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Selective Oxidation of Alcohols to Esters Using Heterogeneous Co_3O_4–N@C Catalysts under Mild Conditions

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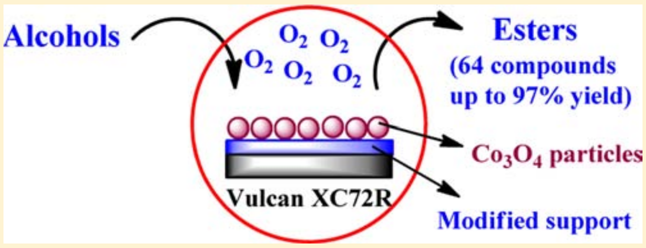
Supporting Information

ABSTRACT: Novel cobalt-based heterogeneous catalysts have been developed for the direct oxidative esterification of alcohols using molecular oxygen as benign oxidant. Pyrolysis of nitrogen-ligated cobalt(II) acetate supported on commercial carbon transforms typical homogeneous complexes to highly active and selective heterogeneous Co_3O_4–N@C materials. By applying these catalysts in the presence of oxygen, the cross and self-esterification of alcohols to esters proceeds in good to excellent yields.



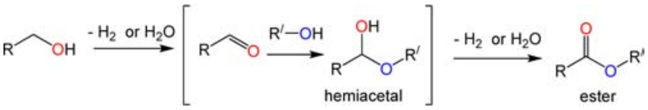
INTRODUCTION

Esters represent an abundant class of compounds in organic synthesis. Moreover, they are used as important building blocks for the fine and bulk chemical industry. Hence, this structural motif is found in numerous pharmaceuticals, agrochemicals, fragrances, and polymers.[1] Both in industry as well as in academic laboratories esters are commonly prepared by the reaction of carboxylic acids or activated acid derivatives, e.g. acid chlorides or anhydrides, with alcohols.[1,2] In addition, Reppe-type carbonylations are used in the chemical industry for the preparation of aliphatic esters.[3] Regarding (hetero)aromatic esters, palladium-catalyzed carbonylations of aryl halides with alcohols are of increasing interest in organic synthesis.[4] Moreover, special methods such as the catalytic esterifications of aldehydes with alcohols are known.[5]

Despite all of these well-established methodologies, the development of environmentally benign and cost-effective procedures for the synthesis of esters continues to attract significant interest. In this respect, the direct transformation of alcohols to esters constitutes an interesting alternative,[6−11] which does not make use of the corresponding acids or acid derivatives (Scheme 1).

Notably, the required alcohols are of increasing importance as renewable feedstock. So far, most of the known catalysts for the synthesis of esters from alcohols under mild conditions are based on precious metals such as palladium,[6] gold,[7] ruthenium,[8] and iridium.[9] Because of the limited availability and high price of noble metals, it is desirable to search for more economical and environmentally friendly alternatives. A possible solution to this problem can be the increased utilization of catalysts based on biorelevant metals, such as iron,[12] cobalt,[13,14] and copper.[15] In addition, the use of heterogeneous catalysts would be beneficial with respect to catalyst recycling and engineering. In this regard, we herein introduce novel, reusable Co_3O_4-based heterogeneous catalysts for the direct oxidative esterification of alcohols. Advantageously, the inexpensive and easily reusable catalyst as well as the use of oxygen as final oxidant make this process cost-effective and environmentally benign.

Scheme 1. Direct Synthesis of Esters from Alcohols



On the basis of our general objective to develop sustainable catalysts for selective organic transformations, we recently started a program to design and apply novel carbon-supported metal−nitrogen catalyst systems, especially those based on iron, cobalt and nickel. In our previous work,[16] we showed that carbon-supported iron− and cobalt−nitrogen materials constitute active catalysts for the selective reduction of a variety of nitroarenes. Here, we demonstrate that Co_3O_4-based particles supported on carbon−nitrogen materials represent excellent heterogeneous catalysts for the selective oxidation of alcohols to esters using benign O_2 as the final oxidant.[17] Notably, these catalysts are easily recycled and can be conveniently reused, which is an important aspect in the development of practical and cost-effective catalytic oxidation processes.

RESULTS AND DISCUSSION

1. Development of the Co_3O_4–N@C Catalyst System.

At the start of our work, the supported Co_3O_4 catalysts were prepared by impregnating in situ generated amino-ligated cobalt(II)−acetate complexes on commercially available Vulcan XC72R carbon powder and subsequent pyrolysis at 800 °C for 2 h (Scheme 2).

