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Cobalt Nanoparticles-Catalyzed Widely Applicable Successive C-C Bond Cleavage in Alcohols to Access Esters

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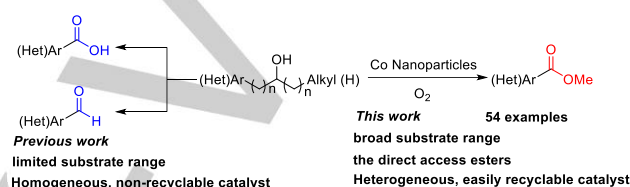
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Supporting information for this article is given via a link at the end of the document.

Abstract: Selective cleavage and functionalization of C-C bonds have important applications in organic synthesis and biomass utilization. However, functionalization of C-C bonds by controlled cleavage remains difficult and challenging because they are inert. Herein, we describe an unprecedented efficient protocol for the breaking of successive C-C bonds in alcohols to form esters with one or multiple carbon atoms less using heterogeneous cobalt nanoparticles catalyst with dioxygen as the oxidant. A wide range of alcohols including inactive long-chain alkyl aryl alcohols undergo smoothly successive cleavage of adjacent $-(C-C)_n-$ bonds to afford the corresponding esters. The catalyst was used for seven times without any decrease in activity. Characterization and control experiments disclose that cobalt nanoparticles are responsible for the successive cleavage of C-C bonds to achieve excellent catalytic activity, while the presence of Co-N_x has just the opposite effect. Preliminary mechanistic reveals that a tandem sequence reaction is involved in this process.

Introduction

Carbon-carbon (C-C) bonds are the fundamental building blocks that make up organic compounds.^[1] Selective cleavage and functionalization of this kind of bond have important applications in organic chemistry, biodegradation, and oil industry.^[2] Among the various C-C bond cleavage, we focus on the cleavage of C-C bonds in alcohols, which are abundant in biomass. For example, lignin structural units contain large amounts of C(OH)-C and C-C bonds, so studying their fracture has important implications for lignin degradation.^[3] However, studies on the degradation and transformation of alcohol compounds through the C-C bond cleavage are limited. The processes of the cleavage of C-C bonds in alcohols involved, either the cleavage of C(OH)-C to form one carbon shorter functional compounds or successive cleavage adjacent $-(C-C)_n-$ bond to form multiple carbon atoms shorter functional compounds. The reports on the breaking of C(OH)-C bonds in alcohols have been well developed with homogeneous transition-metal catalysts. The corresponding functional products aldehydes,^[4] acids,^[5] ketones^[6] or alkanes^[7] are afforded with one carbon less. Very recently, Shengyong Yang and co-workers reported the ^tBuOK (3 equiv.)-O₂ transition-metal-free catalytic system for the C(OH)-C bond cleavage reaction with the disadvantage that the substrates are



Scheme 1. Successive C-C bond cleavage of alcohols.

restricted to heteroarylalcohols.^[8] Buxing Han and co-workers reported the cleavage of C(OH)-C bonds of alcohols into the corresponding acids with nitrogen dioxide as catalyst, but the substrate range is limited to secondary alcohols.^[9] In contrast, there have been few reports on the adjacent $-(C-C)_n-$ bond successive cleavage to form multiple carbon atoms shorter functional compounds.^[10] Recently, Yang and co-workers reported the use of ^tBuONa (3 equiv.)-O₂ system for converting primary alcohols to acids with more carbon atoms less in dry hexamethylphosphoramide (HMPA).^[10a] Han and co-workers disclosed PdCl₂/CuCl catalyst system for the successive cleavage of C-C bonds in alcohols to aldehydes.^[10b] However, both of these catalytic systems are still suffering from limited substrate range and exhibit low catalytic activity or even fail to work for inactive long-chain alkyl aromatic alcohols. So it is still a challenge to address functionalization of C-C bonds in such inactive substrates. Up to now, there has been no method to provide a complete substrate range including functional aromatic, aliphatic, heterocyclic, allylic, propargylic primary and secondary alcohols for the successive cleavage and functionalization of C-C bonds. In addition, despite some splendid achievements have been made in the cleavage of C-C bonds in alcohols to acids or aldehydes (Scheme 1), the direct transformation of alcohols to esters through C-C bond cleavages is still unknown. Thus, the development of a cost-effective, applicable catalyst that enables a highly efficient successive cleavage of adjacent $-(C-C)_n-$ bonds apart from the cleavage of C(OH)-C bond is highly desirable, but challenging.

Our recent reports using cobalt-based nanoparticles or single atom catalysts (SACs) prepared from a well-defined cobalt complex promoted us to investigate the utilization of the heterogeneous cobalt/nitrogen-doped carbon catalyst for the oxidative cleavage of C-C bonds in alcohols.^[11] To the best of our knowledge, neither homogeneous nor heterogeneous cobalt-based catalysts were used for the target transformation.

