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# A sustainable oxidative esterification of thiols with alcohols by a cobalt nanocatalyst supported on doped carbon

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Here, we developed a new cobalt nanocatalyst supported on N-SiO<sub>2</sub>-doped activated carbon (Co/N–SiO<sub>2</sub>–AC), which exhibits excellent catalytic performance towards the oxidative esterification of (hetero)aryl and alkyl thiols with alcohols. A wide array of sulfinic esters were efficiently afforded in an exclusive chemoselective manner. The developed synthetic method proceeds with merits of mild reaction conditions, broad substrate scope, operational simplicity, good functional group tolerance, earth-abundant and reusable cobalt catalysts, the utilization of renewable alcohols as the coupling partners and molecular O<sub>2</sub> as the sole oxidant, which offers a practical way for sustainable synthesis of sulfinic esters.

#### Introduction

Sulfinic esters constitute an important class of organic compounds, which exhibit diverse biological and therapeutic activities such as stimulating the glucose uptake in muscle cells,<sup>1a</sup> and regulating the mitochondrial function of the Parkinsonism protein DJ-1.<sup>1b</sup> In addition, due to the two faces of chemical property,<sup>2</sup> sulfinic esters can serve as both electrophiles and nucleophiles, which have been extensively employed for the preparation of a wide array of functional products such as sulfonylmethyl isonitriles,<sup>3</sup>  $\alpha$ ,  $\beta$ -unsaturated ketones,<sup>4</sup> sulfinamides and sulfonamides<sup>5</sup> sulfonimidamides,<sup>6</sup> sulfoxides<sup>7</sup> and sulfonyl allenes<sup>8</sup>.

Due to the interesting applications, the development of alternative approaches to access sulfinic esters is of high importance in synthetic chemistry. The early representative protocols are mainly based on the oxidation of diaryl disulfides with excess oxidants [i.e., N-bromosuccinimide (NBS),<sup>9a</sup> Br<sub>2</sub><sup>4</sup> or Phl(OCOCF<sub>3</sub>)<sub>2</sub><sup>9b</sup>] in the presence of alcohols (Scheme 1a). Later, the base-promoted reaction of sulfinic acid chlorides with alcohols at -78 °C<sup>10</sup> (Scheme 1b) and the condensation of sulfinic acids with alcohols in the presence of *N*,*N'*-dicyclohexylcarbodiimide (DCC) (Scheme 1c)<sup>11</sup> have offered useful alternatives to realize the related end. In 2015, Sun and the co-workers have demonstrated a new method via *in situ* NBS-mediated C-S bond cleavage of *t*-Butyl sulfoxide to form sulfinyl bromide followed by alcoholysis (Scheme 1d).<sup>12</sup> More recently, the group of Menezes and Oliveira has illustrated a sulfuric acid-promoted coupling of sulfinic acid salts

with methanol in the presence of molecular sieves (Scheme 1e).<sup>13</sup> Interestingly, the aerobic copper-catalyzed cross-coupling of sulfonyl hydrazides (Scheme 1f)<sup>14</sup> or thiols (Scheme 1g)<sup>15</sup> with alcohols have also been nicely demonstrated. Despite the significant utility, most of these transformations suffer from one or more drawbacks such as the need for excessive amount of wastegenerating agents [i.e., NBS, Br<sub>2</sub>, PhI(OCOCF<sub>3</sub>)<sub>2</sub>, DCC, H<sub>2</sub>SO<sub>4</sub>, etc.], difficult catalyst reusability, harsh reaction conditions, poor functional group tolerance, limited chemoselectivity and tedious synthetic procedures to access substrates. Hence, there is a high demand for efficient and environmentally benign new methods for the synthesis of sulfinic esters from readily available starting materials with natural abundant metal catalysts, preferably recyclable and reusable ones.