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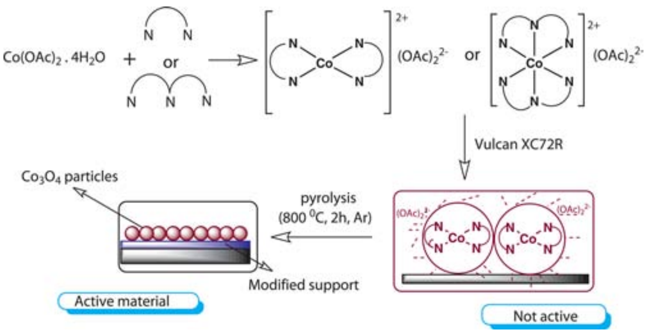
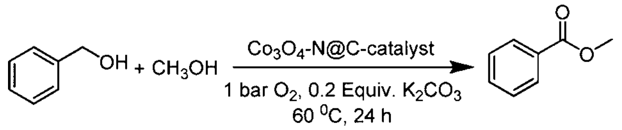
Scheme 2. Preparation of Co_3O_4–N@C Materials with Different Ligands[a]



[a]Co–**L**/C pyrolyzed at 800 °C for 2 h under Ar (Co = 3 wt %, Co:**L** = 1:2).

Table 1. Co_3O_4–N@C-Catalyzed Cross Esterification of Benzyl Alcohol and Methanol[a]–[e]



entry	carbon support	cobalt salt	L^f	pyrolysis [°C, h, gas]	C^f [%]	Y^f [%]
1[a]	–	–	–	–	<2	<1
2[a]	–	$Co(OAc)_2 \cdot 4H_2O$	–	–	5	<1
3[a]	–	$Co(OAc)_2 \cdot 4H_2O$	**L1**	–	12	<1
4[b]	Vulcan XC72R	$Co(OAc)_2 \cdot 4H_2O$	–	–	7	2
5[b]	Vulcan XC72R	$Co(OAc)_2 \cdot 4H_2O$	**L1**	–	12	2
6[b]	Vulcan XC72R	$Co(OAc)_2 \cdot 4H_2O$	–	800, 2, Ar	20	12
7[b]	Vulcan XC 72R	$Co(OAc)_2 \cdot 4H_2O$	**L1**	800, 2, Ar	>99	97
8[b]	Vulcan XC72R	$Co(OAc)_2 \cdot 4H_2O$	**L2**	800, 2, Ar	80	74
9[b]	Vulcan XC72R	$Co(OAc)_2 \cdot 4H_2O$	**L3**	800, 2, Ar	68	60
10[b]	Vulcan XC72R	–	–	800, 2, Ar	<3	<1
11[b]	Vulcan XC72R	–	**L1**	800, 2, Ar	<4	<1
12[b]	Al_2O_3	$Co(OAc)_2 \cdot 4H_2O$	**L1**	800, 2, Ar	83	79
13[b]	TiO_2	$Co(OAc)_2 \cdot 4H_2O$	**L1**	800, 2, Ar	52	45
14[c]	Vulcan XC72R	$Co(OAc)_2 \cdot 4H_2O$	**L1**	800, 2, Ar	6	4
15[d]	Vulcan XC72R	$Co(OAc)_2 \cdot 4H_2O$	**L1**	800, 2, Ar	40	15
16[e]	Vulcan XC72R	$Co(OAc)_2 \cdot 4H_2O$	**L1**	800, 2, Ar	16	7

C = conversion, Y = yield. L = ligand. [a]Homogeneous catalysis conditions: 0.5 mmol benzyl alcohol, 4 mL CH_3OH, 0.0125 mmol $Co(OAc)_2 \cdot 4H_2O$, 0.025 mmol ligand, 0.1 mmol K_2CO_3. [b]Heterogeneous catalysis conditions: (3 wt % Co): 0.5 mmol benzyl alcohol, 4 mL CH_3OH, 0.1 mmol K_2CO_3, 25 mg catalyst (2.5 mol % Co). [c]Same as '*b*' without base and O_2. [d]Same as '*b*' without base. [e]Same as '*b*' in the absence of O_2. [f]Determined by GC. In case of lower yields, benzaldehyde was detected as a minor product.

