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Oxygenation of Styrenes Catalyzed by N-Doped Carbon Incarcerated Cobalt Nanoparticles

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Abstract

We found that cobalt nanoparticle catalysts supported on nitrogen-doped carbon could facilitate oxygenation of styrenes in a heterogeneous manner. Both the nitrogen dopant and cobalt species were essential to promote the reactions. Based on several mechanistic studies, the formation of radical intermediates on cobalt nanoparticles is proposed.

Keywords: Cobalt nanoparticles, Nitrogen-doped carbon, Olefin oxygenation

1. Introduction

Metal nanoparticle (NP) catalysts have great potential to construct ideal heterogeneous catalysts for organic synthesis due to their high activity, ease of immobilization on a solid support, and high stability. However, their applications to organic synthesis have been limited to systems based on noble metals such as Rh, Pd, Pt, and Au.[1] Although it is desirable to use inexpensive, earth-abundant transition metals such as cobalt, applications of these catalysts have been limited to simple gas phase reactions until recently.[2]

Hydrofunctionalizations of olefins with a metal hydride are useful reactions that enable various types of bond formation including C–C, C–O, C–N, C–halogen, C–S, and C–Se bonds.[3] Among them, C–O bond forming reactions with molecular oxygen are important because they are applied frequently to a wide range of natural product syntheses.[3–4] Inspired by metalloenzymatic systems with cofactors, metalloporphyrin catalyst systems with hydride sources, such as borohydrides and alcohols, were pioneered in the 1980s.[5] Later, Mukaiyama developed simpler cobalt diketonate complex catalyst systems using silanes, which became a valuable tool in organic synthesis.[6] In spite of the usefulness and long history of these reactions,[7] to our knowledge, there is no report of a corresponding heterogeneous catalyst system. In the cases of reported metal complex catalysts, electronic states of metal centers have been tuned by changing counter anions[8] or using porphyrin-type ligands[5,7a,7d] to design suitable catalysts. However, anchoring such anions or ligands on a solid support would be difficult or tedious. Alternatively, decoration of metal NPs by ligand molecules can be considered;[9] however, whether such modification is possible for first-row metal NPs is questionable, as they may form an inert oxide species on the surface.[2a]

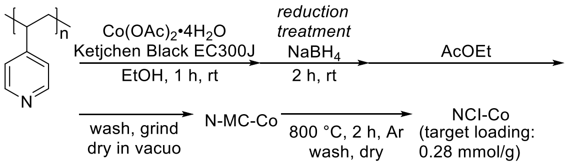
The use of nitrogen-doped carbon as a support is a promising strategy for constructing active cobalt NP catalysts for several organic transformations,[10] such as oxidative esterification of alcohols and aldehydes,[11] oxidation of hydrocarbons,[12] and hydrogenation reactions.[13] However, these reactions can be performed by other metal NPs and the catalytic activity is often not comparable with that of precious metal-based heterogeneous catalysts. Bond forming reactions specifically catalyzed by nitrogen-doped carbon supported cobalt NPs are not well explored,[14] although cobalt has been utilized in a wide range of unique organic reactions in the field of homogeneous metal complex catalysis and is not a mere substitute for precious metals.[15]

We previously developed methods based on a polymer-incarceration strategy[16] to prepare nitrogen-doped carbon supported NP catalysts from poly(4-vinylpyridine) as a nitrogen source.[11a] The process included NP formation by reduction of metal salts in a polymer solution and microencapsulation of NPs by polymer before pyrolysis, expecting efficient stabilization of small NP species. We then found that bimetallic Co/Cu NP catalysts prepared by this method achieved high catalytic performance for oxidative esterification of alcohols and aldehydes that was comparable with that of Au NP catalysts. Motivated by these results, we hypothesized that a nitrogen dopant could work as a good solid ligand to construct catalytically active Co NP species for olefin oxygenation reactions. Herein, we describe these types of heterogeneous reactions using Co NP catalysts supported on nitrogen-doped carbon.

