

Development of N-Doped Carbon-Supported Cobalt/Copper Bimetallic Nanoparticle Catalysts for Aerobic Oxidative Esterifications Based on Polymer Incarceration Methods

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Supporting Information

ABSTRACT: Heterogeneous nitrogen-doped carbon-incarcerated cobalt/copper bimetallic nanoparticle (NP) catalysts, prepared from nitrogen-containing polymers, were developed, and an efficient catalytic process for aerobic oxidative esterification was achieved in the presence of a low loading (1 mol %) of catalyst that could be reused and easily reactivated. This protocol enabled diverse conditions for the bimetallic NP formation step to be screened, and significant rate acceleration by inclusion of a copper dopant was



discovered. The catalytic activity of the bimetallic Co/Cu catalysts is much higher than that for cobalt catalysts reported to date and is even comparable with noble-metal NP catalysts.

The development of highly active and stable heterogeneous catalysts is a crucial subject in modern science. Metal nanoparticle (NP) catalysts have been of great interest because of their unique activity, ease of heterogenization, and robustness. Metal NP catalysts have been widely studied and applied to transformations of complex organic molecules.¹ However, investigations are limited to noble-metal NPs.

Cobalt NP catalysts on conventional supports such as metal oxides and carbon black are useful for bulk chemical synthesis;² however, they are relatively inert with respect to organic reactions.³ A promising strategy to construct active cobalt NP catalysts is the use of a nitrogen-doped carbon support, considering that nitrogen atoms influence the properties of the carbon material and interact with metal species. Nitrogen-doped carbon-supported cobalt NP catalysts have been studied in the field of electrochemistry⁴ and have recently been applied to several organic reactions.⁵ Among these, aerobic oxidative esterification of alcohols or aldehydes is important because esters are stable and useful synthetic intermediates, and it generates only water as a coproduct. Noble-metal-based NP catalysts to achieve this transformation have been investigated.^{6,7} Pioneered by Beller in 2013,⁸ nitrogen-doped carbon-supported cobalt NP catalysts were applied to this process.⁹ However, a base additive was required in most cases and/or a relatively high catalyst loading was needed (>5.5 mol % under base-free conditions). Their catalytic activities were not comparable with noble-metal NP catalysts. Considering formation of bimetallic NPs often tune their activities (and/or selectivities),¹⁰ the introduction of a second metal to cobalt NPs would be a promising strategy to improve their activity. However, this has not been explored for organic transformations.

The structure control of NPs in nitrogen-doped carbonsupported cobalt catalysts is a key to obtaining highly active and selective catalysts.¹¹ NPs are typically synthesized by pyrolysis of a cobalt complex containing nitrogen atoms in a ligand adsorbed on carbon black (Scheme 1a). However, it is difficult to control the structure of NPs using this method because it usually generates a mixture of small NPs, large aggregated NPs, and/or single-metal sites.^{5e,12} This is probably because NPs form during the pyrolysis, and the stabilization ability of the ligand is not sufficient at very high temperatures (500–1000 °C). Metal–

Scheme 1. Preparation of N-Doped Carbon-Supported Metal NP Catalysts



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organic frameworks (MOFs) are highly porous crystalline materials and recognized as relatively stable and rigid templates for this purpose (Scheme 1b).^{9f,11,13} Although several pyrolyzed MOF catalysts have been studied, it remains difficult to flexibly tune the structure of NPs, especially multimetallic NPs because atomic-level ordering in multimetallic MOFs remains challenging.¹⁴ Therefore, a more general method that can be used to access nitrogen-doped carbon-supported metal NP catalysts that are more controllable in structure and is applicable to the preparation of multimetallic NPs is necessary.