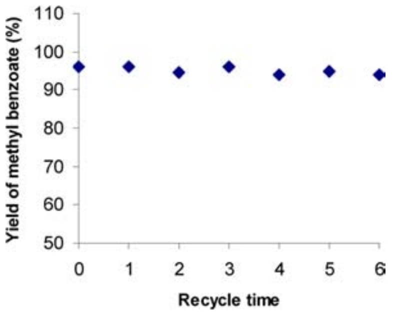


Figure 1. Methyl esterification of benzyl alcohol: recycling of the Co_3O_4–N@C-catalyst. Reaction conditions: 2 mmol benzyl alcohol, 6 mL MeOH, 0.4 mmol K_2CO_3, 100 mg catalyst (2.5 mol % Co), 60 °C, 24 h. Yields were determined by GC.

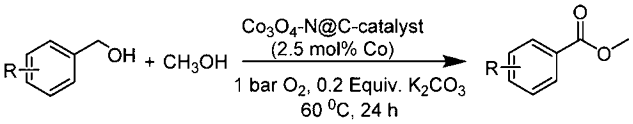
Exploratory catalytic experiments with the different catalytic materials were performed using the oxidative cross esterification of methanol and benzyl alcohol to give methyl benzoate. Typically, this model reaction was performed at 60 °C using simply 1 bar of molecular oxygen in the presence of catalytic amounts of K_2CO_3 as base. As expected, after applying the homogeneous $Co(OAc)_2$ with or without added ligand **L1** no activity toward ester formation is observed (Table 1, entries 2–3). Similarly, the carbon-supported catalysts based on simple hydrated $Co(OAc)_2$ did not show the desired activity (Table 1, entries 4–5).

Interestingly, pyrolyzed carbon-supported $Co(OAc)_2$ showed little activity and produced methyl benzoate in 12% yield (Table 1, entry 6). Unfortunately, no further improvements could be achieved with this catalyst. To our delight, pyrolysis of the in situ generated complex of $Co(OAc)_2$ and **L1** supported on carbon led to a highly active catalyst material for direct oxidative esterification and produced methyl benzoate in 97% yield (Table 1, entry 7)! Notably, the pyrolyzed catalyst system is highly stable and can be reused several times (see below).

Characterization of the metal species in the active catalyst (Co_3O_4–**L1**/C) by XRD, TEM, XPS and EPR revealed the preferential formation of small (2–10 nm) Co_3O_4 particles on a carbon–nitrogen-based support surface (see Supporting Information [SI]). In addition, a few larger particles of 20–80 nm and occasionally of up to 800 nm in size are also present, which consist of a Co and/or CoO core and a Co_3O_4 shell. Interestingly, XPS analysis showed three distinct peaks in the N1s spectra of Co_3O_4–**L1**/C with aelectron binding energies of 399.0, 400.8, and 402.3 eV, respectively. The lowest binding energy peak is attributed to pyridine-type nitrogen, which is bound to a metal ion.[20a] The electron binding energy of 400.8 eV is characteristic for pyrrole-type nitrogen contributing two electrons to the carbon matrix. Some of the nitrogen atoms are also bound to a hydrogen atom. Such types of nitrogen are often found after the carbonization of nitrogen-containing organic materials.[20b] Finally, the small peak at 402.3 eV is typical for quaternary amine species (NR_4^+).[20c] The ratio between all Co atoms and all N atoms in the near surface region is 1:4.7. Deconvolution suggests that around 64% of all N atoms are bound to the metal ions.

While to the best of our knowledge Co_3O_4 on carbon–nitrogen-based materials has not been described as an efficient oxidation catalyst under mild conditions, some oxidations of the parent metal oxide are known. In this respect, the recent work of Schüth and co-workers, who studied in detail the preparation of Co_3O_4 and the catalytic oxidation of CO with these particles, is noteworthy.[18] Furthermore, Co_3O_4 has been used for the oxidation of cyclohexane[19a] and alcohols[19b] under more drastic conditions.

