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N-Doped Sub-3 nm Co Nanoparticles as Highly Efficient and Durable Aerobic Oxidative Coupling Catalysts

Junxing Han,*^[a] Feifei Gu,^[b] and Yuchao Li^[a,c]

Abstract: A nano-coating associated with sulfuric acid leaching protocol was developed to prepare N-doped sub-3 nm Co-based nanoparticle catalyst (Co-N/C) using melamine-formaldehyde resin as the N-containing precursor, active carbon as the support, and Co(NO₃)₂ as the Co-containing precursor. By thermal treatment under nitrogen atmosphere at 800°C and leached with sulfuric acid solution, a stable and highly dispersive Co-N coordination structure was uniformly dispersed on the formed Co-N/C catalyst with a Co loading of 0.47 wt% and Co nanoparticle size of 2.55 nm. The Co-N/C catalyst was characterized with XRD, XPS, Raman, SEM, TEM, ICP, and elemental analysis. The Co-N/C catalyst showed extremely high catalytic efficiency with a TON of 257 for the aerobic oxidative coupling of aldehydes with methanol to directly synthesize methyl esters with molecular oxygen as the final oxidant. The Co-N/C catalyst also showed broad substrate range and stable recyclability. After recycling for 7 times, no obvious deactivation was detected. It was confirmed that the sub-3 nm Co-N coordination structure formed between metallic Co nanoparticles and pyridinic N doping into graphitic layers functions as the active site to activate molecular oxygen for the β -H elimination from generated hemiacetal intermediates to produce methyl esters. The nano-coating associated with acid leaching protocol provides a novel strategy to prepare highly efficient non-precious metal-based catalysts.

Introduction

Oxidation reactions play significant roles in producing highly valuable fine chemicals.^[1] Among them, oxidative coupling of aldehydes with methanol is of high efficiency to directly produce methyl esters in the absence of carboxylic acids or carboxylic acid derivatives.^[2] One of the most representative applications is the oxidative coupling of methylacrolein with methanol to synthesize methyl methacrylate (MMA).^[3] Conventionally, oxidative coupling of aldehydes with methanol is conducted with stoichiometric amount of heavy metal salts, such as CrO_3 , KHSO₅, KMnO₄, or V₂O₅ (Scheme 1).^[4] However, the process

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Scheme 1. Oxidative coupling of aldehydes with methanol to produce methyl esters.

generates a large amount of toxic pollutants. In recent years, aerobic oxidative coupling of aldehydes with methanol using molecular oxygen as the final oxidant has been actively pursued. Up to now, several kinds of precious metal-based catalysts, such as Pd,^[5] Ru,^[6] Ir,^[7] and Au-based catalysts,^[8] have been developed and used for the aerobic oxidative coupling reaction (Scheme 1). But the high cost and scarcity of precious metals limit their industrial applications.

Since Jasinski's pioneering work of using earth-abundant transition metal macrocyclic compounds as the electrolyte of polymer electrolyte membrane cells,^[9] M-N/C hybrids (M represents transition metals, especially iron and cobalt) reaction,^[10] prepared by hydrothermal high-temperature pyrolysis,^[11] or interfacial coordination using various combinations of transition-metal inorganic salts, nitroaen containing compounds and carbon have attracted much attention as promising materials to substitute precious metal catalysts in the electrochemical oxygen reduction and hydrogen evolution reactions,^[12] the selective oxidation of alcohols to nitriles,^[13] the oxidative dehydrogenation of N-hererocycles,^[14] the epoxidation of alkenes,^[15] and the selective hydrogenation of nitroarenes.^[16] Beller and co-workers successfully designed a series of novel CoOx-N/C and FeOx-N/C catalysts by pyrolyzing organometallic Co(II) and Fe(II) complexes.^[13-16] For the first time, they realized the aerobic oxidative coupling of benzyl alcohol with methanol using CoOx-N/C as the catalyst.[17] However, owing to the large size of CoO_x nanoparticles, much excess methanol, high Co loadings, and long reaction time are needed to maintain high product yields.