As our continuous research interests in the transformation of abundant and sustainable alcohol resources into functional

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<sup>&</sup>lt;sup>†</sup>Electronic Supplementary Information (ESI) available: [Experimental details, BET, XRD, TEM, EDX and XPS of catalyst, copies of <sup>1</sup>H NMR, <sup>13</sup>C NMR spectra]. See DOI: 10.1039/x0xx00000x

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molecules<sup>16</sup> and the search for efficient methods to construct Nheterocycles<sup>17</sup> as well as the design of non-noble metal catalysts,<sup>17b</sup> we were therefore motivated to develop a new protocol for the synthesis of sulfinic esters by employing heterogeneous catalysts. In consideration of the natural abundance of cobalt and its capability in activation of inert substrates via oxidation<sup>18</sup> as well as the potential of silica in adjusting the micropore size of carbon materials to favor the mass transfer,<sup>19</sup> we herein report the preparation and characterization of a new cobalt nanocatalyst supported on N–SiO<sub>2</sub>-doped activated carbon (Co/N–SiO<sub>2</sub>–AC), and describe, for the first time, its application on oxidative esterification of thiols with alcohols in the presence of molecular O<sub>2</sub> (Scheme 2).

RSH + R'OH 
$$\xrightarrow{\text{reusable Co/N-SiO}_2\text{-AC}}$$
  $\xrightarrow{O}_{\parallel}$   
60-80 °C, O<sub>2</sub>, K<sub>2</sub>CO<sub>3</sub>  $\xrightarrow{O}_{\parallel}$  R<sup>-S</sup>OR'

Scheme 2 Oxidative esterification of thiols with alcohols.

#### **Results and discussion**

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Typically, the cobalt catalyst was synthesized via the following procedure: The mixture of Co(OAc)<sub>2</sub>·4H<sub>2</sub>O and 1,10-phenanthroline in ethanol was stirred at 100 °C for 1 hour to form the cobalt complex. Then, silica was introduced into the above solution via in situ hydrolysis of the added Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub> (TEOS) with aqueous ammonia. The resulting mixture was followed by successive addition of activated carbon (AC) support, refluxing at 100 °C for 5 h and removal of the solvent, the reaming sample was pyrolyzed at 800 °C under a flow of argon, and etched the non-supported cobalt particles generated during the pyrolysis process with aqueous HCl. The prepared material is named as Co/N–SiO<sub>2</sub>–AC with a Co content of 1.08 wt % (measured by ICP-OES analysis). In addition, for the purpose of comparison, the materials without addition of Si precursor, 1,10-phenanthroline, metal source during the preparing process were denoted as Co/N-AC, Co/SiO<sub>2</sub>-AC and Metal/N-SiO<sub>2</sub>-AC, respectively.

With the catalyst materials prepared, they were then applied to the oxidative esterification of 4-methylbenzenethiol 1a with methanol 2a. By performing the reaction at 60 °C in the presence of molecular O<sub>2</sub> and catalytic amounts of K<sub>2</sub>CO<sub>3</sub>, we tested the effect of Co/N-SiO<sub>2</sub>-AC (without pyrolysis), Co/N-AC, N-SiO<sub>2</sub>-AC, Co/SiO<sub>2</sub>-AC, Co(OAc)<sub>2</sub>·4H<sub>2</sub>O, Co/N-SiO<sub>2</sub>-AC, AC, N-AC, SiO<sub>2</sub>-AC and Co/AC on the reaction (Table 1, entries 1-6 and Table S1, entries 1-4, ESI<sup>†</sup>), only Co/N–AC and Co/N–SiO<sub>2</sub>–AC were able to afford the sulfinic ester 3aa in 70% and 96% yields, respectively (entries 2 and 6), implying that the Co-N species plays a decisive role on the reaction. Then, Co/N-SiO<sub>2</sub>-AC catalyst without pyrolysis and the absence of catalyst or base resulted in no product formation (entries 1, 7 and 8). Further, inspired by the excellent catalytic performance of Co/N-SiO<sub>2</sub>-AC pyrolyzed at 800 °C (entry 6), we further prepared the Cu-, Mn-, Pd- and Fe-catalyst materials. However, they showed no activity under the identical conditions (entries 9-12). Hence, the optimal reaction system is as shown in entry 6 of Table 1.