Table 2. Co_3O_4–N@C-Catalyzed Synthesis of Methyl Esters from Benzylic Alcohols[a]



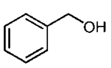
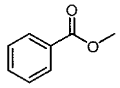
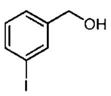
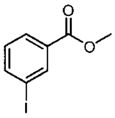
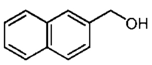
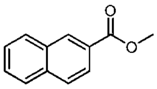
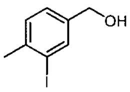
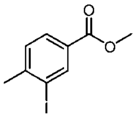
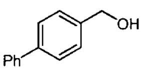
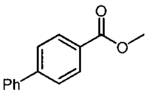
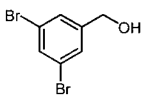
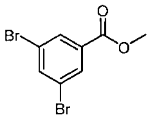
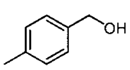
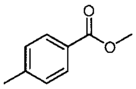
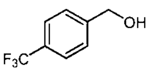
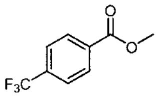
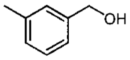
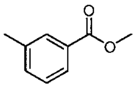
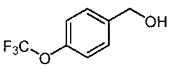
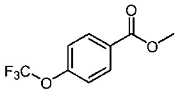
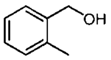
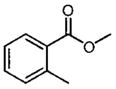
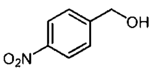
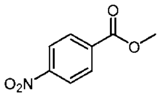
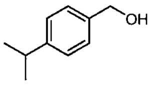
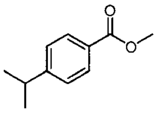
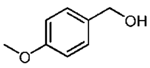
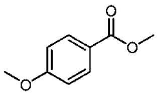
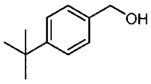
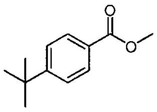
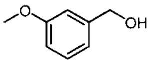
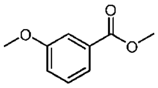
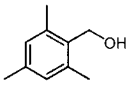
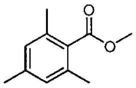
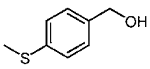
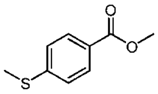
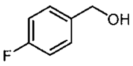
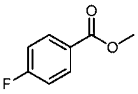
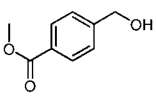
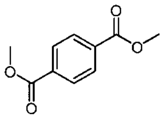
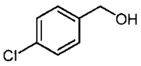
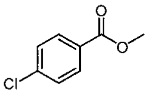
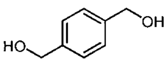
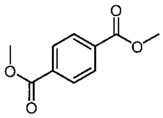
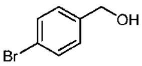
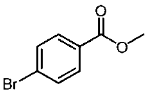
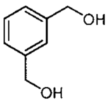
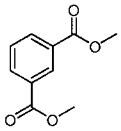
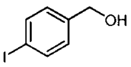
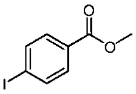
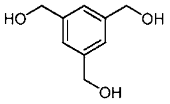
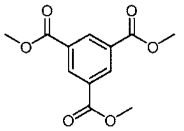
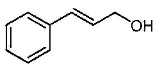
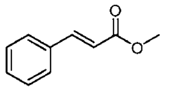
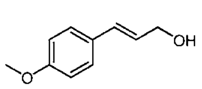
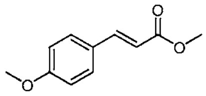
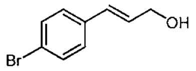
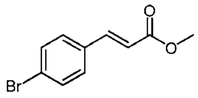
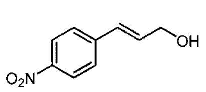
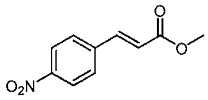
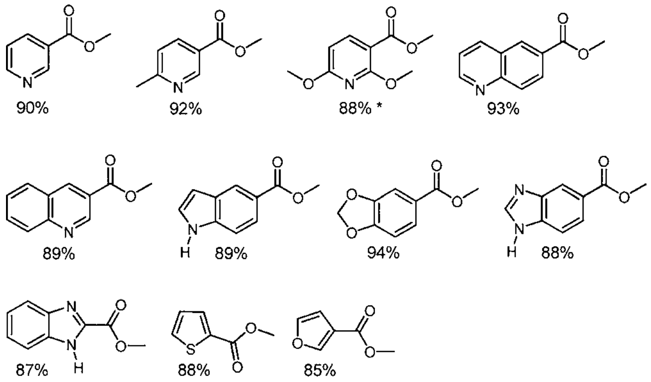
Entry	Benzylic alcohol	Methyl ester	Yield [%]	Entry	Benzylic alcohol	Methyl ester	Yield [%]
1			97 93[c]	14			94
2			95	15			95
3			92	16			91[d]
4			97	17			87
5			90	18			85
6			92[d]	19			88
7			89	20			95
8			89	21			92
9			88[d]	22			94
10			87	23			91
11			92	24			89[e]
12			92	25			85[e]
13			94				

