# **Green Chemistry**

# PAPER

CrossMark

Cite this: DOI: 10.1039/c5gc02082d

# Efficient and selective aerobic oxidation of alcohols catalysed by MOF-derived Co catalysts†

Cuihua Bai, Aiqin Li, Xianfang Yao, Hongli Liu and Yingwei Li\*

A simple and highly efficient nanostructured catalyst system comprising magnetic Co nanoparticles stabilized by N-doped carbon composite (Co/C–N) was synthesized by one-pot thermal decomposition of a Co-containing MOF. The catalysts were characterized by temperature programmed desorption (TPD), N<sub>2</sub> physical adsorption, powder X-ray diffraction (PXRD), Raman spectroscopy, transmission electron microscopy (TEM), scanning electronic microscopy (SEM), and X-ray photoelectron spectroscopy (XPS). The catalytic activity of Co/C–N materials was investigated in the selective aerobic oxidation of alcohols in neat water under an atmospheric pressure of air and base-free conditions. As compared to those prepared by traditional impregnation methods, Co/C–N exhibited an efficient performance with significantly improved catalytic activities. Besides conferring high activity and selectivity to the target products, the proposed catalytic system featured a broad substrate scope for both aryl and alkyl alcohols. Furthermore, the magnetically recoverable Co/C–N catalyst could be easily separated from the reaction system by using an external magnetic field and reused at least five times without any significant loss in catalytic efficiency under the investigated conditions.

Received 3rd September 2015, Accepted 21st October 2015 DOI: 10.1039/c5gc02082d

www.rsc.org/greenchem

### Introduction

Selective oxidation of alcohols to carbonyl compounds is one of the most important transformations in organic chemistry, and a variety of efficient methodologies have been developed to date.<sup>1-3</sup> In many cases, noble metal catalysts such as gold,<sup>4</sup> palladium,<sup>5</sup> platinum,<sup>6</sup> and ruthenium<sup>7</sup> show excellent activities and selectivities for this chemical process. However, because of the high price and limited reserves of noble metals, it is urgent to reduce their usage. Therefore, some non-noble transitional metals, e.g., Co,8 Mn,9 Fe,10 V,11 and Cu,12 have been explored for the oxidation of alcohols, among which the development of efficient and recyclable heterogeneous catalysts has received wide interest.<sup>1b</sup> Nevertheless, when using non-noble metals as heterogeneous catalysts, their efficiencies are generally lower than the noble catalysts in terms of activity and substrate scope.<sup>13</sup> Consequently, a large excess of base additives or explosive oxidizing agents (e.g., peroxy acids, and metal oxidants) are employed to promote the activity and selectivity of this transformation.14 In terms of economy and environmental friendliness, it is highly desirable to catalyze alcohol oxidation by reusable non-noble catalysts under base-

eloped magnetic separation after reactions.<sup>15</sup> Up to now, although a gold,<sup>4</sup> few magnetically heterogeneous catalysts have been developed

oxidant and green media (e.g., water) as the solvent.

for the synthesis of carbonyl compounds from alcohol oxidation, they suffer from inherent problems such as the requirement of base additives, and the uses of alkyl hydroperoxide as terminal oxidants and volatile organic solvents.<sup>13,14b,16</sup> The development of a cost-effective and magnetic catalyst for the selective oxidation of alcohols in an environmentally benign solvent such as water employing air as the oxidant still remains a great challenge.

free conditions using molecular oxygen (ideally air) as the

Containing a magnetic element in heterogeneous catalysts is additionally desirable owing to their facile and efficient

Herein, we report a novel, highly efficient, and reusable Cobased heterogeneous catalyst for the synthesis of carbonyl compounds from the aerobic oxidation of alcohols. To the best of our knowledge, this work represents the first example of a highly active magnetic catalyst for oxidation of alcohols in neat water under an atmospheric pressure of air and base-free conditions. The as-synthesized Co/C–N composites exhibit an outstanding performance in the aerobic oxidation of alcohols, with significantly improved catalytic activities as compared to those prepared by traditional impregnation methods. Besides conferring high activity and selectivity to the target products, the proposed catalytic system features a broad substrate scope for both aryl and alkyl alcohols. Furthermore, the catalyst could be easily recycled by using an external magnetic field.

# ROYAL SOCIETY OF CHEMISTRY

View Article Online

State Key Laboratory of Pulp and Paper Engineering, School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, China. E-mail: liyw@scut.edu.cn

<sup>†</sup>Electronic supplementary information (ESI) available: Additional characterization and reaction results. See DOI: 10.1039/c5gc02082d

The Co-based catalyst was prepared simply by one-pot thermal decomposition of cobalt-containing metal-organic frameworks (MOFs). MOFs are known as a new class of porous materials comprising metal ions and organic linkers, which have exhibited a number of potential applications in many fields such as gas storage/separation, catalysis, sensing, and biomedicine.<sup>17-21</sup> More recently, MOFs have been considered as alternative precursors to construct new metal oxides or carbon nanomaterials due to their orderly structures, high porosities, and isolated metal nodes.<sup>22</sup> Porous materials with high surface areas and porosities that could be utilized in many practical applications (*i.e.*, heterogeneous catalysis, electrochemistry, gas adsorption, and sensors) have been successfully derived from MOFs.<sup>23-26</sup> However, the reports on the employment of such MOFderived materials for liquid-phase catalytic oxidation reactions are scarce.23c,27