Although the nature of the active sites remains unclear, it has been verified that the performance of M-N/C catalysts are closely related to the structure of N-containing ligands, transition metal precursors, carbon support morphology, and thermal treatment method.^[18] Herein, we describe a N-doped sub-3 nm Co nanoparticle catalyst with a Co loading of 0.47 wt% and Co nanoparticle size of 2.55 nm by using a melamine-formaldehyde resin (MF resin) nano-coating associated with sulfuric acid

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Scheme 2. Schematic diagram for the synthesis of Co-N/C catalyst.

leaching protocol. The prepared Co-N/C catalyst showed high activity and stability for the aerobic oxidative coupling of aldehydes with methanol to directly produce methyl esters. It was confirmed that the sub-3 nm Co-N coordination structure formed between metallic Co nanoparticles and pyridinic N doping into graphitic layers functions as the active site to activate molecular oxygen for the β -H elimination from generated hemiacetal intermediates to produce methyl esters.

Results and Discussion

As shown in Scheme 2, Co-N/C catalyst was prepared as follows: (A) adsorbing Co(II) cations onto active carbon; (B) nano-coating Co(II)/C with MF resin; (C) pyrolyzing under nitrogen atmosphere to form the primary CoO_x-N/C hybrid; and (D) leaching with sulfuric acid solution to obtain the final Co-N/C catalyst.

Figure 1A shows XRD patterns of primary CoO_x-N/C hybrids pyrolyzed in the range of 600 to 900°C. It could be seen that when the pyrolyzing temperature increased to 700°C, diffraction peaks belonging to Co₃O₄ and CoO appeared at 31.0, 36.6, 42.4, and 61.3°, respectively. After treated at 800°C, besides Co₃O₄ and CoO, new diffraction peaks at 44.0 and 51.4° could be ascribed to the metallic cobalt. The metallic Co might be generated by reducing Co-based precursors with carbon-based species at high temperatures. Further increasing the pyrolyzing temperature to 900°C, no new diffraction peaks appeared. But the diffraction peaks became sharp, indicating the aggregation of Co-based nanoparticles at high temperatures. Meanwhile, a N-doped graphitic layers derived from MF resin formed and coated on the surface of CoO_x/C.

D band at 1353 cm⁻¹ and G band at 1598 cm⁻¹ of the pyrolyzed materials could be detected in the Raman spectra (Figure 1B). With the increment of pyrolyzing temperature, the I_D/I_G value declined from 1.27 at 600 °C to 1.09 at 900 °C, indicating the increased degree of graphitization of carbon-



Figure 1. (A) XRD patterns of CoO_x -N/C pyrolyzed at different temperatures; and (B) Raman spectra of CoO_x -N/C pyrolyzed at different temperatures.

based materials. Analysis to the element contents demonstrated that elevating the pyrolyzing temperature resulted in the increased content of carbon accompanied by the decreased contents of Co, O, and N (Table S1).

Hence, the pyrolyzing temperature is an important parameter for the synthesis of N-doped Co-based hybrids. At low pyrolyzing temperatures, Co-based species could not be reduced to metallic Co and the degree of graphitization of carbon materials was at a low level. On the contrary, at high pyrolyzing temperatures, the leaching of Co and N occurred accompanied by the aggregation of Co-based nanoparticles. Therefore, in the further work, the pyrolyzing temperature of 800°C was used to maintain the reduction of Co-based species and the doping of N species into graphitic layers.

After leaching CoO_x -N/C with sulfuric acid, the Co-N/C catalyst was obtained. Figure 2A shows the SEM image of Co-N/C catalyst. The rough surface of active carbon indicates the formation of Co-N-C hybrid structure (Figure S1). Diffraction peaks belonging to metallic Co, CoO, and Co₃O₄ particles could be detected on the CoO_x-N/C hybrid (Figure 1A, 800°C). The sharp diffraction peaks indicates the high contents of Co-containing species and large particle size. After sulfuric acid leaching, only a weak diffraction peak ascribed to metallic Co was detected at 44.0° on Co-N/C catalyst (Figure 2B, red), suggesting the low Co content and small particle size. The Co contents for CoO_x-N/C and Co-N/C measured by ICP-AES were 4.9 wt% and 0.47 wt%, respectively (Table S2).