2. Results and Discussion

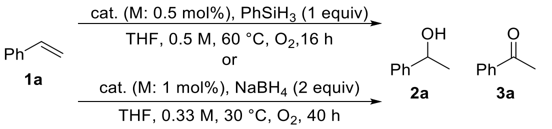
2.1. Development of catalysts. Nitrogen-doped carbon incarcerated NP catalysts (NCI-M) were prepared from poly(4-vinylpyridine) based on a previously reported procedure (Scheme 1). Their catalytic activity was tested on the oxygenation of styrene **1a** in the presence of phenylsilane as a hydride source under an atmosphere of oxygen (Table 1). Gratifyingly, **1a** was fully consumed to produce the oxygenated products as a mixture of alcohol **2a** and ketone **3a** in the presence of NCI-Co (entry 1). The catalyst prepared without the reduction treatment significantly decreased the activity (entry 2), and X-ray diffraction (XRD) and scanning transmission electron microscopy (STEM) analysis of this catalyst revealed that aggregation of NPs occurred.[17] As a control, other metal NPs, including a precious metal, were examined and neither NCI-Cu nor NCI-Au catalyzed this type of reaction (entries 3 and 4). The reaction barely proceeded in the absence of any catalysts or reductants (entries 5 and 6). These findings suggested that this reaction was specifically enhanced by the cobalt species.

To obtain one of the products selectively, the effect of hydride sources was examined. When $NaBH_4$ was used instead of $PhSiH_3$, only alcohol adduct **2a** was obtained in excellent yield (entry 7). The reaction could proceed even under air without loss of the yield (entry 8). To confirm the importance of the nitrogen dopant on the support, several catalysts were prepared as controls and examined under these conditions. Polymer-microencapsulated Co catalyst (N-MC-Co), that is a precursor before pyrolysis to produce NCI-Co, barely promoted the reaction (entry 9). Moreover, carbon black (Ketjen Black EC300J)-supported Co NP catalysts (Co/C and Co/C-800), prepared by the same procedure as for N-MC-Co or NCI-Co respectively without using the polymer, barely catalyzed the reaction either regardless of whether pyrolysis was performed during the catalyst preparation or not (entries 10 and 11). These results clearly showed that the presence of nitrogen-doped carbon enables Co NPs to catalyze olefin oxygenation reactions.



Scheme 1. Preparation of NCI Co catalysts.

Table 1. Effect of catalysts in oxygenation of styrenes.

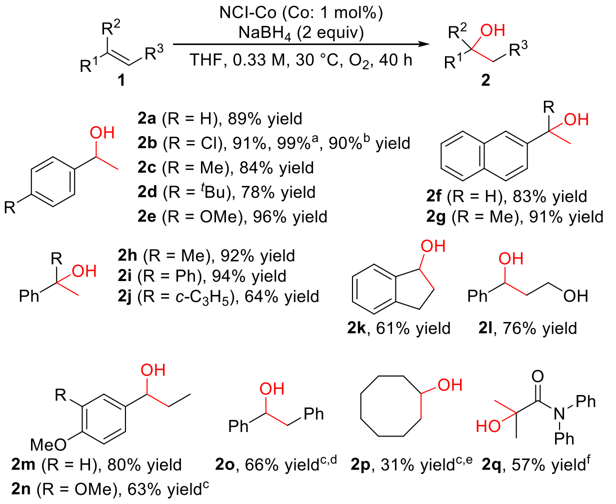


Entry	Catalyst	Reductant	2a (%)[a]	3a (%)[a]
1	NCI-Co	$PhSiH_3$	37	57
2	NCI-Co[b]	$PhSiH_3$	22	40
3	NCI-Cu	$PhSiH_3$	1	4
4	NCI-Au	$PhSiH_3$	trace	trace
5	no catalyst	$PhSiH_3$	0	2
6	NCI-Co	no reductant	0	0
7	NCI-Co	$NaBH_4$	89	0
8[c]	NCI-Co	$NaBH_4$	89	0
9	N-MC-Co	$NaBH_4$	1	0
10	Co/C[d]	$NaBH_4$	4	0
11	Co/C-800[e]	$NaBH_4$	3	0

[a] Determined by GC analysis. [b] The catalyst was prepared without reduction treatment. [c] The reaction was conducted under air. [d] The catalyst was prepared by following the method to access N-MC-Co without using poly(4-vinylpyridine). [e] The catalyst was prepared by following the method to access NCI-Co without using poly(4-vinylpyridine).