Table 2. continued

Entry	Benzylic Alcohol	Methyl ester	Yield [%]
26			84^{f}
27			88
28			89
29			84
30			80

[a] Reaction conditions: 0.5 mmol benzylic alcohol, 4 mL CH_3OH, 0.1 mmol K_2CO_3, 25 mg catalyst (2.5 mol % Co). [b] Yields were determined by GC. [c] Scaled up by a factor of 4 and isolated yields. [d] Same as '*a*' at 80 °C. [e] Same as '*a*' with 0.2 mmol K_2CO_3. [f] Same as '*a*' with 0.3 mmol K_2CO_3.

Scheme 3. Co_3O_4–N@C-Catalyzed Synthesis of Methyl Esters of Heterocyclic Alcohols[a]



[a] Reaction conditions: 0.5 mmol heterocyclic alcohol, 4 mL CH_3OH, 0.1 mmol K_2CO_3, 25 mg catalyst (2.5 mol % Co), yields were determined by GC. *Similar reaction conditions at 80 °C.

In order to demonstrate the stability and reusability of the catalyst material, six consecutive oxidation experiments of the model system were performed. In fact, the Co_3O_4–N@C-catalyst (Co_3O_4–**L1**/C) was successfully recycled without any significant loss of activity (Figure 1).

Other pyrolyzed carbon-supported Co-catalysts using related nitrogen ligands such as terpyridine, and bis(benzimidazolyl)-pyridine showed also activity, producing methyl benzoate in 60–74% yield (Table 1, entries 8–9). Next, pyrolysis of Co-**L1** on Al_2O_3 and TiO_2 supports gave also active catalyst materials, which produced methyl benzoate in 45–79% (Table 1, entries 12–13). From all these results, the Co-**L1** supported on carbon found to be the most active catalyst. Using the latter catalyst we performed the direct oxidative esterification of different alcohols. It is evident from the Table 1 (Table 1, entries 14–16) that both the oxidant (O_2) and base are crucial for the oxidative esterification process.

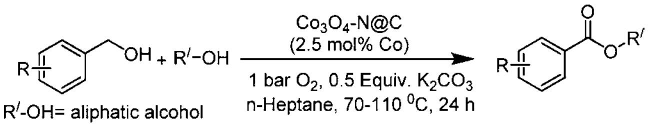
2. Synthesis of Methyl Esters. After having demonstrated the excellent activity of the Co_3O_4–N@C-catalyst (Co_3O_4–**L1**@C) in the model reaction, we investigated the oxidative methyl esterification of a series of structurally diverse benzylic alcohols. As shown in Table 2, good to excellent yields of the corresponding methyl esters are obtained. Apart from simple and alkyl-substituted benzyl alcohols (Table 2, entries 1–9), also halide-, trifluoromethyl-, nitro-, ether-, and even thioether-substituted benzylic alcohols were selectively esterified (Table 2, entries 10–22). The latter reaction is especially remarkable from the viewpoint of chemoselectivity. Furthermore, di- and triesters can be obtained in a straightforward manner in up to 91% yield (Table 2, entries 23–26). Notably, also more sensitive allylic alcohols undergo this cross esterification in high yields (Table 2, entries 27–30).

Next, the oxidative esterification of heterocyclic alcohols was investigated. Gratifyingly, heterocyclic carboxylic acid esters, which constitute important intermediates especially for agrochemicals, were obtained in up to 94% yield (Scheme 3).

3. Synthesis of Different Alkyl Esters. After the successful cross esterification of methanol and various benzylic alcohols, we were interested in demonstrating similar selective oxidative couplings for different alkyl esters. Not surprisingly, such cross esterifications have been scarcely studied in the past due to the potential problem of oxidizing one alcohol in the presence of another.