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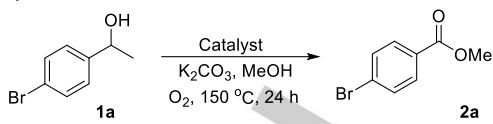
Herein, we describe an unprecedented efficient protocol for converting primary and secondary alcohols to one or more carbon atoms shorter esters using heterogeneous Co nanoparticles catalyst with dioxygen as the environmentally benign terminal oxidant (Scheme 1). The ability to successive cleavage adjacent -(C-C)_n-bonds apart from C(OH)-C bond is significant advantage. The directly accessible ester via successive C-C bond cleavage in alcohols is another feature. The catalytic system showed an unprecedented broad substrate range compared to previously reported systems. In particular, the present catalyst system can successfully achieve the transformation of inactive substrates. The wide range of application is extended to various functionality aromatic, aliphatic, heterocyclic, allylic, propargylic primary and secondary alcohols. The robust catalyst was used for seven times without any decrease in activity. Catalyst characterization and KSCN poison experiments gave deep insights into the active species. Accordingly, we definitely elucidate the destroyer role of Co-N_x sites and the pivotal role of graphene encapsulated Co nanoparticles in the Co-NC materials for the successive C-C bond cleavage in alcohols. Based on a large number of control experiments, a reasonable C-C bond cleavage reaction path is proposed.

Results and Discussion

The catalyst was prepared by a simple method of support-sacrificial. In brief, cobalt acetate and 1,10-phenanthroline (1,10-phen) was dissolved into distilled water, and then the mixture was supported on colloidal silica. After removing the solvent, the obtained powder was pyrolyzed at 700-900 °C under a constant nitrogen flow for 2 h. Then the silica template was etched away by acid leaching. The catalysts pyrolyzed at varying temperatures were labeled as Co-NC-X (X: pyrolysis temperature).

To evaluate the catalytic performances of the Co-NC catalysts for the oxidative cleavage C-C bonds of secondary alcohols, 1-(4-bromophenyl)ethanol (**1a**) was chose as a model substrate (Table 1). The blank experiment indicated that the reaction did not work without catalyst (Table 1, entry 1). The pyrolysis temperature for the preparation of the catalysts has a great influence on the reactivity (Table 1, entries 2-4), with Co-NC-900 affording the best performance. Control experiments were performed using commercially available Co(OAc)₂·4H₂O, 1,10-phenanthroline and Co(OAc)₂·4H₂O with 1,10-phenanthroline as catalysts for the reaction all showed lower activity with the formation of methyl 4-bromobenzoate (**2a**) (Table 1, entries 5-7). O₂ was demonstrated to be necessary for the conversion (Table 1, entry 8). The reaction can also be carried out without adding K₂CO₃, affording the **2a** in 85% yield (Table 1, entry 9). By decreasing the reaction temperature, the yield of **2a** fell to 80% (Table 1, entry 10). Only 18% of **2a** was obtained when template SiO₂ was not removed (Table 1, entry 11), indicating that mesoporous structure is primarily responsible for this reaction. Further, as a more convincing comparison, we evaluated the performance of a series of reported nitrogen-doped carbon-supported cobalt nanoparticles (Supporting Information, Table S1). The results indicated that the use of Co-NC-900 is the most suitable choice for the reaction.

The most attractive merit of the heterogeneous catalyst is its capability for recycling. The reusability of the Co-NC-900 was evaluated by using 1-(4-bromophenyl)ethanol as substrate. As shown in Supporting Information, Figure S1, catalytic activity

Table 1. Optimization of the Reaction Conditions.^[a]


Entry	Catalysts	Conv. [%] ^[b]	Yield [%] ^[b]
1	-	-	-
2	Co-NC-900	>99	97
3	Co-NC-800	>99	82
4	Co-NC-700	>99	56
5	1,10-Phen	-	-
6	Co(OAc) ₂ ·4H ₂ O	-	-
7	Co(OAc) ₂ ·4H ₂ O/1,10-Phen	17	1(16)
8 ^[c]	Co-NC-900	37	(36)
9 ^[d]	Co-NC-900	>99	85
10 ^[e]	Co-NC-900	>99	80
11 ^[f]	Co(phen) ₂ (OAc) ₂ @SiO ₂ -900	93	18(54)

[a] Reaction conditions: 1-(4-bromophenyl)ethanol (0.25 mmol), K₂CO₃ (10 mol%), catalyst (7.5 mol%), MeOH (4 mL), 0.6 MPa O₂, 150 °C, 24 h. [b] Determined by GC analysis using biphenyl as internal standard and the products were confirmed by GC-MS, values in parentheses correspond to yield of ketones. [c] 0.6 MPa N₂. [d] without K₂CO₃. [e] 130 °C. [f] not washed with HF.

