



Oxidative amination of benzylic alkanes with nitrobenzene derivatives as nitrogen sources



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ABSTRACT

The oxidative amination of inert C–H bonds has the potential to fundamentally change chemistry but is severely limited by the low chemo- and regio-selectivity under oxidation conditions. Until now, no efficient methodology for the direct intermolecular amination of terminal sp³-C–H bonds to *N*-alkyl amines has existed. Here, a new concept is proposed for the oxidative amination of the terminal sp³-C–H bond in alkanes via the construction of a complex reaction system composed of a carbon-supported Co–Ni bimetallic catalyst, an alkane, nitrobenzene, *tert*-butyl hydroperoxide and hydrogen. This system allows the reduction of nitrobenzene to aniline and the further oxidative amination of the alkane. Nitrobenzene and toluene derivatives can be successfully transformed into the corresponding *N*-benzyl aniline derivatives with up to 95% isolated yields, and the reaction shows excellent functional group tolerance. This approach offers a new concept for catalyst design and may strongly promote the study of inert C–H bond activation and the synthesis of functional *N*-containing compounds.

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Introduction

Alkanes are the most plentiful organic bases that are easily accessible. Almost all chemical intermediates or products, i.e., fuels, solvents, pharmaceuticals and new materials, are generated via multi-step transformations of alkanes.¹ Among these transformations, the selective functionalization of the sp³-C–H bond is a major challenge.^{2–6} In fact, to date, the sole perfect catalyst system for methane activation is the specific enzyme found in nature, which has been elucidated and mimicked by chemists for a long time.⁷ Over the last decades, rapid progress has been made, and excellent results have been obtained in this field.

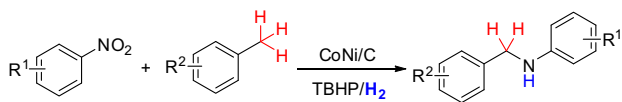
In the field of fine chemicals, a classical route for alkane conversion to nitrogen compounds is through chemical synthesis. Generally, multi-step chemical reactions were used, and a large amount of byproducts were produced if the reaction was initiated from the halogenation or oxidation of the alkane molecule to an alkyl halide, alcohol or aldehyde, followed by aminations with amines to generate *N*-alkyl amines.⁸ Over the last years, numerous approaches for the direct amination of alcohols have been demonstrated, either via nucleophilic substitution or via the borrowing hydrogen reaction mechanism. Typically, metal triflates/halides could promote

nucleophilic substitution pathways in the amination of allylic alcohols,⁹ whereas transition-metal, carbon and enzyme catalysts were used in the borrowing hydrogen reaction mechanism.^{10–22}

Undoubtedly, the one-pot amination of alkanes is highly desirable both in academic and industrial fields. In fact, extensive efforts have been made for the aminations of alkanes with specific *N*-containing molecules.²³ The oxidative amination of alkanes and sulfonamides catalyzed by Mn-,²⁴ Ag-,²⁵ Rh-,²⁶ Ru-,²⁷ Co-²⁸ and Cu-²⁹based catalysts has been demonstrated. Oxidative C–N bond formation between a carboxamide and an alkane over Pd,^{30–32} Ag,³³ Co,³⁴ Ni,³⁵ and Cu,^{36,37} as well as under metal-free conditions, has been developed.^{38,39} C–N bond formation reactions occurred with nitrogen sources containing active groups such as –N₃,^{40,41} PhI=,⁴² and –OH.⁴³ Good results were obtained in the α -amination of aldehydes and secondary sp³-C tertiary carbons; in addition, the cyclization reaction promoted C–H activation of aliphatic amines for strained nitrogen heterocycle synthesis.^{44–47} However, only a few results were reported for the direct reaction between the terminal sp³-C–H and an amine to form *N*-alkyl amine, and no general methodology exists for the one-pot synthesis of *N*-benzyl aniline with aniline/nitrobenzene and toluene as the starting materials (Scheme 1). This reaction would result in severe tar formation because of aniline oxidation as well as resulting in imine generation because the *N*-benzyl aniline is easily oxidized. Herein, we report the one-pot amination of the primary

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Scheme 1. Oxidative amination of benzylic alkanes with nitrobenzene derivatives as nitrogen sources.

sp³-C–H bond in terminal alkanes with nitrobenzene as the nitrogen source in the presence of a suitable amount of hydrogen, which could restrain the aniline oxidation because it was released slowly and reacted soon after its formation.

Results and discussion

Our investigation starts with the oxidative amination of toluene with aniline as the nitrogen source and *tert*-butyl hydroperoxide (TBHP) as the oxidant.

First, a series of carbon-supported transition metal catalysts with lignin as the carbon source was tested with the oxidative amination of toluene as the model reaction. Moderate yields of *N*-benzyl aniline were obtained (Table 1, Entries 1–4). However, an interesting phenomenon was observed when we checked the results, revealing that a better mass balance was achieved when Ni/C was used as the catalyst; this finding is in agreement with our previous results that Ni is a potential species for nitrobenzene reduction and the alcohol amination reaction.^{18,48} In addition, it has been shown that Co(II) or Co(III) is a good choice for the oxidation of alkanes to alcohols.⁴⁹ These results inspire us because they suggest that we can construct a complex catalyst system by combining Ni and Co into a single system for the reductive-oxidative amination of toluene with nitrobenzene. To our delight, an excel-