2.2. Substrate scope. With the optimized conditions for alcohol selective olefin oxygenation in hand, substrate generality was surveyed (Scheme 2). Styrene derivatives bearing an electron-withdrawing group (**1b**), electron-donating group (**1c**–**1e**), or naphthyl ring (**1f**) were smoothly converted into the corresponding secondary alcohols (**2a**–**2f**). Styrene derivatives **1g**–**1i**, with a substituent at an α-position, were also tolerant to afford the corresponding tertiary alcohols **2g**–**2i** in excellent yields. In the reaction with α-phenyl vinylcyclopropane **1j**, the corresponding tertiary alcohol **2j** was obtained in good yield without generating a ring-opening adduct. We then examined several β-substituted styrenes. Indene **1k** could be converted to the corresponding secondary alcohol **2k** in moderate yield. Cinnamyl alcohol **1l** was also afforded the diol **2l** in good yield. Although *trans*-anethole **1m** was a good substrate for this reaction system, an additional methoxy group decreased reactivity and higher reaction temperature was required to afford the desired product **2n**. As *trans*-stilbene was also less reactive, probably as the result of a stable conjugated system, we screened catalysts at elevated temperature and found that bimetallic Co/Cu catalyst (NCI-Co/Cu) slightly improved the result to afford the alcohol **2o** in good yield. Although cyclooctene as an aliphatic substrate had much less reactivity, the product **2p** could be observed in low yield with higher catalyst loading. Not only styrene derivatives, but also an unsaturated carbonyl compound was tested. Because $NaBH_4$ was a sufficiently strong enough reductant to reduce carbonyl groups under the optimized condition, $PhSiH_3$ was used for the reaction with methacrylamide derivative **1q** to afford the corresponding α-hydroxy carbonyl compound **2q** in moderate yield. We examined the reusability of our catalyst in the reaction with **1b** and found that high yields could be maintained until the third run. Since full conversion of **1b** could not be achieved in the third run, we treated the recovered catalyst at 500 ˚C for 2 h under vacuum to reactivate the catalyst.[11a] However, further decrease of the yield in fourth and fifth runs was observed (63% and 67%, respectively).

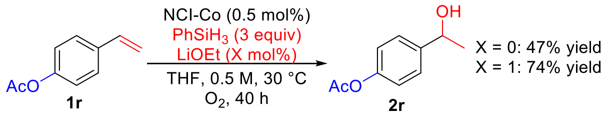
We were then interested in controlling alcohol/ketone selectivity in the reaction with silane. Such milder conditions are important in the reaction with a substrate bearing strong reductant-sensitive functional groups, such as an ester. 4-Acetoxy styrene **1r** was chosen as a model for this purpose; however, almost no selectivity between **2r** and **3r** was observed in the absence of any additives (Scheme 3). We then screened several additives, and it was found that catalytic amounts of lithium halide and lithium alkoxide changed the selectivity to produce **2r** as a major product.[17] Finally, 1 mol% of lithium ethoxide was determined as the best additive, and the alcohol adduct **2r** was obtained in good yield without decomposition of the acetoxy group. Considering that lithium triflate and perchlorate did not affect the selectivity, a coordinative anion might work as a strong electron donor to the metal to tune the reactivity.[18]



[a] 2nd run. [b] 3rd run. [c] 60 ˚C. [d] NCI-Co/Cu was used. [e] NCI-Co

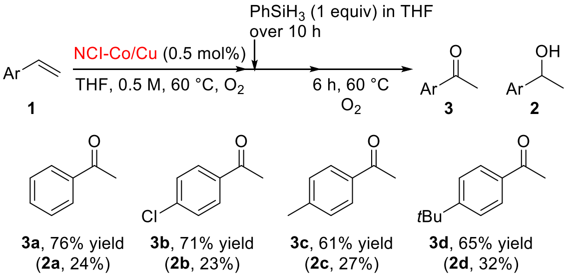
(2 mol%) was used. [f] $PhSiH_3$ was used instead of $NaBH_4$.

Scheme 2. Substrate scope in hydration of olefins.



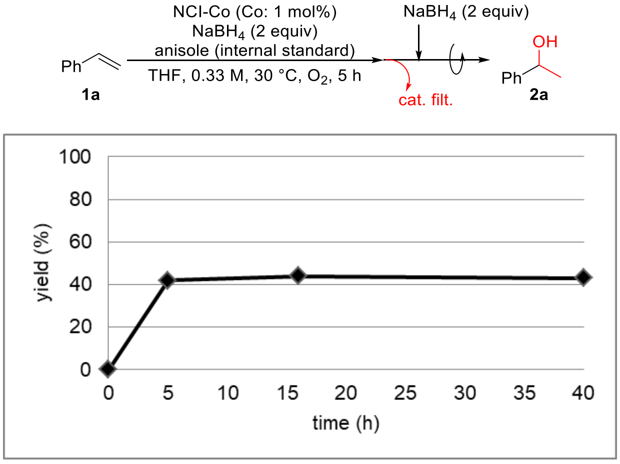
Scheme 3. Hydration of 4-acetoxystyrene.