Our group previously investigated a polymer-incarceration (PI) method to immobilize metal NPs by using a polystyrenebased copolymer with a cross-linking moiety and carbon black.¹⁵ In this method, metal NPs were physically enveloped by the polymer and stabilized by multiple interactions from the polymer (so-called microencapsulation). Further heating then promoted cross-linking to afford an insoluble solid material that "locked up" metal NPs. We envisioned that the PI method might be used to construct structurally controlled NP catalysts supported by Ndoped carbon. Thus, nitrogen-containing polymer-encapsulated metal NPs formed by the chemical reduction might be "crosslinked" by the pyrolysis to afford a nitrogen-doped carbonincarcerated metal NP catalyst (NCI-M). Herein, we report earth-abundant-metal-based bimetallic NP catalysts for aerobic oxidative esterification with high activity that is comparable to noble-metal catalysts. Metal NPs can be effectively stabilized by the multiple interactions from the polymer, and diverse conditions for generation of metal NPs, including multimetallic NPs, can be screened by changing the reduction conditions that might affect the structure of the NPs (Scheme 1c).

Poly(4-vinylpyridine) was chosen as a precursor of a nitrogendoped carbon and a temporal stabilizer of NPs (Scheme 2).

Scl	heme	2.	Pre	para	tion	of	NCI	Cata	lysts
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NaBH₄ as a reductant was added to the mixture of the polymer, metal salts and carbon black to form cobalt NPs stabilized by multiple interactions from the polymer. A poor solvent was added to generate a precipitation of the polymer matrix enclosing cobalt NPs (microencapsulation). The obtained polymer matrix was then pyrolyzed at 800 °C to afford the desired catalyst (NCI-Co 1). As a control, a catalyst (NCI-Co 2) was prepared without using a reductant. In this case, the cobalt complex was enclosed in the polymer matrix and directly pyrolyzed. Inductively coupled plasma (ICP) analysis revealed that both catalysts contained cobalt levels close to the target loading.¹⁶ The catalytic activities were evaluated in the aerobic oxidative esterification of alcohol **1a** in methanol (Table 1). Gratifyingly, the reaction proceeded in the presence of 1 mol % of NCI-Co 1 to afford ester 2a in moderate yield (entry 1), whereas NCI-Co 2 gave almost half the yield of that with NCI-Co 1 (entry 2). These results indicate that the reduction treatment during the catalyst preparation significantly enhanced the catalytic activity. Bimetallic NP catalysts were also screened,¹⁶ and the catalyst NCI-Co/Cu 3 prepared from Co(II) acetate and Cu(II) acetate improved the yield dramatically (entry 3). The importance of the reduction

Table 1. Aerobic Oxidative Esterification by NCI Catalysts

\square	OH NCI-Co/M ca MeOH, 0.125	at. (Co: 1 mol %) M, 60 °C, 16 h, 0		e Ar H
1a			2a	3a
entry	Co cat.	$t (^{\circ}C)^{a}$	$2a (\%)^{b}$	3a (%) ^b
1	NCI-Co 1	rt	47	10
2	NCI-Co 2	С	24	12
3	NCI-Co/Cu 3	rt	73	6
4	NCI-Co/Cu 4	С	42	17
5	NCI-Co/Cu 5	50	79	6
6	NCI-Cu 6	rt	0	7
7^d	NCI-Co/Cu 5	50	92 ± 2^{e}	1

^{*a*}t is a parameter used for catalyst preparation, shown in Scheme 2. ^{*b*}Determined by GC analysis. ^{*c*}The catalyst was prepared without reduction treatment. ^{*d*}The esterification was performed at 70 °C. ^{*e*}The average yield of eight reactions using different batches of the catalyst was shown.

treatment in the preparation of the bimetallic NP catalyst was again confirmed because the bimetallic catalyst NCI-Co/Cu 4, prepared without using a reductant, showed moderate activity (entry 4).