remained very well in the six consecutive runs. The composition and structure of the reused Co-NC-900 catalyst were characterized with TEM (HRTEM), HAADF-STEM and XRD (Supporting Information, Figure S2-4). The results unambiguously demonstrate the catalyst possess excellent stability. More detailed results and discussions are shown in the Supporting Information, Figures S2-4. In addition, the heterogeneous nature of Co-NC-900 was examined through a hot-filtration test. Once Co-NC-900 was filtered from the reaction solution after 6 h, no further formation of product could be observed in the next time (Supporting Information, Figure S5). The N₂ adsorption-desorption analysis demonstrate that the Co-NC-900 catalyst possess a mesoporous structure (Supporting Information, Figure S6). BET surface area is 1149 m²·g⁻¹, and the average pore diameter is 9.5 nm. The X-ray diffraction (XRD) pattern of the Co-NC-900 discloses the diffraction peaks located at 2θ degrees of 44.2 and 51.5, which is assigned to the (111) and (200) lattice planes of metallic Co (JCPDS no. 15-0806), respectively (Supporting Information, Figure S7).^[12] Scanning electron microscopy (SEM) images reveal honeycomb mesoporous structure of the Co-NC-900 catalyst (Figure 1a). The cobalt nanoparticles were investigated by BED-C mode (Figure 1b). Meanwhile, energy-dispersive X-ray (EDX) mapping with SEM demonstrates that C, N, O and Co atoms are homogeneously distributed in the whole structure (Supporting Information, Figure S8 and S9). The transmission electron microscope (TEM) image provided solid evidence for the presence of abundant cobalt nanoparticles with an average size of 10 nm that surviving from the acid treatment (Figure 1c). Spherical aberration corrected HAADF-STEM was further carried out to ascertain the dispersion of Co species. The low-magnification HAADF-STEM images further support the presence of cobalt nanoparticles (Figure 1d). From the zoom-in

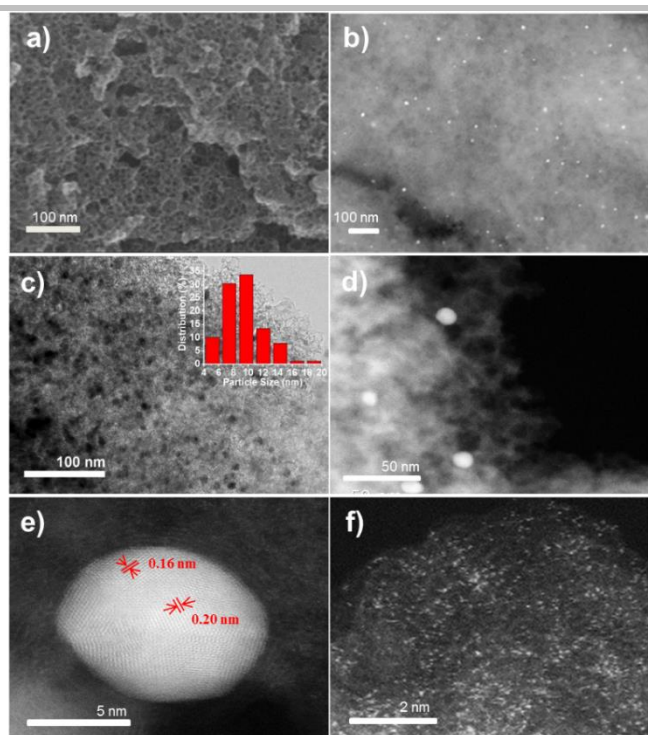


Figure 1. a) SEM images under UED mode, b) SEM images under BED-C mode and c) HR-TEM images (the inset shows the size distribution of metallic Co nanoparticles) of Co-NC-900. d) low-magnification HAADF-STEM image of Co-NC-900. e) atomic-resolution HAADF-STEM image of encapsulated Co nanoparticles in Co-NC-900. f) HAADF-STEM image of Co-NC-900 in the nanoparticle-free region, which single Co atoms are clearly seen.

HAADF-STEM image of an encapsulated cobalt nanoparticle, we clearly observed the lattice spacing of 0.20 and 0.16 nm is consistent with the Co (111) and (200) planes (Figure 1e), which was in good accordance with XRD.^[13] In addition, we also found numerous bright dots distributed on the carbon matrix in the nanoparticle-free region, indicating the existence of single Co atoms (Figure 1f). Although high temperature pyrolysis caused most of the cobalts to aggregate into cobalt nanoparticles, there were still lots of atomically dispersed cobalt that could coordinated with nitrogen atoms to form Co-N_x.^[14]