Table 1 Optimization of reaction conditions<sup>a</sup>

Entry	Catalyst	t (h)	Yield (%) <sup>b</sup>
1	Co/N-SiO <sub>2</sub> -AC	24	0 <sup><i>c</i></sup>
2	Co/N-AC	24	70
3	N-SiO <sub>2</sub> -AC	24	0
4	Co/SiO <sub>2</sub> -AC	24	0
5	Co(OAc) <sub>2</sub> ·4H <sub>2</sub> O	24	trace
6	Co/N-SiO <sub>2</sub> -AC	24	96
7	-	24	0
8	Co/N-SiO <sub>2</sub> -AC	24	$0^d$
9	Cu/N-SiO <sub>2</sub> -AC	24	0
10	Mn/N-SiO <sub>2</sub> -AC	24	0
11	Pd/N-SiO <sub>2</sub> -AC	24	0
12	Fe/N-SiO <sub>2</sub> -AC	24	0

<sup>*a*</sup> Conditions: unless otherwise stated, the reaction of **1a** (0.5 mmol), K<sub>2</sub>CO<sub>3</sub> (0.1 mmol), catalyst (40 mg, Co: 1.46 mol %) in CH<sub>3</sub>OH (1.5 mL) was charged with O<sub>2</sub> and stirred at 60 °C for 24 h. <sup>*b*</sup> GC yield using hexadecane as an internal standard. <sup>*c*</sup> Catalyst without pyrolysis. <sup>*d*</sup> Without base.



**Fig. 1** TEM images of Co/N–SiO<sub>2</sub>–AC and the corresponding elemental mapping images of C, N, Si and Co, respectively.

Characterization of Co/N–SiO<sub>2</sub>–AC was performed by XRD, BET, TEM, XPS, EDX and ICP-OES, respectively. The XRD pattern (Fig. S1, ESI†) showed no peaks ascribing to the Co metal. Except for two peaks of carbon at  $26^{\circ}$  and  $43^{\circ}$ , which are denoted to the (002) and (100) planes, the diffraction pattern of graphite-like carbon structure.<sup>20</sup> However, the existence of cobalt was confirmed by EDX detection (Fig. S2, ESI†) and the transmission electron microscopy (TEM, Fig. S3, ESI†). These results indicate that the cobalt particles are highly dispersed with low density and small size. In comparison with Co/N–AC, Co/N–SiO<sub>2</sub>–AC has a regular morphology although both samples have highly dispersed metal particles (Fig. S3, ESI†). The mean size of the Co particles in Co/N–SiO<sub>2</sub>–AC was measured as 0.52 nm by TEM (Fig. S4, ESI†). In addition, the element mapping images reveal the uniform distribution of Co, N, Si and C (Fig. 1), which is in accordance with the result of EDX (Fig. S2, ESI†).

The specific surface area of Co/N–SiO<sub>2</sub>–AC detected by the Brunauer-Emmett-Teller (BET) is 566.2  $m^2g^{-1}$  (Table S2, ESI†), and Co/N–SiO<sub>2</sub>–AC mainly contains mesopores with a total pore volume

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of 0.69 cm<sup>3</sup>g<sup>-1</sup> and an average pore width of 4.9 nm, whereas the Co/N–AC mainly has micropores with a total pore volume of 0.33 cm<sup>3</sup>g<sup>-1</sup> and a mean pore width of 1.9 nm, the totally different material parameters reflect the capability of the doped SiO<sub>2</sub> in modification of the catalyst structure and change of the catalytic performance. Further, the cobalt content of the Co/N–SiO<sub>2</sub>–AC was detected as 1.08 wt % by means of ICP-OES analysis.