#### **Results and discussion**

 $[Co_9(btc)_6(tpt)_2(H_2O)_{15}]$  solvent (MOF 1) (btc = 1,3,5-benzenetricarboxylate, tpt = 2,4,6-tris(4-pyridyl)-1,3,5-triazine) was selected as the MOF precursor (Fig. S1<sup>†</sup>) due to the mixed rigid triangular ligands in the MOF, highly symmetrical structure, and good thermal stability.<sup>28</sup> The organic linkers in the MOF structure would be carbonized gradually following the slow heating procedure, and the resulting carbon composite could prevent serious aggregation of Co to facilitate the synthesis of monodisperse nanostructured porous Co/C-N materials. To disclose the effect of the N element on the properties of the derived nanomaterials, [Co<sub>3</sub>(H<sub>2</sub>O)<sub>6</sub>(btc<sup>3-</sup>)(btc<sup>2-</sup>)-(btc<sup>1-</sup>)]·2H<sub>2</sub>O (MOF 2) was also selected as the precursor to prepare the N-free Co/C materials (Fig. S2<sup>†</sup>).<sup>29</sup> Considering that MOF 1 begins to decompose when the temperature increases to ca. 400 °C (Fig. S3†), the applied calcination temperatures are varied from 500 to 900 °C.28 The as-synthesized materials are denoted as Co/C-Nx, where x represents the MOF pyrolysis temperature. The Co contents in the Co/C-Nx materials were about 30-45 wt%, while 53.2% of Co was found in the Co/C700 (Table 1).

Alcohol oxidations were performed under base-free conditions using an atmospheric pressure of air as the oxidant. The reaction results are summarized in Table 2. First, the assynthesized Co/C–N materials were examined as catalysts for the aerobic oxidation of 1-phenylethanol in toluene at 100 °C. Under the conditions, although the conversions were somewhat low, it was noteworthy that the ketone selectivities achieved by the Co/C–N composites were all 100% (Table 2, entries 1–5). Among the five Co/C–N materials, Co/C–N700, *i.e.*, the material prepared at 700 °C, was the most active for 1-phenylethanol oxidation (Table 2 entry 3). Using the Co/ C–N700 catalyst, different solvents were tested, and water was

 
 Table 2
 Optimization of reaction conditions for oxidation of 1-phenylethanol to acetophenone



Entry	Catalyst	Solvent	Conv. <sup>a</sup> (%)	Yield <sup><math>a</math></sup> (%)
1	Co/C-N500	Toluene	10	10
2	Co/C-N600	Toluene	12	12
3	Co/C-N700	Toluene	43	43
4	Co/C-N800	Toluene	24	24
5	Co/C-N900	Toluene	19	19
6	Co/C-N700	Acetonitrile	28	28
7	Co/C-N700	DMF	39	39
8	Co/C-N700	DMA	37	37
9	Co/C-N700	Dimethyl benzene	26	26
10	Co/C-N700	H <sub>2</sub> O	65	65
11	Co/C-N700	DMSO	<5	<5
12	Co/C-N700	<i>n</i> -Heptane	41	41
13	Co/C-N700	<i>n</i> -Hexane	24	24
14	Co/C-N700	Acetone	30	30
15	Co/C-N700	Ethanol	52	52
$16^{b}$	Co/C-N700	$H_2O$	84	84
17 <sup>c</sup>	Co/C-N700	H <sub>2</sub> O	98	98
$18^{c,d}$	Co/C-N700	$H_2O$	68	68
$19^{c,e}$	Co/C-N700	$H_2O$	8	<5

Reaction conditions: 1a (0.5 mmol), catalyst (10 mol% Co), solvent (2 mL), air (1 bar), 100 °C, 24 h. <sup>*a*</sup> Conversion and yield were determined by GC-MS. <sup>*b*</sup> 48 h. <sup>*c*</sup> 110 °C, 48 h. <sup>*d*</sup> 5 mol% Co. <sup>*e*</sup> Filled with  $N_2$  (1 bar).

Sample	$\frac{S_{\text{BET}}}{(\text{m}^2 \text{g}^{-1})}$	Pore volume $(cm^3 g^{-1})$	Pore size (Å)	Content (wt%)			Particle size (nm)		
				$C^{a}$	$N^{a}$	$H^{a}$	$\operatorname{Co}^{b}$	XRD	TEM
1	10	0.01	8.9	42.0	7.2	2.4	19.8	_	_
Co/C-N500	241	0.07	5.0	64.5	1.8	0.8	31.0	5.5	5.4
Co/C-N600	256	0.12	4.9	61.2	1.5	0.7	35.9	6.4	6.6
Co/C-N700	159	0.13	6.2	54.4	1.2	0.7	42.7	9.6	9.8
Co/C-N800	180	0.20	6.4	53.6	1.0	0.6	44.2	10.2	10.3
Co/C-N900	165	0.11	6.1	52.8	1.0	0.6	45.2	18.1	35.8
2	4	0.01	_	34.0		3.0	18.3	_	_
Co/C700	34	0.05	8.8	32.4		0.5	53.2	30.2	95.6

Table 1	Properties of	Co-based	materials
---------	---------------	----------	-----------

<sup>a</sup> Measured by elemental analysis. <sup>b</sup> Measured by AAS.

shown to be the best one among the solvents investigated (Table 2, entry 10).