The X-ray photoelectron spectroscopy (XPS) survey shows Co, C, N and O elements are detectable on the external surface of Co-NC materials (Supporting Information, Figure S10a). The N 1s spectrum displays the peaks with binding energies of 398.6, 400.2, 401.0 and 404.3 eV (Figure 2a), originating from pyridinic or Co-N, pyrrolic, graphitic and oxidized nitrogen, respectively.^[15] The Co 2p spectrum shows the peak at 778.2 eV can be assigned to zero valence Co, while the peak at 782.3 eV correspond to Co in the Co-N_x configuration (Figure 2b).^[16] To further confirm the local chemical state and coordination environment in the catalysts, X-ray absorption spectroscopy (XAS) was performed. The Co K-edge absorption near-edge structure (XANES) spectra shows the peak position for Co-NC materials gradually shifts to the lower energy as the pyrolysis temperature increases (Figure 2c), suggesting that cobalt valence state gradually decreased. The XANES spectrum of Co-NC-900 was closer to that of Co foil reference, revealing the dominant valence state of Co⁰ NPs at 900 °C, being in agreement with the XRD and XPS results. As shown in Figure 2d, the atomic dispersion of Co-NC catalysts is further conformed from the Fourier transform (FT) k²-weighted EXAFS. Compared with the reference sample of Co foil, Co-NC-700 has

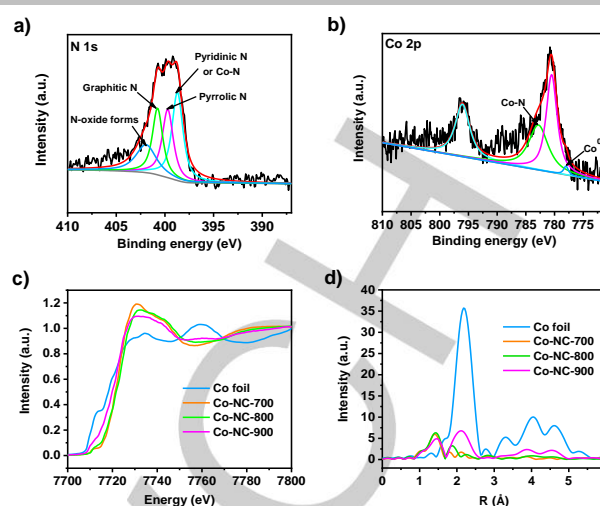
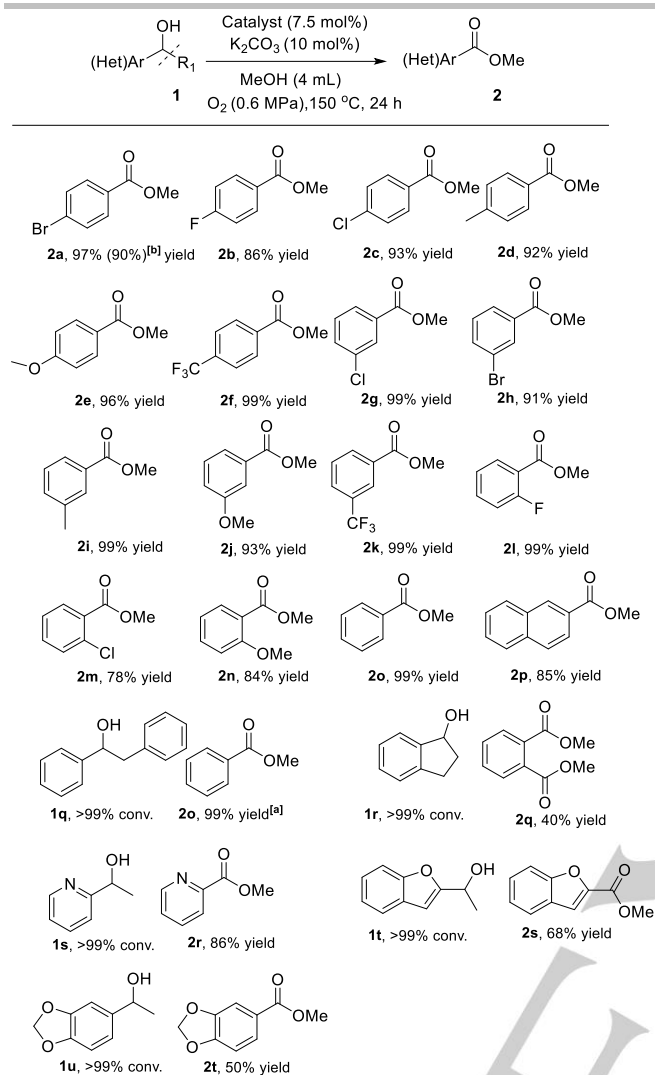


Figure 2. a) N 1s XPS spectra and b) Co 2p XPS spectra of Co-NC-900. c) Co K-edge XANES spectra and d) Fourier transform (FT) EXAFS spectra of the Co-NC catalysts and Co foil as the references.