Subsequently, X-ray photoelectron spectroscopy (XPS) analysis was employed to identify the surface chemistry of the developed Co/N-SiO<sub>2</sub>-AC and Co/N-AC, the Co2p spectra of both catalysts show three peaks with the electron binding energies of 778.2, 780.0 and 782.2 eV, which are assigned to Co, CoO<sub>x</sub> and Co-N, respectively. The content of Co-N and CoO<sub>x</sub> in Co/N-SiO<sub>2</sub>-AC is 63.7% and 13.8%, respectively, while 39.1% of Co-N and 54.3% of  $CoO_x$  were found in Co/N–AC (Figure 2 and Table 2), implying that the Co-N serves as the catalytic active ingredient (Table 1, entries 2 and 6). In the N region of Co/N-SiO<sub>2</sub>-AC, there are three distinct peaks (Figure S5, ESI<sup>+</sup>) with electron binding energies of 398.9 (pyridine-type), 400.7 (pyrrole-type) and 402.2 eV (ammonia N), and the pyridine-type nitrogen in this case is bonded to the cobalt, while the pyrrole-type N originates from the calcination of the 1,10phenanthroline. Deconvolution shows that around 43.9% of the N atoms are bonded to the cobalt metal (see Table S3, Co-N, ESI<sup>+</sup>), which derives from the graphitization of the Co-Phen complex.<sup>21</sup>



Fig. 2 Co2p XPS spectra of the Co/N-SiO<sub>2</sub>-AC (left) and Co/N-AC (right).

 Table 2 The binding energy and content of Co in the catalysts

Sample	Binding Energy / eV (Area/%)				
Sample	Со	CoOx	Co-N	Satellites	
	778.2	780.2	781.8		
CO/N-AC	(6.5)	(54.3)	(39.1)	-	
	778.2	780.0	782.2	786.8	
CO/14 5102-AC	(3.6)	(13.8)	(63.7)	(18.8)	

With the developed Co/N–SiO<sub>2</sub>–AC catalyst in hand, a series of structurally diverse thiols **1** with different alcohols **2** were employed to investigate the generality of the esterification protocol under the optimal conditions. Initially, the reactions of a series of (hetero)aryl thiols with methanol were tested. Gratifyingly, all the reactions proceeded smoothly and furnished the desired sulfinic esters in good to excellent yields upon isolation (Scheme 3, **3aa-3sa**). The substituents on the aryl ring of aryl thiols influenced the product yields to some extent. In general, substrates **1** bearing an electron-donating group (**3aa-3ha**) are able to afford relatively higher yields than those of electron-deficient ones (**3la, 3na, 3oa** and **3pa**). This phenomenon is rationalized as the electron-rich aryl thiols are beneficial to form more stable radical intermediates, thus favoring the coupling process.<sup>15</sup> Interestingly, the less-reactive heterocyclic

substrates such as furan-3-thiol **1r** and thiophene-2-thiol **1s** were also amenable to the transformation to afford the desired products in good yields (**3ra, 3sa**). Moreover, the alkyl thiol **1t** was able to undergo smooth oxidative esterification to couple with methanol, affording the methyl hexane-1-sulfinate **3ta** in a moderate yield (45%). Further, the change of methanol to ethanol, propyl alcohol, butyl alcohol, isopropanol and benzyl alcohol also led to the generation of desired sulfinic ester products at slightly elevated temperature (**3ab, 3gb, 3ac, 3ad, 3ae** and **3ef**). It is worth mentioning that a variety of functional groups such as –Me, –OMe, –*t*-Bu, –F, –Cl, –Br, –CF<sub>3</sub>, –NH<sub>2</sub> and MeCONH– are well tolerated in the transformation, which would offer the potential for molecular complexity via further transformations.