The conditions of coreduction of metal salts can affect both the structure of bimetallic NPs and the catalytic activity. Our method could be used to flexibly tune the conditions of NP formation. Several parameters, such as the reduction temperature, the reductant, the polymer, the pyrolysis temperature, and the ratio of metals, were varied,¹⁶ and improved catalytic activity was observed when the reduction was conducted at 50 °C with $NaBH_4$ (NCI-Co/Cu 5, entry 5). These results demonstrate the importance of the tunability of the conditions in the NP formation to obtain efficient catalysts. The corresponding copper NP catalyst did not give the ester product at all (entry 6). No product formed in the presence of NCI-Cu 6, even in the reaction started from the aldehyde, which indicated that the active sites of NCI-Co/Cu were cobalt species.¹⁶ Finally, a satisfactory high yield was obtained with good reproducibility when the reaction was conducted at 70 °C with NCI-Co/Cu 5 (entry 7). No significant leaching of metals (<0.1%) was detected, and the heterogeneous nature of catalysts was confirmed by a hot leaching test.¹⁶ We confirmed that copper acetate as an additive for the reaction with NCI-Co 1 was less effective for the activity indicating that heterogeneous copper NPs were important to enhance the activity.¹⁰

The comparison of the reaction $profiles^{16}$ between the reactions with the monometallic and bimetallic catalysts revealed dramatic acceleration of the reaction rate aided by a copper dopant. According to the initial rate (from 0 to 1 h), the highest turnover frequency (TOF) of 37.2 h⁻¹ was observed in the reaction catalyzed by NCI-Co/Cu 5, whereas a TOF of only 3.21 h⁻¹ was observed in the case of NCI-Co 1. Such a high TOF has never been achieved by using reported cobalt catalysts, even in the presence of a base,¹⁷ and it is even comparable with noblemetal NP catalysts.^{6,7} We then took the profiles of the reaction started from the aldehyde intermediate, which suggested that both oxidation pathways, an alcohol to an aldehyde and an aldehyde to an ester, were accelerated by the copper dopant.

Several characterizations of the NCI catalysts were conducted to elucidate the effect of the reduction treatment. Powder X-ray diffraction (XRD) patterns of NCI-Co/Cu 4 showed clear, sharp peaks derived from the metallic copper and cobalt (Figure 1a).¹⁸ However, the peaks of metallic cobalt in NCI-Co/Cu 3 and 5

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Figure 1. Characterization of catalysts: XRD and STEM analysis of (a,c) NCI-Co/Cu **4** and (b,d) NCI-Co/Cu **5**, and EDS mapping of (e) NCI-Co/Cu **5**.

were significantly suppressed, indicating that the size of crystalline particles in these catalysts were smaller than those in catalyst 4 (Figure 1b).^{16,19} Scanning transmission electron microscopy (STEM) analysis revealed the existence of large aggregates of metal NPs with several size (ca. 30 to ca. 200 nm) formed during pyrolysis in NCI-Co/Cu 4 (Figure 1c), whereas relatively small metal NPs (ca. 20 nm) were mainly observed in NCI-Co/Cu 5 (Figure 1d). These results are consistent with the XRD patterns, clearly demonstrating that the preformation of NPs prior to pyrolysis is a key to controlling the size of NPs and maintaining a small size. A similar tendency was also observed in the monometallic catalysts.¹⁶ Energy dispersive X-ray spectrometry (EDS) mapping revealed that, in all cases, both alloy NPs and segregated cobalt or copper NPs were observed (Figure 1e).¹⁶ The segregation of two metals might occur because of the differences in the reduction potentials between the metals.²⁰