no obvious peak at the position of Co-Co coordination, suggesting that the Co species exist in atomically dispersed form, without any aggregation. However, conspicuous peak of Co-Co coordination can be observed in Co-NC-900, which was in consistency with the HAADF-STEM result that the formation of Co aggregates. The intensity of the peaks gradually increases along with elevated annealing temperature, indicating the formation of abundant Co nanoparticles during the pyrolysis. Moreover, all three Co-NC samples have a main peak value at 1.47Å, which belongs to the first shell of Co-N_x coordination.^[17] It has been widely accepted that the high-temperature synthesis method leads to the formation of high structural heterogeneity metal-NC materials, which typically compose of metal-N_x sites and graphene encapsulated metal nanoparticles. In this context, HAADF-STEM, XPS, and XAS directly prove the existence of atomically dispersed Co-N_x and graphene encapsulated Co-based nanoparticles in the present Co-NC-900 materials. To shed light on the catalytically active sites for the C-C bond cleavage reaction, a series of reasonable control experiments were performed. To identify the role played by the Co-N_x sites, KSCN was used as the binding molecule to join the reaction system for poisoning experiment. The benchmark reaction was performed with the addition of KSCN under otherwise identical conditions (Supporting Information, Figure S11). In this case, there was barely decline in yield, clearly revealing the negligible contribution of Co-N_x to the catalytic activity and graphene encapsulated Co nanoparticles indeed boost the reaction. To further prove this conclusion, the control experiment was performed with the catalyst amount reduced to 1.6 mol% (kinetically controlled region). The results indicated that 74% yield of ester was obtained without KSCN (no other products were detected), and that 74% yield of ester was also obtained with 26% yield of acetophenone in the presence of KSCN, indicating that Co-N_x indeed is not a truly catalytic active species, and as an unexpected important information that its presence is not conducive to the product of selectivity. And so beyond that, the selectivity was well correlated with the content of Co-N_x in the catalysts Co-NC-X. That is, the lower the content of Co-N_x, the better the selectivity toward the target product (Supporting Information, Figure S12). As a conclusion, these results clearly confirm that cobalt nanoparticles are indeed responsible for the C-C bond oxidative cleavage to achieve excellent activity, while

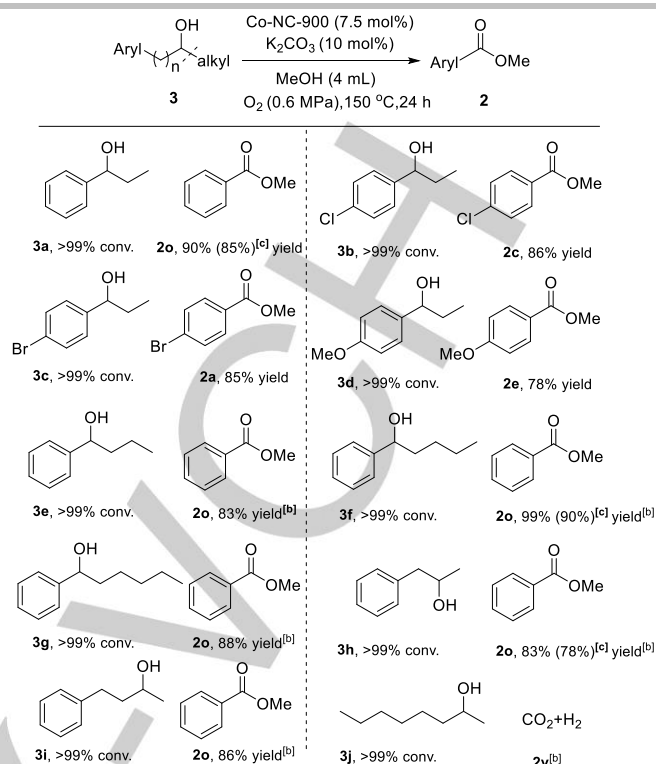


Scheme 2. Substrate Scope of (hetero)aryl methyl alcohols, $R_1 = \text{Me}$ unless noted. Reaction conditions: alcohol (0.25 mmol), K_2CO_3 (10 mol%), Co-NC-900 (7.5 mol%), MeOH (4 mL), 0.6 MPa O_2 , 150 °C, 24 h. [a] The yield was based on both phenyl groups. [b] Isolated yield.

the presence of Co-N_x has just the opposite effect.

After the optimal reaction conditions obtained, the scope of (hetero)aryl methyl alcohols was explored (Scheme 2). A large number of substituted 1-phenylethanol bearing either electron-rich or electron-deficient groups afforded the esters in excellent yields (**2a-2o**). It seems that the nature of substitutional group on the benzene ring of 1-phenylethanol has no obvious influence on oxidative cleavage of C(OH)-C bond cleavage efficiency. 1-(2-naphthyl)ethanol also produced the desired products in good yield (**2p**). For the cyclic aryl alcohol 1-indanol (**1r**), dimethyl phthalate (**2q**) was obtained as the main product. Furthermore, heteroaryl methyl alcohols were also suitable substrates for this transformation (**2r-2t**).