Large CoO_x particles were observed on CoO_x-N/C hybrid with some CoO_x particles larger than 150 nm (Figure S2). After sulfuric acid leaching, large CoO_x particles disappeared. The remaining Co-based nanoparticles with a particle size of 2.55 nm uniformly dispersed on the active carbon support (Figure 2C and inset). In the HR-TEM image, metallic cobalt nanoparticles with a (200) *d*-spacing of 0.176 nm could be clearly observed, which is in line with the XRD measurements. Meanwhile, Co nanoparticles were coated with graphitic layers derived from pyrolyzed MF resin, which might be the reason that these highly dispersed Co nanoparticles could be preserved after sulfuric acid leaching. The *d*-spacing of generated graphitic layers is 0.336 nm, corresponding to the (002) basal plane of carbon materials.

Directly pyrolyzing MF resin under nitrogen atmosphere generated a N-doped carbon material, denoted as CN. The XRD

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Figure 2. (A) SEM image of Co-N/C; (B) XRD patterns of fresh Co-N/C (red), Co-N/C further pyrolyzed under nitrogen atmosphere at 800 $^{\circ}$ C for another 2 h (blue), and Co-N/C used for 7 times (black); (C) TEM image of Co-N/C with the inset showing the particle-size distribution histogram; and (D) HR-TEM image of metallic Co and N-doped graphitic layers on Co-N/C.

pattern of CN showed a diffraction peak at 26.1° (Figure S3). The corresponding lattice spacing is 0.341 nm in accordance with TEM observations. It should be noted that CN showed a positive shift in the C (002) peak in comparison with active carbon (Figure S3), indicating that N-doping promoted the graphitization degree of carbon materials and decreased the lattice spacing of the (002) crystal planes.^[19] When MF resin was supported on active carbon and pyrolyzed under nitrogen atmosphere, the obtained CN@C material showed the same XRD pattern as the active carbon (Figure S3) and no peak position shift was observed.

XP spectra of Co 2p and N 1s are shown in Figure 3. For CoOx-N/C, the Co 2p peaks could be fitted into three peaks located at 780.6, 782.3, and 783.7 eV (Figure 3B), corresponding to metallic Co, Co₃O₄, and CoO, respectively. For Co-N/C, the peak intensity of Co 2p became weak after sulfuric acid leaching, suggesting the low Co content. In addition, the fitted spectrum showed that zero-valenced metallic Co is the main Co-containing species (Figure 3A), indicating that most cobalt oxides (Co₃O₄ and CoO) have been leached in the course of sulfuric acid treatment. Analysis to element contents showed that after sulfuric acid leaching, the contents of Co and O dropped from 1.24 and 7.18 atomic% to 0.34 and 4.85 atomic%, respectively (Table S3). For CoO_x-N/C, the N 1s peaks could be fitted into pyridinic N (398.9 eV), pyrrolic N (400.2 eV), and quaternary N (401.3 eV) (Figure 3E). For Co-N/C, the fitted N 1s spectrum was almost the same as that of CoO_x-N/C. No obvious changes in the peak intensity and the peak numbers were observed, indicating the doped N into graphitic layers are stable.

For CN material, XP spectrum of N 1s could also be fitted into pyridinic N (398.1 eV), pyrrolic N (399.5 eV), and quaternary N (400.7 eV) (Figure 3C), which indicates that the addition of Co did not affect the doping of N into graphitic layers. However, compared with CN, the binding energy of pyridinic N of Co-N/C



Figure 3. Fitted XPS: (A) Co 2p on Co-N/C; (B) Co 2p on CoO_x-N/C; (C) N 1s on CN; (D) N 1s on Co-N/C; and (E) N 1s on CoO_x-N/C.

shifted to 398.9 eV. The positively shifted binding energy suggests the presence of a chemical interaction between highly dispersed metallic Co and pyridinic N,^[20] which preserves the sub-3 nm Co nanoparticles in the course of sulfuric acid leaching.