Inspired by these intriguing results, we further optimized the oxidation reaction conditions. When the reaction time was prolonged to 48 h, acetophenone could be obtained in 84% yield (Table 2, entry 16). A slight increase of temperature to 110 °C led to an almost quantitative transformation (Table 2, entry 17). Note that the reaction also proceeded smoothly when the Co usage was decreased to 5 mol% (Table 2, entry 18). However, it was evident that the oxidant (*i.e.*, air) was crucial for this oxidation process (Table 2, entry 19). Thus, after screening the reaction parameters, the optimized reaction conditions could be obtained as follows: 10 mol% Co/C–N700 as the catalyst, H<sub>2</sub>O as the solvent, air as the oxidant, and at 110 °C for 48 h.

A series of carbon- or Co-based materials were prepared as reference catalysts to verify the unique catalytic characteristics of the Co/C-N composites in aerobic oxidation. It can be seen that in the absence of any catalyst, the reaction hardly occurred (Table 3, entry 1). Similarly, a very low yield was obtained when solely using activated carbon as the catalyst (Table 3, entry 2). Notably, the C-N composite, which was derived from the synthesized Co/C-N700 after being immersed in aqua regia to remove Co, showed some activity in the oxidation of 1-phenylethanol (Table 3, entry 3). Commercial Co-based catalysts including metallic Co powder, Co oxides, and salt were all essentially inactive for this transformation under the investigated conditions (Table 3, entries 4-7). The MOF 1 precursor also showed poor activity toward ketone formation (Table 3, entry 8). A conversion of 15% was obtained when using Co/C as the catalyst, which was prepared by a traditional impregnation method (Table 3, entry 9). For comparison, MOF 2 that has a similar structure as MOF 1 but containing no N elements

 Table 3
 Aqueous oxidation of 1-phenylethanol catalyzed by various catalysts

ОН		0 II
	catalys	
<u> </u>	H <sub>2</sub> O a	ir 🗖 🔰
1a		2a

Entry	Catalyst	Conv. <sup><i>a</i></sup> (%)	Yield <sup>a</sup> (%)
1	_	<5	<5
2	С	6	<5
3 <sup>b</sup>	C-N	55	55
4	Со	<5	<5
5	CoO	5	5
6	$Co_3O_4$	<5	<5
7	$Co(NO_3)_2 \cdot H_2O$	<5	<5
8	MOF 1	<5	<5
9 <sup>c</sup>	Co/C	15	13
10	Co/C700	34	34

Reaction conditions: **1a** (0.5 mmol), catalyst (10 mol% Co),  $H_2O$  (2 mL), air (1 bar), 110 °C, 48 h. <sup>*a*</sup> Conversion and yield were determined by GC-MS. <sup>*b*</sup> The synthesized Co/C–N700 was immersed in aqua regia to remove Co. <sup>*c*</sup> Co/C was prepared by an impregnation method.

was also pyrolyzed at 700 °C to afford Co/C700. Interestingly, the Co/C700 catalyst showed a much lower activity and produced acetophenone in only 34% yield (Table 3, entry 10) under identical conditions, demonstrating the importance of N-doping in the composite for the oxidation reaction. These control experiments suggested that the synergic interactions between the C–N composite and Co played an important role in determining the high activity of Co/C–N700 in the oxidation of alcohols.

To elucidate reasons for the remarkable catalytic activity of the Co/C-N materials in aerobic alcohol oxidation, we examined the composites with a series of characterization techniques. Basicity is reported to play a crucial role in promoting the activity of liquid phase oxidation of alcohols with molecular oxygen.14c,30 Here, the basic properties of Co/C-N700 and Co/C700 were investigated by CO<sub>2</sub>-TPD (Fig. 1). In general, the strength of basic sites may be determined from CO<sub>2</sub> desorption temperatures, i.e., the higher the desorption temperature, the stronger the basicity. A few desorption peaks were observed in the CO2-TPD curve of Co/C-N700. The peak at ca. 245 °C was attributed to the basic site associated with weak chemical adsorption of CO2 molecules. Co/C-N700 exhibited broad peaks within the temperature range of 330-530 °C, with the main desorption located at about 460 °C and one shoulder peak at ca. 380 °C. In contrast, only one sharp peak (at ca. 445 °C) was observed for the Co/C700. These results indicated that pyrolysis of MOFs with N-containing ligands could enhance the basicity of the resulting materials. The CO2-TPD curves of Co/C-Nx materials prepared at different pyrolysis temperatures are summarized in Fig. S4.† It can be seen that all the curves showed a main desorption peak at around 450 °C, and Co/C-N700 had the most amount of basic sites. The results suggested that the high activity of Co/C-N700 could be mainly attributed to the strong basicity of the material.

The specific surface areas and porosities were analyzed by  $N_2$  adsorption-desorption isotherms at 77 K and the results are summarized in Table 1. Both MOFs 1 and 2 exhibited a non-porous structure as reported in the literature.<sup>28,29</sup> But after carbonization, the obtained materials possessed high specific surface areas. As compared to MOF 1, remarkable increases in the specific surface areas from around 10 m<sup>2</sup> g<sup>-1</sup> to 256 m<sup>2</sup> g<sup>-1</sup> and total pore volumes from 0.01 cm<sup>3</sup> g<sup>-1</sup> to



Fig. 1 CO<sub>2</sub>-TPD profiles of Co/C-N700 (a) and Co/C700 (b).

*ca.* 0.20 cm<sup>3</sup> g<sup>-1</sup> were observed for the Co/C–N composites (Table 1). The lower surface area observed on the Co/C–N700 was probably attributed to the decomposition of the microporous structure. For the Co/C700 derived from MOF 2, the specific surface area and pore volume were, however, not enhanced as obviously as observed for the Co/C–N materials.