Having established the broad substrate scope, more challenging substrates were investigated (Scheme 3). Aryl long-chain alkyl secondary alcohols containing various substituents could be effectively transformed, generating esters in good to excellent yields (**3a-3g**). Intriguingly, employing more catalyst and longer reaction time, reactions with aliphatic methyl alcohols **3h** and **3i** afforded methyl benzoate **2o** in good yields. Except for benzylic substrates, n-octanol (**3j**), an alkyl aliphatic alcohol, can also be

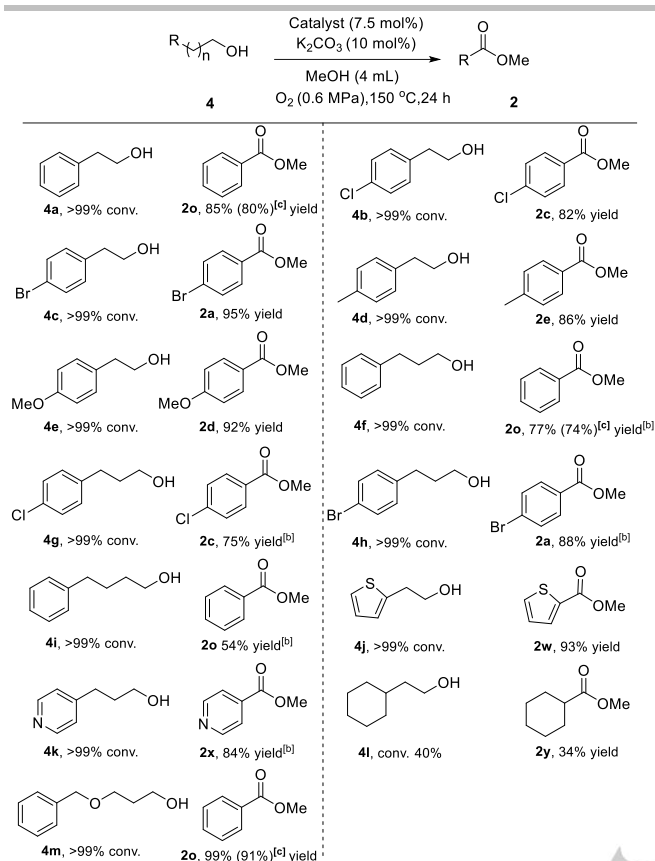


Scheme 3. Substrate Scope of secondary aliphatic alcohols. Reaction conditions: alcohol (0.25 mmol), K_2CO_3 (10 mol%), Co-NC-900 (7.5 mol%), MeOH (4 mL), 0.6 MPa O_2 , 150 °C, 24 h. [b] Co-NC-900 (15 mol%), 48 h. [c] Isolated yield.

degraded to afford H_2 and CO_2 , which were detected with gas chromatography, mass spectrometer and by the lime-water test, respectively (Supporting Information, Figure S13-15). As we all know, this is the first example of heterogeneous catalyst for a complete degradation of an aliphatic alcohol to H_2 and CO_2 .

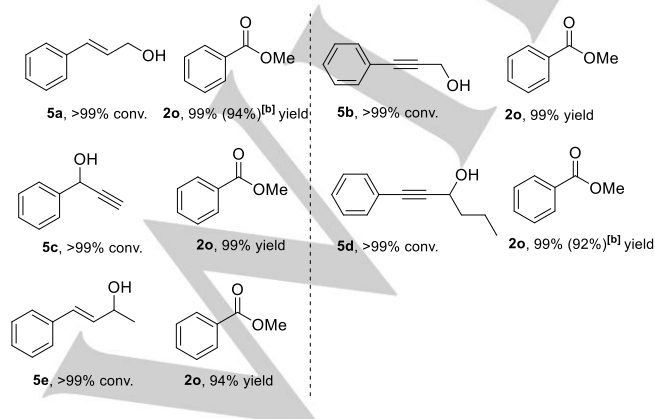
The capacity of the catalyst for more challenging inactive primary aliphatic alcohols were evaluated (Scheme 4). The reactions of substrates that the substituents on the aromatic ring of 2-phenylethanol worked well, regardless of the electron properties of the substituent groups (**4a-4e**). To our delight, reactions with **4f-4i** proceeded to give the corresponding methyl benzoate in the case of increasing the loading of catalyst and prolonging the reaction time. Moreover, the length of the alkyl chain influences their reactivity. For instance, 4-phenylbutan-1-ol (**4i**) is lower reactive in comparison to 3-Phenyl-1-propanol (**4f**). Heteroaryl alcohols also successfully gave the corresponding products in good yields (**4j**, **4k**). Importantly, 2-cyclohexylethanol was also transformed into methyl cyclohexanecarboxylate in moderate yield (**4l**). In addition, 3-Benzyloxy-1-propanol was also examined, which gave methyl benzoate in 99% yield (**4m**). Unexpectedly, the catalytic system can effectively oxidize cleavage of C=C and C≡C of allylic and propargylic alcohols into corresponding esters in almost quantitative yields (Scheme 5, **5a-5e**). Overall, this method indicates the wide range of substrates, highlighting its practical value in direct synthesis of esters from alcohols under sustainable reaction conditions.

