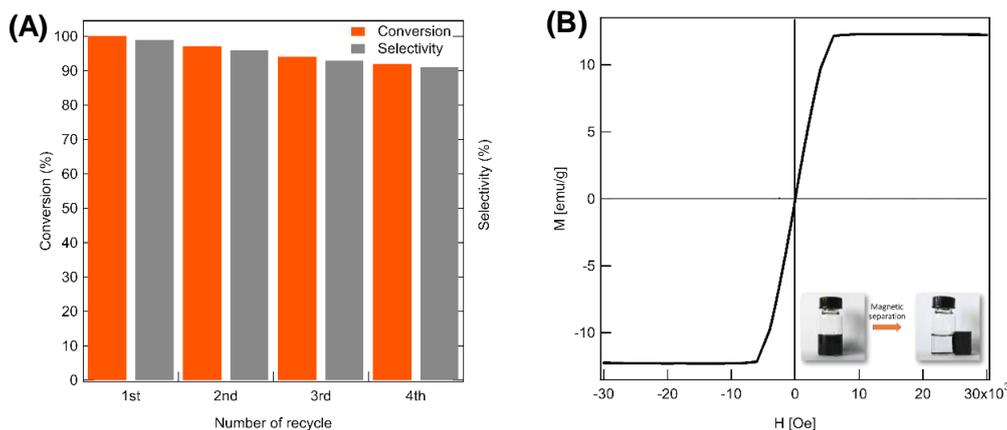


Figure 1. (A) The recycling performance of the reductive coupling of nitrobenzene with benzyl alcohol under standard reaction conditions and (B) magnetic hysteresis loop (300 K) of the catalyst $\text{CoO}_x\text{@NC-800}$; inset is the illustration of separation by external magnet.

To gain insight into the reaction pathway, additional experiments were performed (Scheme S3 (See Supplementary Materials)). A control experiment of acceptorless dehydrogenation of benzyl alcohol revealed that the combination of *t*BuOK and $\text{CoO}_x\text{@NC-800}$ is essential for efficient benzaldehyde formation (See Supplementary Materials), which is generally considered the rate-determining step in the coupling of anilines with benzyl alcohols [17,18,57]. Of note is that the dehydrogenation reaction rate is considerably slower, mainly due to the lack of a hydrogen acceptor to drive the reaction equilibrium to the desired aldehyde. The reduction of nitrobenzene in the presence of one atmosphere of molecular hydrogen did not proceed under standard reaction conditions (See Supplementary Materials), indicating that nitrobenzene is reduced by in-situ generated cobalt hydride species rather than molecular hydrogen. No hydrogen was detected out for the headspace gas after reaction by GC analysis, in support of cobalt hydride formation. Furthermore, in a separate reaction, we reacted freshly prepared *N*-diphenylmethanimine (**3a**) with benzyl alcohol and *t*BuOK (1 equivalent to alcohol) under otherwise identical conditions, which resulted in 93% isolated yield of the desired *N*-benzylaniline (**4a**) together with quantitative formation of benzaldehyde (Scheme S3e (See Supplementary Materials)). This experiment indicates that a hydrogen borrowing mechanism is operative. The reaction profiles for the synthesis of amine and imine as a function of reaction time were performed, and the respective results are shown in Figure 2. From these results, we were able to find that the reaction rate for the reduction of nitrobenzene is relatively faster in the presence of 4 equivalents of benzyl alcohol and *t*BuOK than that with 3 equivalents of them under otherwise identical conditions. For the synthesis of amine, nitrobenzene was rapidly converted toward imine (**3a**) without formation of amine (**4a**) at the early stage (e.g., 4 h). With an elapse of the reaction time, the remaining nitrobenzene was further converted; meanwhile, the formation of **4a** began to dominate the reaction due to the reduction of **3a**. However, for the synthesis of imine, a negligible formation of **4a** was observed over the whole reaction process. Apparently, the additional 1 equivalent of benzyl alcohol and *t*BuOK in the reaction preferentially facilitates the reduction of the formed **3a** to **4a**. The results above indicated that the amount of *t*BuOK made a significant contribution to producing enough cobalt hybrid species for the reduction of nitrobenzene or imine, which accounts for the reaction selectivity and the switch of product distribution between imine and amine. In addition, the reductive coupling of nitrobenzene with benzyl alcohol in the presence of TEMPO as a radical scavenger showed negligible difference in activity and selectivity under standard reaction conditions (See Supplementary Materials), thereby excluding the possibility of a radical pathway based on a single electron transfer (SET).