To elucidate details of the surface composition, X-ray photoelectron spectroscopy (XPS) analysis was conducted.² The quantitative analysis based on the Co $2p^{3/2}$ and Cu $2p^{3/2}$ XPS spectra revealed that a copper-rich surface formed in NCI-Co/ Cu 4, whereas a cobalt-rich surface formed in NCI-Co/Cu 3 and 5, although the bulk ratio of the loaded metals in each catalyst was almost 1:1 on the basis of ICP analysis.¹⁶ We postulated that the copper was reduced faster than the cobalt and tended to exist in the core of the alloy NPs under the current mild chemical reduction conditions. These results suggest that the reduction treatment also impacted the structure of the bimetallic NPs and that a modification of the chemical reduction conditions may be used to tune the process. However, XPS spectra of N 1s revealed that pyrrolic nitrogen and pyridinic nitrogen²² were mainly detected, and that their ratio was almost constant regardless of the reduction treatment and the deposition of mono- or bimetallic NPs. A different ratio appeared when the pyrolysis was conducted at lower temperatures that led to a lower ratio of pyrrolic nitrogen. The catalysts pyrolyzed at lower temperature

showed significantly lower activity though no aggregates might form based on XRD analysis.¹⁶ These observations indicated that a higher ratio of pyrrolic nitrogen might be important for high catalytic activity.

With the optimized conditions in hand, the substrate scope was surveyed (Scheme 3). Both electron-donating and -with-





^{*}Isolated yield. ^{*a*}GC yield. ^{*b*}K₂CO₃ (20 mol %) was used. ^{*c*}48 h. ^{*d*}NCI-Co/Cu **5** (2 mol %) was used. ^{*c*}At 110 °C. ^{*f*}At 120 °C.

drawing group substituted benzyl alcohols were smoothly converted into the corresponding methyl esters in high yields under the base-free conditions (2a-g). Whereas substituents at the *m*- or *p*-position were tolerated (2h-i), the presence of a substituent at *o*-position decreased the reactivity $(2\mathbf{j}-\mathbf{k})$; in one case, a catalytic amount of base could be used to promote the reaction (2j). A diol was converted into the corresponding diester 2l in high yield. Various aryl alcohols, including naphthyl alcohol, heteroaryl alcohols, and cinnamyl alcohol, were also suitable substrates, giving the products in good yields under the base-free conditions (2m-2p). Other alcohol solvents were examined, and the corresponding esters were obtained in good to high yields (2q-t). Unfortunately, the reaction with aliphatic alcohol gave a low yield.¹⁶ We then applied NCI-Co/Cu to the synthesis of heteroaryl esters from aldehydes (Scheme 4). Heteroaryl aldehydes are more readily available than the corresponding alcohols because of many direct synthetic methods, such as formylation and the Vilsmeier-Haack reaction. Various substrates, including pyridine, thiophene, furan, quino-



^{*}Isolated yield. ^{*a*}48 h.

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line, and indole derivatives, were converted into the desired esters under the base-free conditions.

NCI catalysts were easily recovered by filtration, and the reusability of the catalyst was examined.¹⁶ A slight loss of activity was observed after several runs, and the catalyst could be reactivated by heating at 500 °C. Consequently, the catalyst could be reused for the tenth run, and around 90% yields were obtained in every run. We assumed that such a heating treatment could destroy and eliminate contaminations derived from organic molecules.

In conclusion, we have developed nitrogen-doped carbonsupported cobalt NP catalysts based on a PI strategy. The chemical reduction of metal salts to form NPs before the pyrolysis is essential to form a highly active catalyst for aerobic oxidative esterification, and these conditions can be flexibly tuned. We discovered for the first time that bimetallic Co/Cu NP catalysts showed an order of magnitude higher TOF than those of cobalt NP catalysts in aerobic esterification reactions, although copper NPs themselves did not catalyze the reaction. The esterification reactions proceeded in the presence of only 1 mol % of the catalyst under base-free conditions for most substrates, including various heteroaryl compounds. Such a remarkable catalytic performance under relatively mild conditions for a wide variety of substrates has never been achieved, even with noblemetal NP catalyst systems. The catalyst was reusable for 10 runs and easily reactivated. These protocols are suitable for the construction of more active nitrogen-doped carbon-supported metal NP catalysts that can be used in various catalysis fields.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b02118.

Experimental procedures, characterization data, and copies of NMR charts (PDF)

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