The above-encouraging results prompted us to evaluate the ability of the catalysts to the oxidative cleavage of lignin model compounds. The results are summarized in Scheme 6. Various β -O-4 linkages lignin model compounds were used as substrates and both the C-C and C-O bonds were successfully cleaved. The corresponding aromatic esters were obtained in

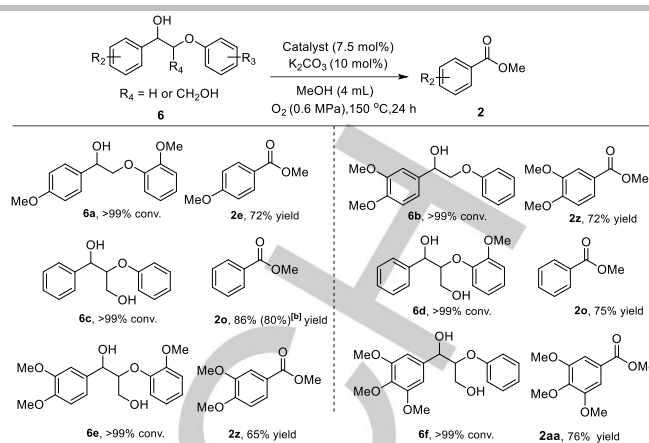


Scheme 4. Substrate Scope of primary aliphatic alcohols. Reaction conditions: alcohol (0.25 mmol), K_2CO_3 (10 mol%), Co-NC-900 (7.5 mol%), MeOH (4 mL), 0.6 MPa O_2 , 150 °C, 24 h. [b] Co-NC-900 (15 mol%), 48 h. [c] Isolated yield.

good to moderate yields. Specifically, the catalytic system can also effectively oxidize cleavage of complex lignin models with Cy-OH into corresponding esters in moderate yields. However, the lower yield of the desired phenolic compounds was afforded (10-30% yield), possibly due to over-oxidization and/or the formation of low polymer. This observed result is in accordance with previous reports on the oxidative cleavage of lignin model compounds.^[18-23] To better elucidate the mechanism of the oxidative cleavage of secondary alcohols to esters, we first



Scheme 5. Substrate Scope of allylic and propargylic alcohols. Reaction conditions: alcohol (0.25 mmol), K_2CO_3 (10 mol%), Co-NC-900 (15 mol%), MeOH (4 mL), 0.6 MPa O_2 , 150 °C, 48 h. [b] Isolated yield.

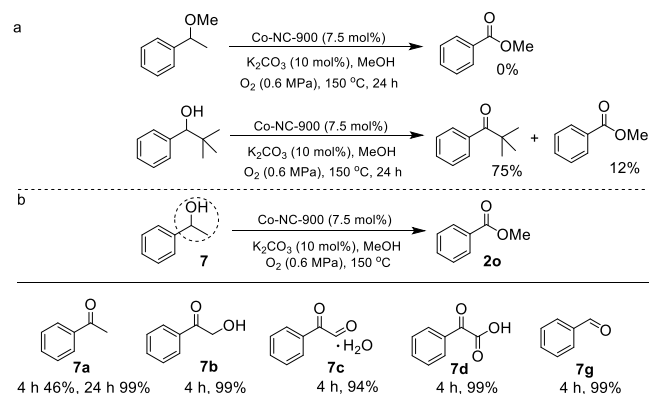


Scheme 6. Substrate Scope of lignin model compounds. Reaction conditions: lignin model compounds (0.25 mmol), K_2CO_3 (10 mol%), Co-NC-900 (7.5 mol%), MeOH (4 mL), 0.6 MPa O_2 , 150 °C, 24 h. [b] Isolated yield.

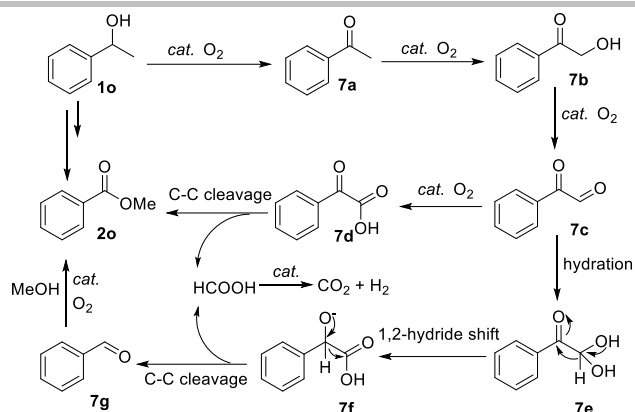
implemented a radical inhibition experiments to determine whether the reaction involves free radicals. The results showed that the radical scavengers 2,6-di-tertbutyl-4-methylphenol (BHT) or (2,2,6,6-tetramethyl-1-piperidinyloxy) (TEMPO) had no effect on the formation of target products (Supporting Information, Scheme S1), thus suggesting that the radical reaction process can be ruled out.