The catalytic performance of Co-N/C catalyst as well as other relevant catalysts was evaluated by using the aerobic oxidative coupling of benzaldehyde with methanol as a model reaction. The results were summarized in Table 1. The blank experiment showed that almost no benzaldehyde was converted. In the absence of catalysts, both the benzaldehyde conversion and the methyl benzoate yield are negligible, indicating that catalysts play important roles in activating oxygen molecules. In the presence of active carbon supports or CN, the conversion of benzaldehyde was less than 10%, while using CN@C as the catalyst the substrate conversion dropped to less than 2%, though it was reported that the presence of quaternary N on CN facilitates the activation of molecular oxygen.^[22] Calcinating Co(NO₃)₂ under nitrogen atmosphere at 800 °C generated a mixture of CoO and Co₃O₄ (Figure S4), denoted as CoO_x. No diffraction peaks belonging to metallic Co could be detected. The catalytic activity of CoO_x was low with a benzaldehyde conversion of 6%. No improvements were observed using the combination of CoO_x and CN@C as the catalyst. Calcinating active carbon supported Co(NO₃)₂ produced a hybrid material denoted as CoOx@C. Metallic Co, CoO and Co3O4 were

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detected in the XRD pattern with metallic Co as the main crystal phase (Figure S4), suggesting that active carbon could reduce the Co precursor at high temperatures. Compared with CoO_x-N/C, the sharper diffraction peaks of metallic Co on CoOx@C indicate the larger metallic Co particle size on CoO_x@C, which manifests that the coating of MF resin on Co(II)/C could effectively inhibit the aggregation of Co-based species. The large Co-based particle size of CoOx@C resulted in the low catalytic activity with a substrate conversion less than 10%. Calcinating the combination of MF resin and Co(NO₃)₂ under the same conditions generated a hybrid material denoted as CoO_x-CN. The diffraction peaks in the XRD pattern of CoO_x-CN could be attributed to metallic Co, CoO, and Co₃O₄, respectively (Figure S4). The CoO_x-CN catalyst provided a benzaldehyde conversion of 50% with a product selectivity of 74%, which suggests that after N doping the catalytic performance of Cobased catalyst could be greatly improved. Using Co(NO₃)₂, the combination of Co(NO₃)₂ and CN, or the combination of Co(NO₃)₂ and CN@C as the catalyst, almost no substrate conversion occurred.

In a series of CoO_x-N/C hybrids treated in the range of 600 to 900°C, the CoO_x-N/C pyrolyzed at 800°C showed the best performance with a benzaldehyde conversion of 94% and a methyl benzoate selectivity of 96%. According to the discussion on XRD and Raman spectra in Figure 1, the optimal pyrolyzing temperature of 800°C benefits for the reduction of Co precursor to metallic Co and the doping of N into graphitic layers.

We then evaluated the performance of Co-N/C catalyst for the aerobic oxidative coupling reaction. To our surprise, no obvious decline in catalytic activity was observed, though the Co loading dropped from 4.9 to 0.47 wt% after sulfuric acid leaching. The Co-N/C catalyst offered a benzaldehyde conversion of 92% with a methyl benzoate selectivity of 89%. The calculated TON, defined as the total number of product moles formed per mole of Co, of Co-N/C reached up to 257, nearly 10 times higher than that of CoO_x-N/C (Table S2). The much higher TON of Co-N/C demonstrates that the leached large Co-based particles had marginal effect on the aerobic oxidative coupling of benzaldehyde with methanol and the remaining sub-3 nm Co-N coordination structure functions as the active site for the aerobic oxidative coupling reaction.

In the absence of K₂CO₃, the benzaldehyde conversion declined to 3%, which demonstrates that the alkalinity of K₂CO₃ also plays an important role in improving the oxidative coupling reaction rate. Based on the proposed oxidative coupling mechanism, $^{\left[2a\right] }$ this reaction begins with the deprotonation of methanol. The formed methoxy group nucleophilically attacks the aldehydic carbon atom to generate the hemiacetal intermediate. The β -H elimination of hemiacetal by activated oxygen species yields the methyl ester product. Hence, the Co-N coordination structure functions as the active site for the activation of molecular oxygen to generate activated oxygen species and K₂CO₃ acts as an alkali to promote the formation of methoxy groups by deprotonation of methanol. The combination of Co-N coordination structure of Co-N/C and K₂CO₃ exhibited extremely high efficiency for the oxidative coupling of benzaldehyde with methanol and provided a TON of 257.