Nevertheless, ethyl esters of both benzylic and heterocyclic alcohols are conveniently obtained in up to 92% yield (Table 3, entries 1–9). The procedure also works well for the synthesis of propyl, butyl, pentyl, and hexyl benzoates in 81–87% yield at

Table 3. Co_3O_4–N@C-Catalyzed Synthesis of Alkyl Esters of Benzylic Alcohols[a]



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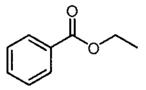
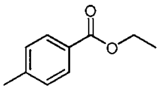
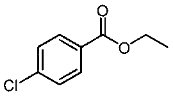
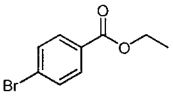
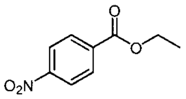
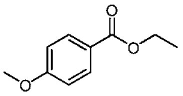
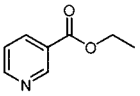
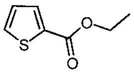
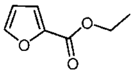
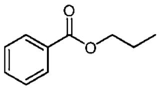
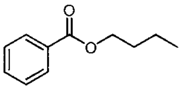
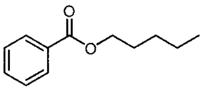
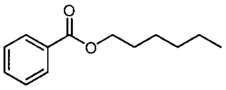
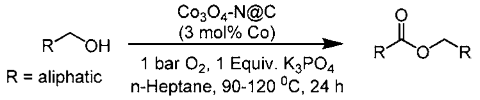
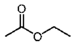
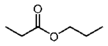
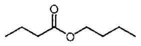
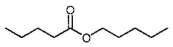
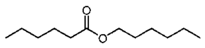
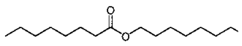
1		70	91 88[c]
2		70	92
3		70	87
4		70	85
5		70	82
6		70	91
7		70	88
8		70	81
9		70	77
10		90	87
11		110	86
12		110	82
13		110	81

[a] Reaction conditions: 0.5 mmol benzylic alcohol, 1 mL aliphatic alcohol, 0.25 mmol K_2CO_3, 25 mg catalyst (2.5 mol % Co), 4 mL *n*-heptane. [b] Determined by GC. [c] Scaled up by a factor of 4 and isolated yields.

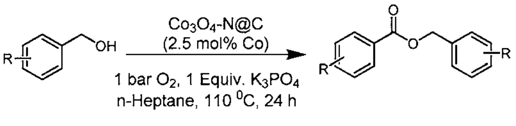
Table 4. Co_3O_4–N@C-Catalyzed Oxidative Esterification of Aliphatic Alcohols[a,b]



Entry	Ester	T [°C]	Yield [%][c]
1[a]		90	65
2[b]		90	71
3[b]		110	72
4[b]		110	73
5[b]		120	75 71[d]
6[b]		120	75

[a] Reagents and conditions: 2 mmol ethanol, 2 mmol K_3PO_4, 120 mg catalyst (3 mol % Co), 8 mL *n*-heptane. [b] Reagents and conditions: 0.5 mmol alkyl alcohol, 0.5 mmol K_3PO_4, 30 mg caytalyst (3 mol % Co), 5 mL *n*-heptane. [c] Determined by GC. [d] Scaled up by a factor of 4 and isolated yield.

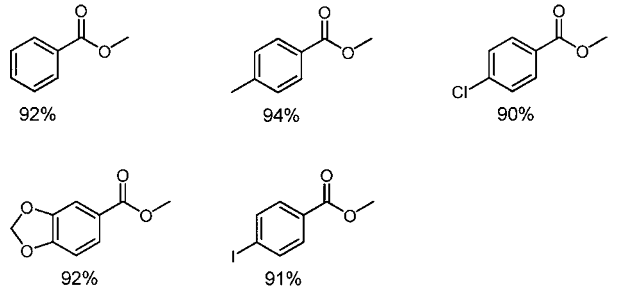
Scheme 4. Co_3O_4–N@C-Catalyzed Oxidative Self-Esterification of Benzylic Alcohols[a]



R	Yield (%)
-H	85
-OMe	70
-Cl	78
$-NO_2$	73

[a] Reaction conditions: 0.5 mmol benzylic alcohol, 0.5 mmol K_3PO_4, 25 mg catalyst (2.5 mol % Co), 5 mL *n*-heptane. Yields were determined by GC.