The time course of the oxidative cleavage of 1-(4-bromophenyl)ethanol was tracked (Supporting Information, Figure S16). It was found that the concentrations of the 4'-bromoacetophenone first increased rapidly and then decreased after 1 h. Meanwhile, the products increased with the increase of reaction time. These results showed that ketone might be the plausible intermediates.

Next, some control reactions were conducted to elucidate the roles of different functional groups in secondary alcohols (Scheme 7a). (1-methoxyethyl)benzene, without an hydroxyl group in the 1-phenylethanol, was unable to undergo oxidative cleavage. 2,2-dimethyl-1-phenylpropan-1-ol, in which the α -H position of 1-phenylethanol is blocked by three methyl groups, producing 75% yield of corresponding ketone and 12% yield of **2o**. The above two reactions confirm that the presence of the hydroxyl group and α -H in the secondary alcohol is of crucial importance for the access to the C-C bond cleavage.



Scheme 7. Control experiments. a) The role of different functional groups in secondary alcohols was clarified. b) Reactions of 1-phenylethanol derivatives.



Scheme 8. Proposed mechanism of the oxidative cleavage C-C bonds of secondary alcohols to ester over the Co-NC-900 catalyst.

Subsequently, some representative 1-phenylethanol derivatives were selected and examined in the reaction system (Scheme 7b). It was observed that the reaction of acetophenone (**7a**) afforded **2o** in lower yield, while reactions of α -mono-(hydroxy)acetophenone (**7b**), phenylglyoxal (**7c**) and benzoylformic acid (**7d**) gave excellent yield in a short time, indicating a oxygenation of the α -methyl group and then stepwise oxidation of **7a** to **7b**, then to **7c**, and further to **7d**. Furthermore, the possible intermediate benzaldehyde (**7g**) was subjected to the given condition, affording the yield of **2o** in 99%. According to the above results and our previous work, we can provide a plausible reaction mechanism of the oxidative cleavage of secondary alcohols to esters over the Co-NC-900 catalyst (Scheme 8). Initially, the substrate is oxidized to **7a** through the reactive oxygen species produced by activation of oxygen by cobalt nanoparticles.^[24] Subsequent aerobic oxidation of **7a** generates **7b** which is further oxidized to **7c**. Then, there are two possible reaction pathways. On one hand, the generated **7c** is oxidized to **7d**, and then the cleavage of C-C bond affords the ester **2o** with release of formic acid followed by the decomposing to CO₂ and H₂ (Supporting Information, Figure S17 and 18).^[11a, 25] On the other hand, **7c** reacts with water to form the hydrated α,α -bis(hydroxy)acetophenone (**7e**). C-C bond cleavage occurs via 1,2-hydride shift, generating **7g** and CO₂. Then, nucleophilic addition takes place between **7g** and MeOH to form the hemiacetal intermediate. Finally, the hemiacetal intermediate is transformed to **2o** catalyzed by the Co/O₂ system. The similar reaction pathway of Co-catalyzed adjacent -(C-C)n-bond cleavage of primary alcohols is verified by some control experiments using 3-phenyl-1-propanol (**4f**) as a typical substrate, and detailed discussions are given in the Supporting Information, Scheme S2 and S3.

Conclusion

In summary, we have successfully prepared heterogeneous Co-NC catalysts for the aerobic oxidative successive C-C bond cleavage of various functionality aromatic, aliphatic, heterocyclic, allylic, propargylic primary and secondary alcohols to one or multiple carbon atoms shorter esters with O₂ as the oxidant. The catalyst was used for seven times without any decrease in activity. Catalyst characterization and control experiments demonstrated that cobalt nanoparticles are responsible for excellent catalytic activity, while the presence of Co-N_x has just

the opposite effect. Preliminary mechanistic research revealed the reaction sequence in a tandem manner. This work not only exhibits the ability to successive cleavage adjacent -(C-C)n-bonds but also provides a new practical method for directly accessible ester through C-C bond cleavage in alcohols, which is still challenging to the existing methods.

Acknowledgements

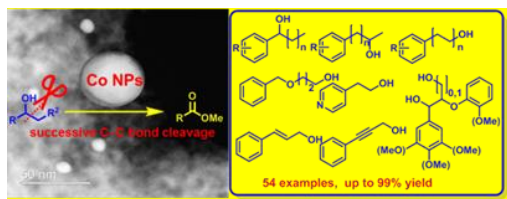
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Keywords: C-C bond • aerobic oxidative cleavage • alcohols • heterogeneous cobalt catalyst • esters

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Nanoparticle scissors: Cobalt nanoparticles-catalyzed aerobic oxidative cleavage of adjacent $-(C-C)_n-$ bonds in succession in a wide range of alcohols as well as inactive long-chain alkyl aryl alcohols to afford esters was developed. Control experiments disclose that metallic cobalt nanoparticle is responsible for the outstanding catalytic performance rather than single atom cobalt.