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**Scheme 3** Oxidative esterification of thiols.<sup>a</sup> <sup>a</sup> Standard conditions: unless otherwise stated, the reaction of **1** (0.5 mmol), **2** (1.5 mL), catalyst (40 mg, 1.46 mol %), K<sub>2</sub>CO<sub>3</sub> (0.1 mmol) was stirred at 60 <sup>o</sup>C for 24 h under O<sub>2</sub>. <sup>b</sup> At 80 <sup>o</sup>C. <sup>c</sup> At 70 <sup>o</sup>C. <sup>d</sup> At refluxing temperature.

To check the stability of the developed catalyst material (Co/N–SiO<sub>2</sub>–AC), it was recycled and reused for six consecutive runs with the model reaction. As illustrated in Fig. 3, the catalytic activity maintains very well. After six recycles, the ICP-OES analysis showed only a slight decrease of Co content from 1.08 wt % to 1.05 wt %.

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Meanwhile, a slight decrease of the specific surface area, pore volume and width of the Co/N–SiO<sub>2</sub>–AC was found, which still belongs to mesopore structure and causes no obvious decrease in catalytic activity (Table S2, ESI $^{+}$ ).



Fig. 3 The reusability of the Co-N-SiO<sub>2</sub>/AC catalyst.

To gain insight into the mechanistic information, the model reaction under standard conditions was terminated after 1 h to analyze the product system. **3aa** was detected in 8% yield along with diaryl disulfide **1a-1** and thiosulfinate **1a-2** in 91% and 1% yields, respectively (Scheme 4, eq 1). Then, the prepared **1a-1** and **1a-2** were able to couple with alcohol **2a** to give product **3aa** in excellent yields (eq 2 and 3), showing that both diaryl disulfide **1a-1** and thiosulfinate **1a-2** serve as the key reaction intermediates. Further, addition of excess TEMPO into the reaction significantly suppressed the product formation (eq 4), reaveling that the reaction involves a radical mechanism.



Scheme 4 The control experiments.

On the basis of the above findings, a possible reaction pathway is depicted in Scheme 5. The active Co-N sites of the catalyst Co/N–SiO<sub>2</sub>–AC (simplified as [Co-N]) captures the molecular oxygen under the assistance of the doped nitrogen, the single electron oxidation<sup>[17a]</sup> of thiol **1** by [Co-N]/O<sub>2</sub> initially forms species **A** and the thiol radical **1'**. Then, another single electron oxidation of thiol **1** by **A** also gives radical **1'** and regenerates the catalytic species. The homo-coupling of **1'** forms the disulfide **1-1** *in situ*. Further, the oxidation of **1-1** by [Co-N]/O<sub>2</sub> results in species **B** and its tautomer **C**,<sup>[15]</sup> and the interaction between **C** and radical **1'** would lead to generation of thiosulfinate **1-2**. Finally, the desired sulfinic ester **3** is

afforded via  $K_2CO_3$ -promoted necleophilic substitution of **1-2** by the high concentration of alcohol **2** (solvent).



Scheme 5 The possible reaction pathway.

#### Conclusions

In conclusion, by developing a cobalt nanocatalyst supported on N–SiO<sub>2</sub>-doped activated carbon, which exhibits excellent catalytic performance towards the oxidative esterification of aryl, heteroaryl and alkyl thiols with alcohols. A wide array of sulfinic esters were efficiently afforded in an exclusive chemoselective manner. The developed synthetic protocol proceeds with the merits of mild reaction conditions, broad substrate scope, operational simplicity, good functional group tolerance, high atom-efficiency earth-abundant and reusable cobalt catalyst, the utilization of renewable alcohols as the coupling partners and molecular  $O_2$  as the sole oxidant, which offers a practical way for sustainable synthesis of sulfinic esters.