Scheme 5. Gram-Scale Reactions[a]



[a] Reagents and conditions: 5 g benzylic alcohol, 0.2 equiv K_2CO_3, weight of Co_3O_4–N@C corresponds to 2.5 mol % Co, 150-200 mL MeOH, 60 °C, 24–30 h, isolated yields.

slightly higher temperatures (90–110 °C) (Table 3, entries 10–13).

4. Self-Esterification of Aliphatic and Benzylic Alcohols.

So far, only few examples are known for the direct self-esterification of aliphatic alcohols.[6a,8,10] In this respect, recently, we described homogeneous palladium and ruthenium complexes for the self-esterification of 1-octanol and ethanol to produce octyl octanoate and ethyl acetate.[6a,8c] Furthermore, Milstein and co-workers performed the self-esterification of 1-butanol, 1-pentanol, and 1-hexanol using homogeneous ruthenium pincer catalysts.[8a,b] In addition, the oxidative dimerization of some aliphatic alcohols to esters has also been reported using organocatalysts.[10]

As seen from Table 4, different aliphatic alcohols undergo oxidative self-esterification in presence of our Co_3O_4−N@C-catalyst using only 1 bar of molecular oxygen. It should be noted that the bulk chemical ethyl acetate can be obtained from ethanol in good yield under such mild conditions (Table 4, entry 1). No further optimization has been done on this industrially important intermediate. Similarly, the oxidative self-esterification of other aliphatic alcohols was also achieved in a straightforward manner and we obtained the corresponding esters in 71−75% yield (Table 4, entries 2−6).

Finally, we also performed the self-esterification of benzylic alcohols. Here, again the catalyst is highly selective, and we obtained the corresponding substituted benzyl benzoates in up to 85% yield (Scheme 4).

Because most of the catalytic experiments were run on 0.5−2 mmol scale, we wanted to demonstrate the synthetic utility of our catalyst system more clearly. Thus, we performed 5-g scale reactions for selected substrates. As shown in Scheme 5 in all these cases the previous yields were verified and we obtained the corresponding products in up to 94% (Scheme 5).

SUMMARY

In summary, a stable, inexpensive, and reusable Co_3O_4 supported on nitrogeneous carbon surface catalyst is shown to be active and selective for the direct oxidative esterification of alcohols using 1 bar of molecular oxygen as benign oxidant. The novel supported catalyst is prepared by pyrolysis of amino-ligated cobalt(II) acetate on commercial Vulcan XC72R. It allows for the synthesis of a series of structurally diverse methyl esters as well as other alkyl esters in good to excellent yields. The oxidative self-esterification of both aliphatic and aromatic alcohols has been well demonstrated. In general, the process is simple, cost-effective, and environmentally benign.

EXPERIMENTAL SECTION

Methyl Esterification. Twenty-five milligrams of Co_3O_4−N@C (Co-**L1**/C) catalyst (2.5 mol % Co) and K_2CO_3 (0.1 mmol) were added to an oven-dried Schlenk tube. Then, methanol (4 mL) and a corresponding benzylic alcohol (0.5 mmol) were added sequentially. The Schlenk tube was evacuated, refilled with 1 bar O_2, and closed with septum. The reaction was stirred at 60 °C (refluxed condenser was fixed for the reactions carried out at 80 °C) for 24 h by passing 1 bar O_2. After cooling the reaction mixture to room temperature, 100 μL of *n*-hexadecane as internal standard was added and diluted with ethyl acetate. Then, the catalyst was filtered off, and the sample of the mixture was directly subjected to GC analysis. Conversion and yields were determined by GC-FID (HP6890 with FID detector, column HP530 m × 250 mm × 0.25 μm) and compared with authentic samples. Quantitative and qualitative analyses of all esters were made by GC and GC−MS and identified by comparison with authentic samples.

For methyl esterification of benzyl alcohol, the reaction was scaled up by a factor of 4, and the corresponding methyl benzoate was isolated. After completion of the reaction, the solid catalyst was filtered off and washed thoroughly with ethyl acetate. The solvent was evaporated, and the reaction product was treated with water. The mixture was then extracted with ethyl acetate, the combined organic layers were dried over $MgSO_4$, and the solvent was removed in vacuo. Finally, the methyl benzoate was purified by column chromatography (silica; *n*-hexane−ethyl acetate mixture).

ASSOCIATED CONTENT

Ⓢ Supporting Information

Catalyst preparation. Detailed procedure for oxidative esterification. EPR TEM XPS and XRD analysis. ^{1}H NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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