We then attempted to obtain a ketone adduct selectively (Scheme 4). Slow addition of silane was crucial to lead the selective production of a ketone. Moreover, the use of a bimetallic catalyst (NCI-Co/Cu), that is the better catalyst for oxidation than NCI-Co, improved the result. Several acetophenone derivatives **3a**–**3d** could be produced in moderate to good yields.



Scheme 4. Substrate scope in oxygenation of olefins to ketones

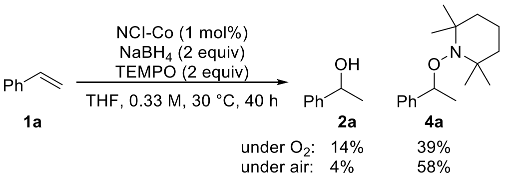
2.3. Mechanistic insights. We were interested in how the reaction was promoted by the nitrogen-doped carbon supported cobalt NP catalyst. At first, we confirmed the heterogeneity of the current catalyst system. No metal leaching into the reaction solution was detected by an ICP analysis, whose detection limit was 0.083% of cobalt. Moreover, a hot leaching test was conducted (Scheme 5). The solid materials were removed by filtration in the middle of the reaction (5 h) and the reaction was continued in the filtrate. As a part of the $NaBH_4$ was also removed, so a new portion of $NaBH_4$ was added to the filtrate. Even though an excess amount of the reducing agent existed, the reaction did not proceed any further, indicating that the catalysis occurred in a heterogeneous manner.



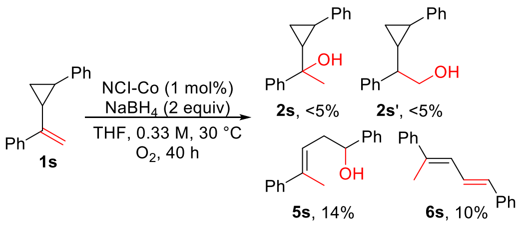
Scheme 5. Hot leaching test.

Because conventional oxygenation of olefins was suggested to proceed via radical intermediates,[3] we examined this possibility in our heterogeneous catalyst system. In the presence of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) as a radical trapping agent, the formation of the TEMPO inserted adduct **4a** was observed; however, alcohol product **2a** was also obtained, probably because insertion of molecular oxygen and TEMPO to the benzyl radical intermediate remained competitive (Scheme 6). The reaction in the presence of TEMPO under air could further suppress the formation of **2a**, and the yield of **4a** was increased. A radical clock experiment using the cyclopropylbenzene substituted styrene **1s** was performed (Scheme 7). Compared with α-cyclopropylstyrene **1j**,[19] no cyclopropyl substituted alcohol adducts **2s** and **2s′** were observed and several ring opening products, such as **5s** and **6s**, were obtained instead.

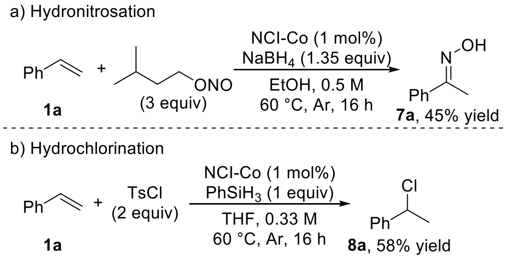
Other singly occupied molecular orbital-philic reagents (SOMOphiles), instead of molecular oxygen, were tested (Scheme 8). We found that nitrite[20] or tosyl chloride[7b] could insert to the benzylic position to form the corresponding oxime **7a** or benzyl chloride **8a** in moderate yield. These experiments supported a reaction pathway via radical intermediates and showed the possibility that the catalyst systems could be applied to various bond formation reactions.



Scheme 6. Radical trapping experiments.



Scheme 7. Radical clock experiments.



Scheme 8. Hydrofunctionalization of styrene with other SOMOphiles.