XRD patterns of the Co/C-N materials prepared at different pyrolysis temperatures are shown in Fig. 2. The weak peak at ca. 25° could be assigned to a typical (002) interlayer of graphite-type carbon sheets, while the peaks at around 44.2°, 51.5°, 75.8°, 92.2°, and 97.6° were assignable to the well-crystallized Co with a face-centered cubic (fcc,  $Fm\bar{3}m$  (225), a = 0.355 nm) structure (JCPDS no. 15-0806).<sup>30</sup> At lower carbonization temperatures, only one peak at *ca.* 44.2° was observed. More intense diffraction peaks were detected at elevated temperatures, implying the formation of a Co phase with a higher crystallization degree. Interestingly, the Co/C700 nanocomposite showed similar peaks as Co/C-N700 (Fig. S5<sup>†</sup>). However, the mean particle size (ca. 30.2 nm) of metallic cobalt in Co/C700 (Table 1), which was calculated from the broadening of the Co(111) plane using the Scherrer equation,<sup>31</sup> was much bigger than that in Co/C-N700 (ca. 9.6 nm).

Fig. 3 shows the Raman spectra of Co/C-N and Co/C700 nanocomposites. For the MOF-derived materials, the D band



Fig. 2 Powder XRD patterns of (a) Co/C–N500, (b) Co/C–N600, (c) Co/ C–N700, (d) Co/C–N800, and (e) Co/C–N900.



Fig. 3 Raman spectra of (a) Co/C700, (b) Co/C-N500, (c) Co/C-N600, (d) Co/C-N700, (e) Co/C-N800, and (f) Co/C-N900.

could be seen at 1315 cm<sup>-1</sup> due to the disorder induced features caused by lattice defects.<sup>31,32</sup> The G band at 1590 cm<sup>-1</sup> represents the first-order scattering of the  $E_{2g}$  vibrational mode within aromatic carbon rings.<sup>31,32</sup> The relative ratio of D band to G band ( $I_D/I_G$ ) in the Raman spectra of Co/C–N500, Co/C–N600, Co/C–N700, Co/C–N800 and Co/C–N900 materials was 2.53, 2.49, 1.71, 1.24, and 1.20, respectively, indicating that the crystallization degree of graphitic carbon was increased with an increase in pyrolysis temperature, which was in good agreement with those observed in XRD measurements. Moreover, the appearance of the 2D band indicated that graphitic structures were well developed in the Co/C–N800 and Co/C–N900 composites. Notably, a similar profile was also observed for the Co/C700 (Fig. 3).

SEM and TEM images were taken to investigate the morphology and structure of the materials. As seen in Fig. 4, with an increase in the pyrolysis temperature, the Co/C–N surfaces were distorted with rougher surfaces, indicating the decomposition and carbonization of the MOF frameworks. Interestingly, nanotubes were observed on the Co/C–N900 (Fig. S6†). SEM images of Co/C700 also showed rough surfaces as the Co/C–Nx. From TEM images (Fig. 5), it can be seen that Co was highly dispersed on the N-doped carbon in Co/C–N700 with a uniform particle size of  $9.8 \pm 2.6$  nm, while Co nanoparticles in the Co/C700 nm). A high-resolution TEM image of Co/C–N700 confirmed the existence of crystallized Co nanoparticles tightly surrounded by graphitized carbon. The Co nanoparticles tended to aggregate gradually with an increase



Fig. 4 SEM images of (a) MOF 1, (b) Co/C-N500, (c) Co/C-N600, (d) Co/C-N700, (e) Co/C-N800, (f) Co/C-N900, (g) MOF 2, and (h) Co/C700.



Fig. 5 TEM images and the size distribution of Co particles for Co/C–N700 (a, d), Co/C700 (b), and Co/C (c).

in pyrolysis temperature (Fig. S7†). These results suggested that the thermolysis temperature and N-containing ligands played important roles in reducing the particle size of Co particles.

To gain further insight into the catalyst structure and especially the nitrogen location, XPS characterization was performed on the materials. Three distinct peaks were observed in the N 1s spectra of Co/C-Nx with electron binding energies of 398.8, 400.5, and 402.8 eV, which were attributed to pyridine-type, pyrrole-type, and ammonium species nitrogen, respectively (Fig. 6).<sup>30,34</sup> In Co/C-N700, the percentage of pyridinic nitrogen bonded to metal was higher than that in the other two samples, i.e., Co/C-N800, and Co/C-N900. Such a coordination interaction between the nitrogen and cobalt was advantageous in preventing a serious aggregation of Co in the course of MOF pyrolysis, in good accordance with the TEM observations. In the cobalt region for all samples, only two main peaks at ca. 793.5 and 778.7 eV were observed, characteristics for Co  $2p_{1/2}$  and Co  $2p_{3/2}$  of metallic Co (Fig. S8<sup>†</sup>).<sup>33</sup> Deconvolution revealed that the Co region at ca. 778.7 eV consisted of three peaks at 778.7 eV, 780.1 eV, and 782.7 eV, respectively (Fig. S9†). The observation suggested that some of the Co atoms on the surface could have some interaction with the nitrogen or carbon atoms surrounding the Co nanoparticles.



Fig. 6 N 1s spectra for (a) Co/C–N700, (b) Co/C–N800, and (c) Co/C–N900.

The above characterization results suggested that the introduction of N-containing ligands would be the key to facilitate the formation of uniformly dispersed Co particles. Overall, N-doping in the materials promoted the basic properties and played an important role in reducing the particle size of Co, which may lead to materials with excellent performances in catalytic reactions.