Table 1. Aerobic oxidative coupling of benzaldehyde with methanol to synthesize methyl benzoate. $^{\left[a\right] }$

$ \begin{array}{c} & & \\ & & $) + H ₂ O)—
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Entry	Catalyst	$T[^{\circ}C]^{[b]}$	Conv. [%]	Selec. [%]
1 ^[c]	None		< 2	< 2
2	None		< 2	< 2
3	С		7	46
4	CN	800	8	28
5	CN@C	800	< 2	< 2
6	CoO _x	800	6	33
7	CoO _x + CN@C	800	8	20
8	CoO _x @C	800	8	51
9	CoO _x -CN	800	50	74
10	Co(NO ₃) ₂		< 2	< 2
11	Co(NO ₃) ₂ + CN	800	< 2	< 2
12	Co(NO ₃) ₂ + CN@C	800	< 2	< 2
13	Co(NO ₃) ₂ + C		29	93
14	CoO _x -N/C	600	16	74
15	CoO _x -N/C	700	67	82
16	CoO _x -N/C	800	94	96
17	CoO _x -N/C	900	88	90
18	Co-N/C	800	92	89
19 ^[c]	Co-N/C	800	3	36
20 ^[d]	Co-N/C-FT	800	33	81
21 ^[e]	Pd ₂ Pb ₈ /alumina		94	90

 $^{[a]}$ Typical reaction conditions: Catalyst (0.2 g), benzaldehyde (9.4 mmol), methanol (625 mmol), K₂CO₃ (1.4 mmol), 0.1 MPa of oxygen, 30 mL min⁻¹ of oxygen flow rate, 60 $^{\circ}$ C, 2.0 h. $^{[b]}$ *T* represents the pyrolyzing temperature. $^{[c]}$ In the absence of K₂CO₃. $^{[d]}$ The obtained Co-N/C catalyst was further calcined at 800 $^{\circ}$ C under nitrogen atmosphere for another 2.0 h. $^{[e]}$ The Pd₂Pb₈/alumina catalyst was prepared according to the literature method. $^{[21]}$

If the Co-N/C hybrid was further treated under nitrogen atmosphere at 800 °C for another 2 h, the obtained material, denoted as Co-N/C-FT, displayed obvious diffraction peaks belonging to CoO and Co₃O₄ in the XRD pattern (Figure 2B, blue). The Co-N/C-FT catalyst showed inferior activity to Co-N/C with the benzaldehyde conversion dropped to 33%, which further suggests that the Co-N coordination structure between metallic Co and pyridinic N functions as the active site for the oxidative coupling reaction. To be highlighted, the TON of Co-



Scheme 3. Catalytic performance of Co-N/C for the aerobic oxidative coupling of various aldehydes with methanol. Reaction conditions: Co-N/C Catalyst (0.2 g), aldehyde (4.7 mmol), methanol (625 mmol), K₂CO₃ (1.4 mmol), 0.1 MPa of oxygen, 30 mL min⁻¹ of oxygen flow rate, 60° C.

N/C was nearly two times higher than the traditional Pd-Pb bimetallic catalyst. The latter offered a TON of 126 (Table S2).

Besides benzaldehyde, Co-N/C catalyst also showed high activity for the aerobic oxidative coupling of substituted benzaldehyde with methanol. The results were listed in Scheme 3. Complete conversion was achieved using 4.7 mmol of benzaldehyde as the substrate in one hour with a methyl benzoate yield of 96%. It was found that methyl group substituted benzaldehyde with the substituent group located at 2-, 3-, and 4-position, respectively, showed different activity. Complete conversion was achieved in 2 hours for the 3- and 4-position methyl substituted benzaldehyde, while the yield of 2-methyl benzaldehyde was only 37%. After prolonging reaction time to 12 h, the yield of 2-methyl benzaldehyde indicates that the ortho-substituent groups showed strong steric hindrance effect