NCI-Co was characterized to elucidate the role of the nitrogen dopant and active species. STEM analysis of NCI-Co and Co/C-800 were conducted to compare the size of Co NPs (Figure 1). Regardless of the presence of the nitrogen dopant, Co NPs were well distributed all over carbon black and were kept to small size. This indicated that the role of nitrogen dopant was not just as a stabilizer of NPs to prevent them from aggregation.

XPS analysis of these two catalysts was then performed (Figure 2). To check the possibility of a reaction between the Co surface and the reductant, the Co $2p^{3/2}$ spectra of the pristine catalysts and the catalyst treated with $PhSiH_3$ at 60 °C were recorded. In NCI-Co before the treatment with silane, two major peaks assigned to Co^{3+} (779.6 eV) and Co^{2+} (781.9 eV) and a satellite peak corresponding to Co^{2+} were observed (Figure 2a).[21] On the other hands, no peak corresponds to Co(0) (~778 eV) was observed indicating that cobalt oxide species mainly existed on the surface of the catalyst.[22] After the treatment with silane, the satellite peak diminished and only one peak corresponding to Co^{3+} (779.7 eV) was observed (Figure 2b). This indicated that $PhSiH_3$ reacted with the Co surface to change its oxidation state. We assumed that silane could reduce Co^{3+} species to Co^{2+} species. Because the treated catalyst was shortly exposed to air during work-up and analysis, Co^{2+} species might react with absorbed O_2 and silane to give Co^{3+} species.[23] By contrast, no change of the Co $2p^{3/2}$ spectra was observed before or after the treatment in the case of Co/C-800 (Figures 2c and 2d). These results suggested that the nitrogen dopant facilitated the reaction between a hydride source and Co surface to form an active Co intermediate.

Based on these investigations, a similar mechanistic scenario with a homogeneous cobalt complex system (Scheme 9)[6a,23] can be assumed for our heterogeneous NCI-Co system. By the aid of nitrogen-dopant, Co(III)-H species form from a hydride source on the surface of NPs and insert to an olefin substrate to generate a radical intermediate. After molecular oxygen reacts with this intermediate, further reaction with a hydride source affords products and regenerates the Co(III)-H species.

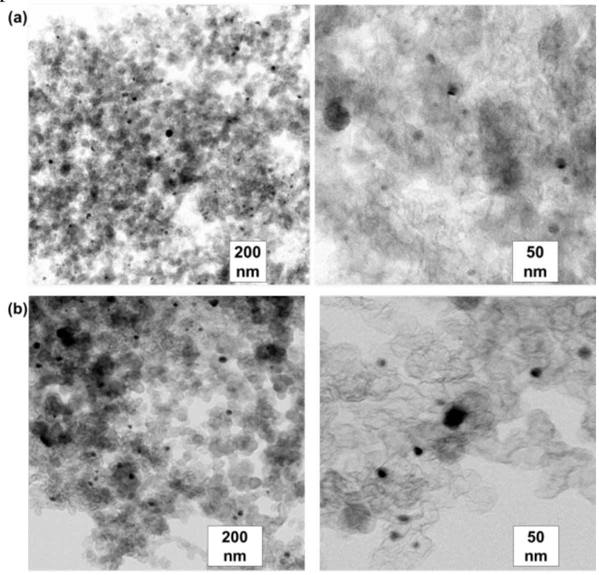
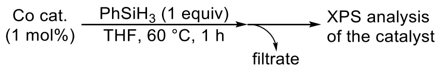


Figure 1. STEM images of (a) NCI-Co and (b) Co/C-800.



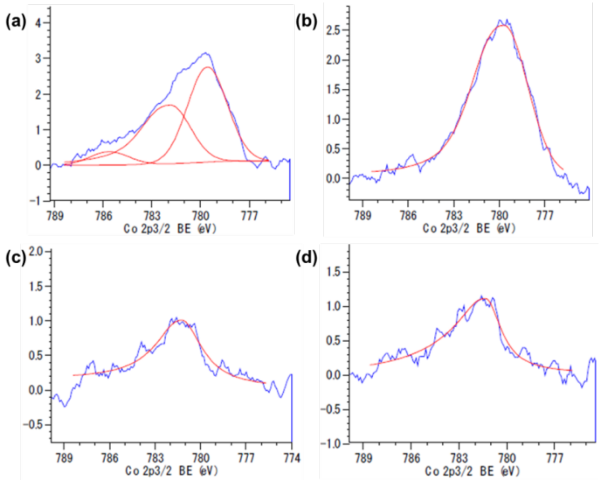
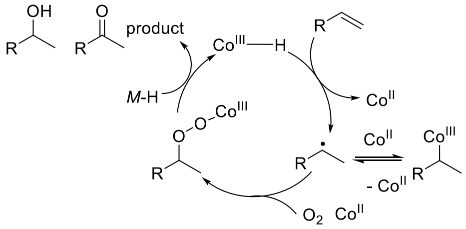