The substrate scope of the selective alcohol oxidation over the Co/C-N materials was investigated under an atmospheric pressure of air and base-free conditions (Table 4). Different secondary benzylic alcohols bearing electron-donating or -withdrawing functional groups afforded the corresponding substituted ketones in good to excellent yields within 48 h (entries 2-7). Diphenylmethanol (1h), which is sterically hindered, was converted to the corresponding ketone (2h) in 97% yield (entry 8). 1-(Naphthalen-1-yl)-ethanol also underwent oxidation smoothly and gave 2i in 68% yield (entry 9). The Co/ C-N700 catalyst was also active in the aerobic oxidation of 2,3dihydro-1*H*-inden-1-ol (1j), furnishing 2j in 81% yield (entry 10). Notably, even 1-phenylprop-2-en-1-ol (1k) bearing activated double bonds also worked well and afforded the desired oxidation product in ca. 52% yield (entry 11). Moreover, a range of aliphatic alcohols were suitable for the formation of the corresponding ketones 2j-o, achieving moderate to good yields within 60 h (entries 12-15). It was noteworthy that excellent selectivities to the target oxidation products were obtained for all the investigated substrates. Although in some cases the conversion was not satisfying, it could be significantly improved simply by prolonging the reaction time, without any remarkable changes in selectivity. For example, 2-butyl alcohol was efficiently oxidized to 2-butanone in excellent yield (95%) after 96 h of reaction (entry 16). The present catalytic system was also applicable to the oxidation of primary alcohols, giving the corresponding aldehydes 2p-t in excellent yields (Table 4, entries 17-21).

Finally, we investigated the reusability of the highly active Co/C–N700 catalyst in the aerobic oxidation of 1-phenylethanol

Table 4	Aqueous	oxidation	of various	secondary	alcohols	catalyzed	by
Co/C-N	700						

Table 4 (Contd.)





Reaction conditions: substrate (0.5 mmol), Co/C–N700 (10 mol% Co), H<sub>2</sub>O (2 mL), air (1 bar), 110 °C, 48 h. <sup>*a*</sup> Yield was determined by GC-MS. <sup>*b*</sup> 60 h. <sup>*c*</sup> 96 h. <sup>*d*</sup> H<sub>2</sub>O (0.5 mL), 65 h.

in aqueous medium. After the reaction, the catalyst was dispersed in water, but it was easily separated with the assistance of an external magnet (Fig. S11<sup>†</sup>). AAS analysis of the reaction solution confirmed that the content of Co in the solution was below the detection limit, indicating that there was no significant leaching of the active Co during the reaction process. The used catalyst was washed several times with acetic ester and alcohol, and then dried in air. The catalytic activity of the used catalyst was significantly reduced (Table S1<sup>†</sup>). The PXRD data (Fig. S12<sup>†</sup>) indicated that the diffraction peaks of the Co phase apparently decreased in strength. However, after being reduced in H<sub>2</sub> at 400 °C for 1 h, the PXRD profile was similar to the fresh one (Fig. S12<sup>†</sup>), and no apparent Co aggregation could be observed (Fig. S13<sup>†</sup>). As shown in Table S2,<sup>†</sup> upon hydrogen treatment, the catalyst could be reused at least five times without any significant loss of activity for the aerobic oxidation of 1-phenylethanol under the investigated conditions.

## Conclusions

In summary, we have developed a novel, highly efficient, and reusable Co-based heterogeneous system for selective aerobic oxidation of alcohols. The Co/C–N composites are synthesized by one-step thermolysis of Co-containing MOFs under an inert atmosphere. It was found that the N element could be introduced into the carbon matrix during pyrolysis of the MOFs with N-containing ligands, and the presence of N is beneficial for the improvement of basicity and metal dispersion of the Co-carbon nanocomposites. The Co/C–N materials exhibit an excellent performance in the aerobic oxidation of alcohols in neat water under an atmospheric pressure of air and base-free conditions. Besides conferring high activity and selectivity to the target products, the proposed catalytic system features a broad substrate scope for both aryl and alkyl alcohols. Furthermore, the catalyst could be easily recycled by using an external magnetic field and reused. The present reaction system might provide a simple, cost effective, and environmentally friendly procedure for the preparation of carbonyl compounds from selective alcohol oxidation.

#### Experimental

#### **General information**

All starting materials and solvents were obtained from commercial suppliers and used without further purification.

Atomic absorption spectroscopy (AAS) was performed on a Hitachi Z-2300 instrument. Elemental analysis was performed on an Elementar Vario EL III equipment. Powder X-ray diffraction patterns of the samples were obtained on a Rigaku diffractometer (D/MAX-IIIA, 3 kW) using Cu K $\alpha$  radiation (40 kV, 30 mA,  $\lambda = 0.1543$  nm). XPS data were obtained on an Axis Ultra DLD using Mono Al K $\alpha$  (1486.6 eV, 10 mA × 15 kV) as an X-ray source.

The size and morphology of materials were characterized by using a scanning electronic microscope (SEM, 1530 VP of LEO) equipped with an energy dispersive X-ray detector (EDX, Inca 300 of Oxford), and a high-resolution transmission electron microscope (HR-TEM, C/M300 of Philips). BET surface area and pore size measurements were performed with N<sub>2</sub> adsorption/desorption isotherms at 77 K on a Micromeritics ASAP 2020 instrument. Mass spectra were recorded on a GC-MS spectrometer (Shimadzu GCMS-QP5050A equipped with a 0.25 mm × 30 m DB-WAX capillary column). CO<sub>2</sub>-TPD data were obtained on a Micromeritics AutoChem II 2920 instrument. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Bruker Avance III 400 spectrometer using CDCl<sub>3</sub> as the solvent and tetramethylsilane (TMS) as the internal standard.