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Figure 4. Kinetic data for aerobic oxidative coupling of aldehydes with methanol: benzaldehyde (black), 2-chlorobenzaldehyde (red), and 2-methylbenzaldehyde (blue).

on the oxidative coupling reaction. The same phenomenon was also observed by using 2-chlorobenzaldehyde and 2-methoxy benzaldehyde as the substrate. Kinetic measurements showed that the oxidative coupling of benzaldehyde with methanol was a pseudo first order reaction (Figure 4). With the increase of the steric hindrance of the ortho-position substituent groups (CH₃ > Cl > H), the reaction rate constant decreased from 3.31 to 0.22 h⁻¹ (Figure 4). For 2-methoxy benzaldehyde, the oxidative coupling reaction no longer displayed the pseudo first order behavior (Figure S5). Based on the proposed oxidative coupling mechanism mentioned above,[2a] the nucleophilically attack of the methoxy group to the aldehydic carbon atom might act as a rate determining step for the oxidative coupling reaction. Because the β -H elimination of formed hemiacetal intermediates by active oxygen species on the Co-N coordination structure is a fast reaction step.^[2a] When the ortho-position H of benzaldehyde was substituted by a bulk groups, the steric hindrance effect of the substituent group inhibited the attack of methoxy group to the aldehydic carbon atom and resulted in the decrease of the reaction rate. By elevating reaction temperature and prolonging reaction time, the substrate conversion and product selectivity could be improved.

On the other hand, no obvious electronic effect was observed. Co-N/C catalyst showed high activity for the oxidative coupling of 4-methyl benzaldehyde, 4-chlorobenzaldehyde, and 3-nitrobenzaldehyde with methanol. Complete conversion was achieved within 2 hours. Due to the stronger electron-donating effect of the methoxy group, complete conversion of 4-methoxy benzaldehyde was achieved after reacting for 6 hours. The coexistence of steric hindrance effect and electron-donating effect resulted in the conversion of 2-methoxy benzaldehyde no longer displayed the pseudo first order behavior.

Kinetic data manifest that on Co-N/C catalyst the steric hindrance effect of ortho-substituent groups plays a more important role than the electronic effect in determining the

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Figure 5. Recycling tests of Co-N/C for the aerobic oxidative coupling of benzaldehyde with methanol.

reaction rates. This phenomenon clearly demonstrates that the nucleophilic attack of methoxy group to the aldehydic carbon atoms to form the hemiacetal intermediates acts as the rate-determining step for the oxidative coupling of aldehydes with methanol.

Due to the coating of N-doped graphitic layers, Co-N/C catalyst showed excellent stability and could be recycled for 7 times without deactivation for the oxidative coupling of benzaldehyde with methanol (Figure 5). No aggregation of Co-based species was observed in the TEM image of the recycled Co-N/C catalyst and the Co nanoparticles still uniformly dispersed on the support (Figure S6). The XRD pattern of the recycled Co-N/C resembled that of the fresh one. Only a weak diffraction peak attributed to metallic Co was detected at 44.0° for the recycled Co-N/C catalyst (Figure 2B, black), further suggesting the stability of the Co-N/C catalyst.

Conclusions

In conclusion, a nano-coating associated with acid leaching protocol was developed to prepare N-doped sub-3 nm Co-based nanoparticle catalyst using MF resin as the N-containing precursor, Co(NO₃)₂ as the Co-containing precursor, and activated carbon as the support. After pyrolysis under nitrogen atmosphere at 800°C, a primary CoO_x-N/C hybrid material was formed. Further treating the CoOx-N/C hybrid with sulfuric acid solution leached unstable Co-based species and obtained the final Co-N/C catalyst with highly dispersed Co nanoparticles. After sulfuric acid leaching, the Co loadings dropped from 4.9 wt% to 0.47 wt%. The reserved metallic Co nanoparticles with a particle size of 2.55 nm chemically interacted with pyridinic N derived from pyrolysis of MF resin to form a stable Co-N coordination structure, which functions as the active site for the activation of molecular oxygen and provides high activity, broad substrate range as well as stable recyclability for the aerobic oxidative coupling of benzaldehyde with methanol. The nanocoating associated with acid leaching protocol provides a novel strategy to prepare highly efficient non-precious metal-based catalysts.