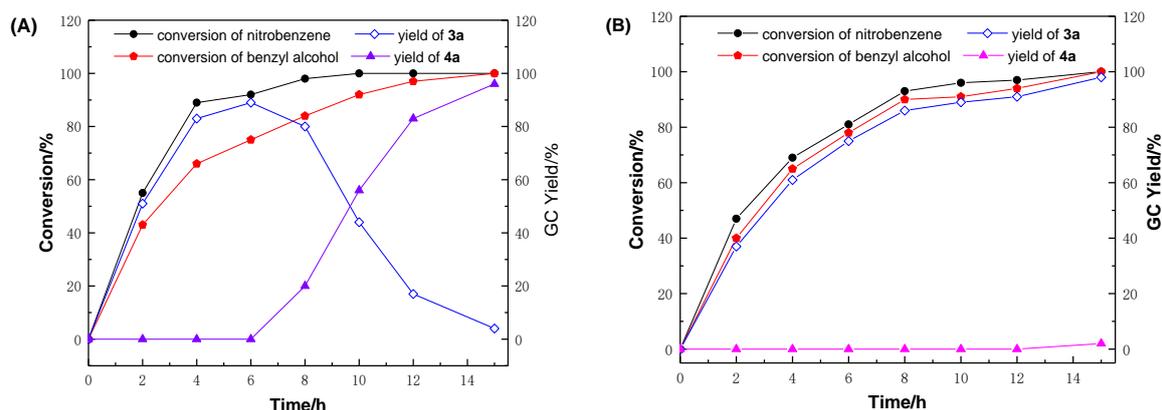
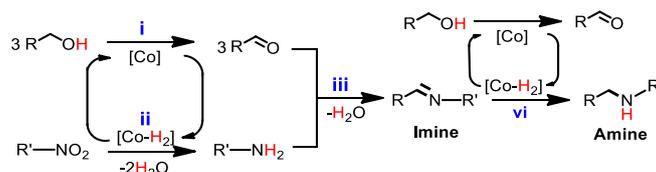


Figure 2. Kinetics of Amine 4a and Imine 3a. Reaction conditions: (A) nitrobenzene (0.2 mmol), benzyl alcohol (0.8 mmol), $\text{CoO}_x\text{@NC-800}$ (10 mol%), *t*BuOK (0.8 mmol), 120 °C, toluene (5 mL), 15 h; (B) nitrobenzene (0.2 mmol), benzyl alcohol (0.6 mmol), $\text{CoO}_x\text{@NC-800}$ (10 mol%), *t*BuOK (0.6 mmol), 120 °C, toluene (5 mL), 15 h.

Based on these experiments, a plausible reaction pathway is proposed as shown in Scheme 3, which involves (i) dehydrogenation of the alcohol to generate 3 equiv. aldehyde and cobalt hydride species with assistance of a base, (ii) reduction of nitroarenes to anilines via the in-situ formed hydride, (iii) condensation of aldehyde and aniline to form imine with excess aldehyde remaining, and (vi) further reduction of imine to amine in the presence of excess amounts of alcohol and base.



Scheme 3. Proposed reaction pathway of the reductive coupling of nitroarenes with alcohols via the borrowing hydrogen strategy.

3. Conclusions

In conclusion, we have developed an inexpensive, active, and heterogeneous hybrid nanostructured cobalt catalyst modified with N-doped hierarchical porous carbon derived from biomass. The resultant catalyst allows for efficient and selective synthesis of various amines and imines directly from the reductive coupling of readily available nitroarenes with benzyl alcohols via the borrowing hydrogen strategy, and it is easily separable and recyclable. To our knowledge, this is the first example of using a heterogeneous base metal catalyst for such organic transformation. Further investigation regarding the applications of this base metal's NPs supported on N-doped porous carbon hybrid material is currently underway in our laboratory.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4344/9/2/116/s1>: Scheme S1: The schematic illustration of the fabrication of $\text{CoO}_x\text{@NC}$ catalyst; Scheme S2: Switchable product selectivity for coupling of nitrobenzene and benzyl alcohol catalyzed by $\text{CoO}_x\text{@NC-800}$ by simple modification of reaction conditions; Scheme S3: Control experiments; Figure S1: High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image and elemental mapping of Co, C, O, and N for the catalyst $\text{CoO}_x\text{@NC-800}$; Figure S2: XRD patterns of $\text{CoO}_x\text{@NC-700}$, $\text{CoO}_x\text{@NC-800}$, and $\text{CoO}_x\text{@NC-900}$; Figure S3: N_2 sorption isotherms and pore size distribution calculated using a nonlocal density function theory (NLDFT) method for the catalysts $\text{CoO}_x\text{@NC-700}$, $\text{CoO}_x\text{@NC-800}$, and $\text{CoO}_x\text{@NC-900}$; Figure S4: Raman spectra of the catalysts $\text{CoO}_x\text{@NC-700}$, $\text{CoO}_x\text{@NC-800}$, and $\text{CoO}_x\text{@NC-900}$; Figure S5: Co 2p_{3/2}, C 1s, N 1s, and O 1s XPS spectra of the catalysts $\text{CoO}_x\text{@NC-700}$, $\text{CoO}_x\text{@NC-800}$, and $\text{CoO}_x\text{@NC-900}$; Table S1: Chemical composition of the catalysts $\text{CoO}_x\text{@NC-T}$ by elemental analysis; Table S2: The textural properties of the catalysts $\text{CoO}_x\text{@NC-T}$; Table S3: The nitrogen types and respective contents in the carbon matrix for the catalysts $\text{CoO}_x\text{@NC-T}$ by XPS analysis; Table S4: The different cobalt phases and respective contents in the catalysts $\text{CoO}_x\text{@NC-T}$ by XPS

analysis; Table S5: Screening of solvents; Table S6: Screening of reaction temperature; Table S7: Screening of CoO_x@NC-T catalysts; Table S8: Effect of amount of benzyl alcohol.

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Conflicts of Interest: The authors declare no conflict of interest.

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