#### **Catalyst preparation**

Synthesis of MOF 1. In a typical synthesis,  $Co(NO_3)_2 \cdot 6H_2O$  (464 mg) was added to 48 mL 1:1:1 (v/v) mixture of *N*,*N'*-dimethylmethanamide (DMF), ethanol and water containing tpt (124 mg) and H<sub>3</sub>btc (168 mg) under stirring in a vial. The vial was then sealed and allowed to stand at 100 °C. After heating for 24 h, red cubic shaped crystals were formed. The crystals were collected by filtration, washed with DMF and ethanol and then dried in air. Powder X-ray diffraction analysis indicated that the resultant compound exhibited the same crystalline structure as that prepared by Bu *et al.* (Fig. S1†).

Synthesis of MOF 2. A mixture of 1,3,5-benzenetricarboxylic acid (3 mmol), cobalt( $\pi$ ) chloride hexahydrate (6 mmol), potassium hydroxide (3 mmol) and water (5 mL) was added to a 25 mL Teflon container. The container was then sealed and placed in an oven heated at 180 °C for 3 days. After cooling, dark violet needle crystals were obtained as a homogeneous solid phase. The solid was collected by filtration, and dried in air.

Synthesis of Co/C–N materials by thermolysis of MOF 1. The typical procedure for the preparation of the Co/C–N materials is described as follows: 0.5 g of 1 was pyrolyzed at a high temperature for 8 h with a heating rate of 1 °C min<sup>-1</sup> at room temperature under an argon atmosphere. The prepared material was denoted as Co/C–N*x*, where *x* indicated the MOF pyrolysis temperature.

Synthesis of Co/C700 by thermolysis of MOF 2. MOF 2 (0.5 g) was placed in a tubular furnace and calcined up to 700 °C under an argon gas flow at a heating rate of 1 °C min<sup>-1</sup>. Maintaining the targeted-temperature for 8 h, the resulting solid was cooled to room temperature to give Co/C700.

**Synthesis of C–N.** The prepared Co/C–N700 was dispersed in aqua regia. After 12 h, the supernatant was decanted and replaced with fresh aqua regia. The exchange process was repeated several times. The solid was washed several times with water and collected by centrifugation, and finally dried at 100 °C overnight in an oven. The obtained material was denoted as C–N.

Synthesis of Co/C by impregnation. An aqueous solution of  $Co(NO_3)_2$ ·H<sub>2</sub>O (0.7 g) was added dropwise to the activated carbon. The sample was aged at room temperature for 24 h and then washed twice with deionized water (30 mL). The assynthesized sample was dried under vacuum at 100 °C for 2 h and then was treated in a stream of H<sub>2</sub> at 400 °C for 2 h to yield Co/C.

#### Catalytic reaction

**Procedures for the aerobic oxidation of alcohols.** Alcohols (0.5 mmol),  $H_2O$  (2 mL), and catalyst (Co 10 mol%) were added into the Schlenk tubes. The reaction mixture was stirred at 110 °C and under atmospheric conditions for 48 h. After completion of the reaction, 100 µL of *n*-hexadecane as the internal standard was added. Then, the products were extracted with ethyl acetate from the liquid mixture, subsequently subjected to GC-MS analysis. The products were isolated by preparative TLC using *n*-hexane/ethyl acetate (20:1, v/v) as an eluent.

#### **Recycling of catalyst**

The recyclability of the Co/C–N700 catalyst was tested for the aerobic oxidation of 1-phenylethanol maintaining the same reaction conditions as described above, except for using the recovered catalyst. Each time, the catalyst was isolated from the reaction mixture by magnetic separation at the end of catalytic reaction, thoroughly washed with acetic ester and alcohol and then dried in air, treated in  $H_2$  at 400 °C for 1 h before being reused.

#### Acknowledgements

We thank the National Natural Science Foundation of China (21322606, 21436005, and 21576095), the State Key Laboratory

of Pulp and Paper Engineering (2015TS03), the Doctoral Fund of Ministry of Education of China (20120172110012), Fundamental Research Funds for the Central Universities (2015ZP002 and 2015PT004), and the Guangdong Natural Science Foundation (2013B090500027, and 10351064101000000) for financial support.