lent result was achieved when the Co-Ni/C catalyst was prepared and tested. The isolated yield of *N*-benzyl aniline reached 94% (Table 1, Entry 5). For the other bimetallic catalysts, such as Cu-Ni/C and Fe-Ni/C, only moderate yields were obtained (Table 1, Entries 6 and 7). Relatively good results were also obtained when Co and Ni were supported on activated carbon (XC-72R) or with cellulose as the carbon source (Table 1, Entries 8 and 9). Note that the carbonization ratio of lignin was ~50%, while it was only ~14% when cellulose was used. Therefore, the synthesis will be more valuable with lignin as the carbon source for the preparation of the catalyst. Then, the reaction conditions were further optimized, and 95% isolated yield was achieved with 4 mmol TBHP and 4 MPa H₂ (Table 1, Entry 12). It should be mentioned that this catalyst can be easily recovered and recycled, and 93% yield was maintained when it was used in the 3rd run (Table 1, Entry 13). As control reactions, the activity of Ni₂O₃, Co₃O₄ and Ni₂O₃/Co₃O₄ were tested under the same reaction conditions (Table 1, Entries 14–16), and the yields of *N*-benzyl aniline were 24–27%. Thus Ni₂O₃, Co₃O₄ or Ni₂O₃/Co₃O₄ mixture cannot be used as active catalyst directly.

To reveal the structure of the active Co-Ni/C catalyst, it was extensively characterized using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), N₂-adsorption desorption and transmission electron spectroscopy (TEM). Typically, the cobalt and nickel loadings were approximately 6 wt% (catalyst samples were determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES)), and the BET surface areas ranged

Table 1
Catalyst screening and reaction conditions optimization.^a

Entry	Catalyst	Conversion % ^b	Yield/% ^b
1	Co/C	60	32
2	Ni/C	93	50
3	Cu/C	57	36
4	Fe/C	90	20
5	Co-Ni/C	99	94 ^c
6	Cu-Ni/C	96	58
7	Fe-Ni/C	94	49
8	Co-Ni/C-Cel	95	83
9	Co-Ni/XC-72R	99	81
10	Co-Ni/C ^d	93	82
11	Co-Ni/C ^e	92	77
12	Co-Ni/C ^f	99	95 ^c
13 ^g	Co-Ni/C	99	93
14 ^h	Co ₃ O ₄	62	27
15 ^h	Ni ₂ O ₃	54	24
16 ^h	Co ₃ O ₄ /Ni ₂ O ₃	53	27

^a 0.5 mmol nitrobenzene, 10 mL toluene, 60 mg catalyst, 5.5 mmol TBHP, 5.0 MPa H₂, 160 °C, 36 h.

^b Determined by GC-FID using biphenyl as the external standard material.

^c Isolated yield.

^d 2 mmol TBHP was used.

^e 1 MPa H₂ was used.

^f 40 mg catalyst, 4 mmol TBHP, 4.0 MPa H₂.

^g The catalyst was recovered and used at the 3rd run. Entries 1–7 and 10–13, Carbon source = lignin. Entry 8, Carbon source = cellulose, and were denoted as C-Cel.

^h The same metal loadings as those in 40 mg Co-Ni/C catalyst.

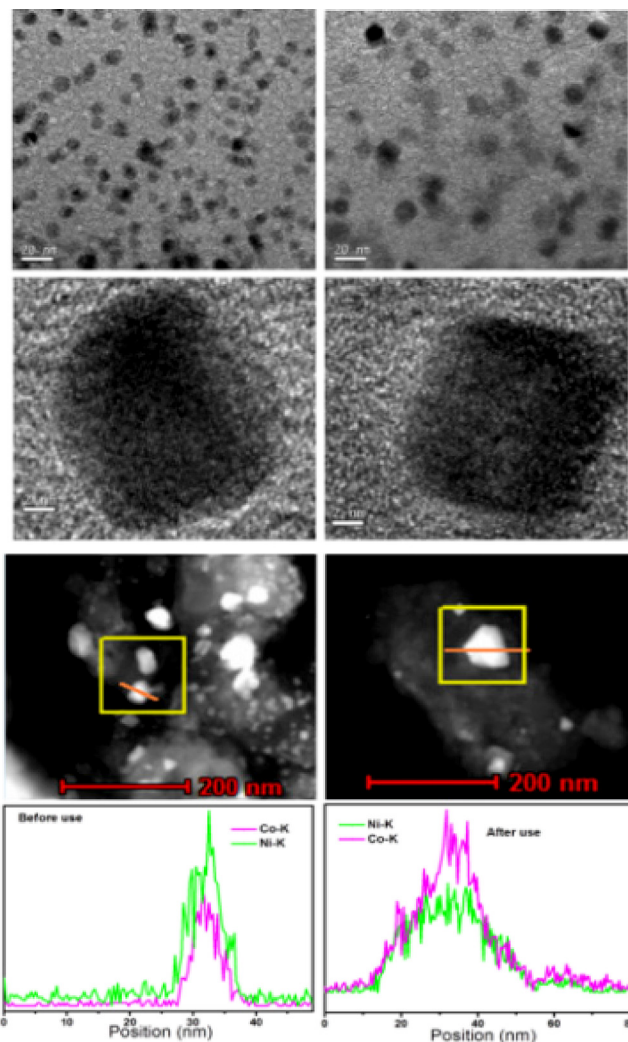


Fig. 1. TEM, HR-TEM and STEM images of Co-Ni/C before (left) and after use (right).

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