Experimental Section

Catalyst preparation

Melamine-formaldehyde resin (MF resin) was synthesized according to the reported method.^[22] Typically, formaldehyde solution (37 wt%, 8.9 mL), deionized water (40 mL) and NaOH aqueous solution (1.0 M, 0.2 mL) were mixed together in a 100 mL round bottom flask and stirred for 10 min at room temperature. Then, melamine (5.0 g) was added to the solution. The flask was transferred into an oil bath and maintained at 90 °C for 1 h. The obtained clear MF resin solution was promptly cooled down to room temperature.

Active carbon powder (Vulcan XC72R, 2.0 g), Co(NO₃)₂+6H₂O (1.46 g, 5 mmol) and a HCl aqueous solution (0.5M, 50 mL) were mixed in a 250 mL round bottom flask and stirred for 30 min at room temperature. Then, the obtained MF resin solution was added into the mixture and stirred for another 5 h at room temperature. Water was removed slowly under vacuum. The residual solid sample was dried at 80 °Cfor 12 h. The raw sample was grinded to a fine powder. The obtained fine powder was pyrolyzed in N₂ atmosphere at 800 °C for 2 h and cooled down to room temperature. The obtained sample was denoted as CoO_x-N/C. The heat-treated sample CoO_x-N/C (1 g) was leached in a H₂SO₄ aqueous solution (0.5M, 75 mL) at 80 °Cfor 12 h and thoroughly washed with deionized water. After dried under vacuum at 80 °Cfor 12 h, the Co-N/C catalyst was obtained.

Characterization

Raman measurements were performed on a LabRAM HR800 equipped with an excitation wavelength of 514 nm and CCD detector. X-ray diffraction (XRD) patterns were recorded on a Rigaku SmartLab diffractometer using Cu Kα radiation at 45 kV and 200 mA. XPS spectra were collected on an ESCALAB 250Xi electron spectrometer using 300 W Al Kα X-ray source and the binding energies were referenced with C 1s at 284.6 eV. Field-emission SEM and HR-SEM images were observed on a JSM 6700F microscope. TEM and HR-TEM images were obtained on a JEM-2100F microscope operated at 200 kV. The cobalt content was measured by ICP-AES with an ICP E-9000 spectrometer. The Co loading in the Co-N/C hybrid is 0.47 wt%. Elemental analysis was conducted on a Varian EL cube equipment. The contents of C, H, and N in the Co-N/C hybrid are 88.65, 0.17, and 3.35 wt%, respectively.

Aerobic oxidative coupling reaction

Co-N/C catalyst (0.2 g), benzaldehyde (1.0 g, 9.4 mmol), methanol (20.0 g, 625 mmol) and K₂CO₃ (0.2 g, 1.4 mmol) were added to a 100 mL autoclave sequentially. After filling the autoclave with 0.1 MPa of oxygen, the reaction was stirred at 60 °C for 2.0 h with the oxygen flow rate of 30 mL min⁻¹. After cooling to room temperature, 1 mL reaction mixture and 0.2 mL ethanol (the internal standard) were mixed together. The obtained sample was directly subjected to GC analysis. Conversion, selectivity and yields were measured by GC-FID (Agilent 6890 equipped with DB-624 capillary column). Qualitative analysis of esters and byproducts was made by GC-MS and identified by comparison with authentic samples. Catalytic oxidative coupling of other aldehydes with methanol was carried

out in a similar way. The reproducibility for each experiment was repeated for three times.

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Keywords: aldehyde • cobalt • methanol • nitrogen • oxidative coupling

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Hybrid catalyst: Highly dispersed N-doped Co nanoparticles with a Co loading of 0.47 wt% and Co nanoparticle size of 2.55 nm function as highly efficient active sites for the aerobic oxidative coupling of aldehydes with methanol and provide an extremely high TON of 257 as well as stable recyclability.



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