## Notes and references

- (a) N. Gunasekaran, Adv. Synth. Catal., 2015, 357, 1990– 2010; (b) C. Parmeggiani and F. Cardona, Green Chem., 2012, 14, 547–564.
- 2 (a) R. Munirathinam, J. Huskens and W. Verboom, Adv. Synth. Catal., 2015, 357, 1093–1123; (b) B. Gutmann, D. Cantillo and C. O. Kappe, Angew. Chem., Int. Ed., 2015, 54, 6688–6728.
- 3 (a) X. Ma, Z. Li, F. Liu, S. Cao and H. Rao, Adv. Synth. Catal., 2014, 356, 1741–1746; (b) Q. Feng and Q. Song, J. Org. Chem., 2014, 79, 1867–1871; (c) S. Chakraborty, P. O. Lagaditis, M. Förster, E. A. Bielinski, N. Hazari, M. C. Holthausen, W. D. Jones and S. Schneider, ACS Catal., 2014, 4, 3994–4003.
- 4 (a) H. Miyamura, R. Matsubara, Y. Miyazaki and S. Kobayashi, Angew. Chem., Int. Ed., 2007, 46, 4151-4154;
  (b) M. Mahyari, A. Shaabani, M. Behbahani and A. Bagheri, Appl. Organomet. Chem., 2014, 28, 576-583; (c) C. Shang and Z. P. Liu, J. Am. Chem. Soc., 2011, 133, 9938-9947;
  (d) S. Rautiainen, O. Simakova, H. Guo, A.-R. Leino, K. Kordás, D. Murzin, M. Leskelä and T. Repo, Appl. Catal., A, 2014, 485, 202-206; (e) H. L. Liu, Y. L. Liu, Y. W. Li, Z. Y. Tang and H. F. Jiang, J. Phys. Chem. C, 2010, 114, 13362-13369.
- 5 (a) X. Wang, G. Wu, N. Guan and L. Li, *Appl. Catal., B*, 2012, **115**, 7–15; (b) B. Karimi, M. Khorasani, H. Vali, C. Vargas and R. Luque, *ACS Catal.*, 2015, **5**, 4189–4200; (c) G. Z. Chen, S. J. Wu, H. L. Liu, H. F. Jiang and Y. W. Li, *Green Chem.*, 2013, **15**, 230–235.
- 6 J. Zhu, T. Wang, X. Xu, P. Xiao and J. Li, *Appl. Catal., B*, 2013, **130**, 197–217.
- 7 H.-B. Ji, Q.-L. Yuan, X.-T. Zhou, L.-X. Pei and L.-F. Wang, Bioorg. Med. Chem. Lett., 2007, 17, 6364–6368.
- 8 (a) J. Zhu, J. L. Faria, J. L. Figueiredo and A. Thomas, *Chem. Eur. J.*, 2011, 17, 7112–7117; (b) J. Zhu, K. Kailasam, A. Fischer and A. Thomas, *ACS Catal.*, 2011, 1, 342–347; (c) K.-I. Shimizu, K. Kon, M. Seto, K. Shimura, H. Yamazaki and J. N. Kondo, *Green Chem.*, 2013, 15, 418; (d) G. Zhang, K. V. Vasudevan, B. L. Scott and S. K. Hanson, *J. Am. Chem. Soc.*, 2013, 135, 8668–8681.
- 9 (a) H.-Y. Sun, Q. Hua, F.-F. Guo, Z.-Y. Wang and W.-X. Huang, *Adv. Synth. Catal.*, 2012, 354, 569–573;
  (b) M. T. Raisanen, A. Al-Hunaiti, E. Atosuo, M. Kemell, M. Leskela and T. Repo, *Catal. Sci. Technol.*, 2014, 4, 2564– 2573.
- 10 (a) H. Song, B. Kang and S. H. Hong, ACS Catal., 2014, 4, 2889–2895; (b) D. Obermayer, A. M. Balu, A. A. Romero,

W. Goessler, R. Luque and C. O. Kappe, *Green Chem.*, 2013, **15**, 1530–1537; (*c*) F. Rajabi, A. Pineda, S. Naserian, A. M. Balu, R. Luque and A. A. Romero, *Green Chem.*, 2013, **15**, 1232–1237.

- 11 S. K. Hanson, R. T. Baker, J. C. Gordon, B. L. Scott, A. D. Sutton and D. L. Thorn, *J. Am. Chem. Soc.*, 2009, 131, 428–429.
- 12 (a) C. Chen, B. Liu and W. Chen, Synthesis, 2013, 3387–3391; (b) L. Liu, J. Ma, L. Ji and Y. Wei, J. Mol. Catal. A: Chem., 2008, 291, 1–4.
- 13 L. Geng, M. Zhang, W. Zhang, M. Jia, W. Yan and G. Liu, *Catal. Sci. Technol.*, 2015, 5, 3097–3102.
- 14 (a) Y. Yan, X. Tong, K. Wang and X. Bai, *Catal. Commun.*, 2014, 43, 112–115; (b) M. Jafarpour, A. Rezaeifard, V. Yasinzadeh and H. Kargar, *RSC Adv.*, 2015, 5, 38460–38469; (c) J. Yu, Y. Luan, Y. Qi, J. Hou, W. Dong, M. Yang and G. Wang, *RSC Adv.*, 2014, 4, 55028–55035.
- 15 (a) J.-M. Yan, X.-B. Zhang, T. Akita, M. Haruta and Q. Xu, J. Am. Chem. Soc., 2010, 132, 5326–5327; (b) D. Wang and Y. Li, J. Am. Chem. Soc., 2010, 132, 6280–6281; (c) J. Liu, S. Z. Qiao, Q. H. Hu and G. Q. Lu, Small, 2011, 7, 425–443.
- 16 (a) S. Wang, Z. Zhang and B. Liu, ACS Sustainable Chem. Eng., 2015, 3, 406–412; (b) B. Liu, Z. Zhang, K. Lv, K. Deng and H. Duan, Appl. Catal., A, 2014, 472, 64–71.
- 17 (a) T. R. Cook, Y. R. Zheng and P. J. Stang, *Chem. Rev.*, 2013, 113, 734–777; (b) M. O'Keeffe and O. M. Yaghi, *Chem. Rev.*, 2012, 112, 675–702.
- 18 Y. He, W. Zhou, G. Qian and B. Chen, Chem. Soc. Rev., 2014, 43, 5657–5678.
- 19 (a) A. Dhakshinamoorthy and H. Garcia, *Chem. Soc. Rev.*, 2014, 43, 5750–5765; (b) V. N. Panchenko, M. M. Matrosova, J. Jeon, J. W. Jun, M. N. Timofeeva and S. H. Jhung, *J. Catal.*, 2014, 316, 251–259.
- 20 Z. Hu, B. J. Deibert and J. Li, *Chem. Soc. Rev.*, 2014, 43, 5815–5840.
- 21 P. Falcaro, R. Ricco, C. M. Doherty, K. Liang, A. J. Hill and M. J. Styles, *Chem. Soc. Rev.*, 2014, 43, 5513–5560.
- 22 (a) B. Liu, H. Shioyama, T. Akita and Q. Xu, J. Am. Chem. Soc., 2008, 130, 5390–5391; (b) W. Chaikittisilp, N. L. Torad, C. Li, M. Imura, N. Suzuki, S. Ishihara, K. Ariga and Y. Yamauchi, Chem. Eur. J., 2014, 20, 4217–4221; (c) W. Chaikittisilp, K. Ariga and Y. Yamauchi, J. Mater. Chem. A, 2013, 1, 14–19; (d) H. L. Jiang, B. Liu, Y. Q. Lan, K. Kuratani, T. Akita, H. Shioyama, F. Q. Zong and Q. Xu, J. Am. Chem. Soc., 2011, 133, 11854–11857.
- 23 (a) F. Zhang, C. Chen, W.-M. Xiao, L. Xu and N. Zhang, Catal. Commun., 2012, 26, 25–22; (b) C. H. Bai, X. F. Yao and Y. W. Li, ACS Catal., 2015, 5, 884–891; (c) W. Zhong, H. Liu, C. Bai, S. Liao and Y. W. Li, ACS Catal., 2015, 5, 1850–1856; (d) X. Wang, W. Zhong and Y. W. Li, Catal. Sci. Technol., 2015, 5, 1014–1020; (e) K. Shen, L. Chen, J. Long, W. Zhong and Y. W. Li, ACS Catal., 2015, 5, 5264–5271; (f) J. Long, Y. Zhou and Y. W. Li, Chem. Commun., 2015, 51, 2331–2334.
- 24 (a) D. Zhao, J.-L. Shui, L. R. Grabstanowicz, C. Chen, S. M. Commet, T. Xu, J. Lu and D.-J. Liu, *Adv. Mater.*, 2014,