#### Experimental

#### **General information**

All the obtained products were characterized by melting points (m.p), <sup>1</sup>H-NMR, <sup>13</sup>C-NMR and infrared spectra (IR). Melting points were measured on an Electrothermal SGW-X4 microscopy digital melting point apparatus and are uncorrected; IR spectra were recorded on a FTLA2000 spectrometer; <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were obtained on Bruker-400 and referenced to 7.27 ppm for chloroform solvent with TMS as internal standard (0 ppm). Chemical shifts were reported in parts per million (ppm,  $\delta$ ) downfield from tetramethylsilane. Proton coupling patterns are described as singlet (s), doublet (d), triplet (t), multiplet (m); TLC was performed using commercially available 100–400 mesh silica gel plates (GF254), and visualization was effected at 254 nm; Unless otherwise stated, all the reagents were purchased from commercial sources (J&K Chemic, TCI, Fluka, Acros, SCRC) and used without further purification.

X-ray diffraction (XRD) was used for crystal structure identification by a Bruker D8 advanced X-ray diffractometer. Micromeritics ASAP 2020 was employed to measure the specific surface area and pore structure (BET) by  $N_2$  adsorption. Transmission electron microscopy (TEM) and Energy Dispersive X-ray spectroscopy (EDX) by a Tecnai-G20 were used to detect the morphology of the samples. The atomic emission spectrometry (ICP) was used to analyse the metal content. And the electronic states were measured by X-ray photoelectron spectroscopy (XPS)

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**Catalyst Preparation** 

using a K-Alpha spectrometer with a monochromatized Al-K $\alpha$  X-ray source (300W).

Initially, a mixture of Co(OAc)<sub>2</sub>·4H<sub>2</sub>O and 1,10-phenanthroline was

added to ethanol and stirred for 1 hour at 100 °C to in situ generate

the cobalt complex. Then,  $Si(OC_2H_5)_4$  was added into the above

solution and followed by hydrolysis of TEOS with aq. ammonia to in

situ form the silica. After refluxing for 2 hours, the activated carbon

suspension was removed under vacuum and the remained solid was

dried overnight. Then, the powdered sample was pyrolyzed at 800

°C under a constant argon atmosphere for 2 h. Subsequently, the

cooled sample was treated with HCl solution to selectively remove

the unsupported cobalt particles generated during the pyrolysis

process, and the remaining catalyst is named as Co-N-SiO<sub>2</sub>/AC (Co

content: 1.08 wt % detected by ICP-OES). Similarly, the other

prepared metal catalysts are denoted as Metal-N-SiO<sub>2</sub>/AC.

Moreover, without addition of Si precursor, 1,10-phenanthroline or

metal source, the resulting materials were donated as Co-N/AC,

The mixture of 4-methylbenzenethiol 1a (0.5 mmol), methanol 2a

(1.5 mL),  $K_2CO_3$  (0.1 mmol) and Co–N–SiO<sub>2</sub>/AC (40 mg, 1.46 mol %

Co) were successively added into a 25 mL Schlenk tube, then stirred

at 60  $^{\circ}$ C for 24 h under O<sub>2</sub> atmosphere. The resulting mixture was

filtered and washed with ethyl acetate, and then concentrated by

removing the solvent under vacuum. Finally the residue was

purified by preparative TLC on silica, eluting with petroleum ether

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Typical procedure for the synthesis of sulfinic ester 3aa

 $(60 - 90^{\circ}C)$  : ethyl acetate (20 : 1) to give the product.

**Conflicts of interest** 

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Notes and references

support.

There are no conflicts to declare.

Co-SiO<sub>2</sub>/AC and N-SiO<sub>2</sub>/AC, respectively.

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By developing new cobalt nanocatalyst supported on N-SiO<sub>2</sub>-doped activated carbon (Co/N–SiO<sub>2</sub>–AC), which exhibits excellent catalytic performance towards the oxidative esterification of (hetero)aryl and alkyl thiols with alcohols. A wide array of sulfinic esters were efficiently afforded in an exclusive chemoselective manner together with merits of mild reaction conditions, broad substrate scope, operational simplicity, good functional group tolerance, earth-abundant and reusable cobalt catalysts, the utilization of renewable alcohols as the coupling partners and molecular  $O_2$  as the sole oxidant.