Figure 2. XPS analysis of (a) NCI-Co, (b) NCI-Co after treatment with silane, (c) Co/C-800, and (d) Co/C-800 after treatment with silane.



Scheme 9. Plausible mechanism for olefin oxygenation.

3. Conclusion

In summary, we developed NCI-Co catalyzed olefin oxygenation reactions. Among the metals examined, including noble metals, the reaction proceeded specifically on cobalt catalysts, and nitrogen dopant was crucial for the catalytic activity. In the presence of $NaBH_4$ as a hydride source, the corresponding alcohols were obtained in high yields. The substrate bearing reductant-sensitive functional group was made tolerant by changing the reductant and using an additive, and furthermore, we could access the corresponding ketones by changing reaction conditions. A preliminary examination of other SOMOphiles suggested that our heterogeneous catalyst systems have the potential to be applied to more general hydrofunctionalization of olefins to form various kinds of bonds. Several mechanistic studies suggested that the reaction proceeded in a heterogeneous manner and formed a radical intermediate on cobalt NP species. To our knowledge, this is the first example of heterogeneous catalyst systems for oxygenation of olefins. This work provides not only synthetic utility, but also new insights into nitrogen-doped carbon supported NP species.

4. Experimental

Preparation of NCI-Co. To a stirring solution of poly(4-vinylpyridine) (200 mg) in ethanol (4 mL), a solution of $Co(OAc)_2 \cdot 4H_2O$ (27.8 mg, 0.112 mmol) in ethanol (1 mL) was added dropwise at room temperature under air. To this solution was added ketjen black (200 mg), and the mixture was stirred for 1 h at room temperature under air. To this mixture, a solution of $NaBH_4$ (21.2 mg, 0.56 mmol) in ethanol (1 mL) was slowly added, and the mixture was continued to stir for 2 h at room temperature under air. To this mixture was added ethyl acetate (50 mL) at room temperature and stirred for 30 min. The catalyst was filtered and washed in water (50 mL). The catalyst was filtered and washed in acetone (50 mL). After filtration, the catalyst was grinded and dried *in vacuo*. The catalyst was treated by pyrolysis at 800 ˚C for 2 h under Ar atmosphere. After cooling to room temperature, the catalyst was washed in ethanol (30 mL) under air. The catalyst was filtered, washed with ethanol, water and acetone and dried *in vacuo* to afford NCI-Co (280 mg). NCI-Co (10 mg) was heated in a mixture of sulfuric acid and nitric acid at 200 ˚C, and the mixture was cooled to room temperature. The amount of Co in the resulting solution was measured by ICP analysis to determine the loading of Co (0.312 mmol/g).

Preparation of NCI-Co/Cu. To a stirring solution of poly(4-vinylpyridine) (200 mg) in ethanol (4 mL), a solution of $Co(OAc)_2\cdot 4H_2O$ (13.9 mg, 0.056 mmol) in ethanol (1 mL) and $Cu(OAc)_2\cdot H_2O$ (11.2 mg, 0.056 mmol) in ethanol (1 mL) was added dropwise at room temperature successively under air. To this solution was added ketjen black (200 mg), and the mixture was stirred for 1 h at 50 ˚C under air. To this mixture, a solution of $NaBH_4$ (21.2 mg, 0.56 mmol) in ethanol (1 mL) was slowly added, and the mixture was continued to stir for 2 h at 50 ˚C under air. To this mixture was added ethyl acetate (50 mL) at room temperature and stirred for 30 min. The catalyst was filtered and washed in water (50 mL). The catalyst was filtered and washed in acetone (50 mL). After filtration, the catalyst was grinded and dried *in vacuo*. The catalyst was treated by pyrolysis at 800 ˚C for 2 h under Ar atmosphere. After cooling to room temperature, the catalyst was washed in ethanol (30 mL) under air. The catalyst was filtered, washed with ethanol, water, THF and acetone and dried *in vacuo* to afford NCI-Co/Cu (280 mg). NCI-Co/Cu catalyst (10 mg) was heated in a mixture of sulfuric acid and nitric acid at 200 ˚C, and the mixture was cooled to room temperature. The amount of Co and Cu in the resulting solution was measured by ICP analysis to determine the loading of Co and Cu (Co: 0.159 mmol/g, Cu: 0.157 mmol/g).