**26**, 1093–1097; (*b*) P. Gai, H. Zhang, Y. Zhang, W. Liu, G. Zhu, X. Zhang and J. Chen, *J. Mater. Chem. B*, 2013, **1**, 2742–2749; (*c*) B. Liu, H. Shioyama, H. Jiang, X. Zhang and Q. Xu, *Carbon*, 2010, **48**, 456–463; (*d*) K. J. Lee, T.-H. Kim, T. K. Kim, J. H. Lee, H.-K. Song and H. R. Moon, *J. Mater. Chem. A*, 2014, **2**, 14393–14400; (*e*) E. Proietti, F. Jaouen, M. Lefevre, N. Larouche, J. Tian, J. Herranz and J.-P. Dodelet, *Nat. Commun.*, 2011, **2**, 416; (*f*) W. Xia, B. Qiu, D. G. Xia and R. Q. Zou, *Sci. Rep.*, 2013, **3**, 1935.

- 25 S. J. Yang, T. Kim, J. H. Im, Y. S. Kim, K. Lee, H. Jung and C. R. Park, *Chem. Mater.*, 2012, 24, 464–470.
- 26 N. L. Torad, Y. Li, S. Ishihara, K. Ariga, Y. Kamachi, H.-Y. Lian, H. Hamoudi, Y. Sakka, W. Chaikittisilp, K. C. W. Wu and Y. Yamauchi, *Chem. Lett.*, 2014, 43, 717–719.
- 27 Y.-X. Zhou, Y.-Z. Chen, L. Cao, J. Lu and H.-L. Jiang, Chem. Commun., 2015, 51, 8292–8295.
- 28 Z. Chang, D.-S. Zhang, T.-L. Hu and X.-H. Bu, *Cryst. Growth Des.*, 2011, 11, 2050–2053.

- 29 (a) O. M. Yaghi, H. Li and T. L. Groy, J. Am. Chem. Soc., 1996, 118, 9096–9101; (b) C. Livage, N. Guillou, J. Marrot and G. Férey, Chem. Mater., 2001, 13, 4387–4392.
- 30 R. V. Jagadeesh, H. Junge, M.-M. Pohl, J. Radnik, A. Brueckner and M. Beller, *J. Am. Chem. Soc.*, 2013, 135, 10776–10782.
- 31 R. Nie, J. Shi, W. Du, W. Ning, Z. Hou and F.-S. Xiao, J. Mater. Chem. A, 2013, 1, 9037–9045.
- 32 N. L. Torad, M. Hu, S. Ishihara, H. Sukegawa, A. A. Belik, M. Imura, K. Ariga, Y. Sakka and Y. Yamauchi, *Small*, 2014, 10, 2096–2107.
- 33 (a) M. C. Biesinger, B. P. Payne, A. P. Grosvenor, L. W. M. Lau, A. R. Gerson and R. S. C. Smart, *Appl. Surf. Sci.*, 2011, 257, 2717–2730; (b) G. H. Jaffari, H.-Y. Lin, C. Ni and S. I. Shah, *Mater. Sci. Eng.*, B, 2009, 164, 23–29.
- 34 G. Lv, L. Cui, Y. Wu, Y. Liu, T. Pu and X. He, *Phys. Chem. Chem. Phys.*, 2013, **15**, 13093–13100.