A typical procedure of olefin hydration with $NaBH_4$. NCI-Co (Co: 1.0 mol%) was added in a Carousel^{TM} tube and dried with heat gun *in vacuo*. $NaBH_4$ (22.7 mg, 0.6 mmol), olefin **1** (0.3 mmol) and THF (0.9 mL) were added to the Carousel tube. The mixture was stirred for 40 h under 1 bar of O_2 atmosphere at 30 ˚C. If necessary, anisole (25~30 mg) as an internal standard was added to the mixture, and an aliquot of the reaction mixture (~0.02 mL) was filtered through a silica gel packed disposable Pasteur pipette and washed with ethyl acetate to inject to the GC analysis. Ethyl acetate was added to the mixture and the solid catalyst was removed by filtration. After that, the solvents were removed *in vacuo* and ^1H NMR analysis of the crude mixture was conducted with tetrachloroethane as an internal standard. The residue was purified by preparative TLC to afford the corresponding alcohol **2**.

A typical procedure of olefin hydration with $PhSiH_3$ and additives. NCI-Co (Co: 0.5 mol%) was added in a Carousel^{TM} tube and dried with heat gun *in vacuo*. 4-Acetoxystyrene **1r** (48.7 mg, 0.3 mmol), LiOEt (0.003 mmol) in THF (0.6 mL) and $PhSiH_3$ (97.4 mg, 0.9 mmol) were added to the Carousel tube. The mixture was stirred for 40 h under 1 bar of O_2 atmosphere at 30 ˚C. Ethyl acetate was added to the mixture and the solid catalyst was removed by filtration. The organic phase was washed with water and dried over Na_2SO_4. The solvents were removed *in vacuo* and ^1H NMR analysis of the crude mixture was conducted with tetrachloroethane as an internal standard. To the crude mixture, methanol was added and treated with a silica gel packed eluting tube. After solvents were removed, the crude mixture was dissolved in diethyl ether and was purified by preparative TLC to afford the corresponding alcohol **2r** (74% yield).

A typical procedure of olefin oxygenation to ketone with $PhSiH_3$. NCI-Co/Cu (Co: 0.5 mol%) was added in a Carousel^{TM} tube and dried with heat gun *in vacuo*. Olefin substrate **1** (0.3 mmol) and THF (0.6 mL) were added to the Carousel tube. The mixture was stirred under 1 bar of O_2 atmosphere at 60 ˚C and $PhSiH_3$ (32.5 mg, 0.3 mmol) in THF (0.3 mL) was added by a syringe pump over 10 h. After completion of the addition, the reaction mixture was further stirred for 6 h. If necessary, anisole (25~30 mg) as an internal standard was added to the mixture, and an aliquot of the reaction mixture (~0.02 mL) was filtered through a silica gel packed disposable Pasteur pipette and washed with ethyl acetate to inject to the GC analysis. Diethyl ether was added to the mixture and the solid catalyst was removed by filtration. The organic phase was washed with water and dried over Na_2SO_4. The solvents were removed *in vacuo* and ^1H NMR analysis of the crude mixture was conducted with tetrachloroethane as an internal standard. After solvents were removed, the crude mixture was dissolved in diethyl ether and was purified by preparative TLC to afford the corresponding ketone **3**.

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Supporting Information

Experimental procedures, characterization data for products and copies of ^1H and ^{13}C NMR spectra of products. This material is available on https://

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Graphical Abstract

<Title>
Oxygenation of Olefins Catalyzed by N-Doped Carbon Incarcerated Cobalt Nanoparticles
<Authors' names>
Tomohiro Yasukawa, Shū Kobayashi*
<Summary>
We found that cobalt nanoparticle catalysts supported on nitrogen-doped carbon could facilitate oxygenation of olefins in a heterogeneous manner. Both the nitrogen dopant and cobalt species were essential to promote the reactions. Based on several mechanistic studies, the formation of radical intermediates on cobalt nanoparticles is proposed.
<Diagram>