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## COMMUNICATION

## Selectivity-tunable Amines Aerobic Oxidation Catalysed by Metal-free N, O-doped Carbons

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Herein, we present a series of N, O-doped mesoporous carbons obtained at different pyrolysis temperature as the first metal-free catalysts successfully switches between imines and nitriles products for amines oxidation. Systematic characterizations and control experiments revealed that the C-O group on the surface could function as catalytic active site for nitriles synthesis and N-doping environment was essential.

Oxidative transformations of amines are an important subject in synthetic chemistry as it leads to a variety of N-containing products such as nitriles, imines and amides,<sup>1</sup> and their derivatives are among the most important and valuable building blocks for a variety of fine chemicals,<sup>2</sup> pharmaceuticals,<sup>3</sup> and as raw materials for engineering materials.<sup>4</sup> For aerobic oxidation of primary amines to nitriles, almost all previously reported homogeneous and heterogeneous catalytic systems employed transition metal-based catalysts.<sup>5</sup> Mizuno et al. have reported effective aerobic oxidation of various amines to the corresponding nitriles catalysed by Ru/Al<sub>2</sub>O<sub>3</sub>,<sup>5a</sup> followed by Ru(OH)<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub><sup>5b</sup> and Ru@POM-IL<sup>5c</sup> catalysts. Recently, Beller et al. have applied their developed Fe<sub>2</sub>O<sub>3</sub>(Co<sub>3</sub>O<sub>4</sub>)/NGR@C to allow for excellent functionalized and structurally diverse nitriles synthesis.<sup>5g, 5h</sup> Nevertheless, metal-free catalytic alternative for the aerobic oxidation of amines to nitriles still remains unknown, to the best of our knowledge, but great significance in fundamental and applied research due to sustainability and eco-friendliness.

In parallel, heteroatom-doped carbons are emerging as versatile metal-free carbocatalysts for aerobic oxidation, reduction and hydrogenation in its own right.<sup>6</sup> For example, N-doped graphene have been recently found to catalyse selective

oxidation of ethylbenzene<sup>7</sup> and epoxidation of trans-stilbene and styrene<sup>8</sup> owing to the more metal-like d band electronic structure of the ortho-carbon atom next to the doped N atom. Heteroatomic doping (such as N, O, B, P etc) to pure carbon can give rise to charge densities changes and structural distortions, and thereby fine-tune its electronic properties and surface physicochemical features, which in principle determine the catalytic performance. So far, few carbocatalysts have been explored in amines aerobic oxidation, but they often give the self-coupling products imines instead of nitriles (Table S1).<sup>9</sup> With 2 equiv. NaClO as oxidant, GO achieved major products benzylidene imines and minor nitriles.<sup>10</sup> More ideally, the selective synthesis of nitriles or imines enabled by handy catalysts design is very challenging and pursuing with molecular oxygen as environmentally benign and abundant oxidant.

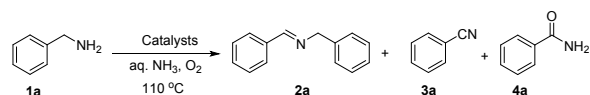
Inspired by "metal-actor" feature of heteroatom-doped carbocatalysts and our continuous interest in nitriles synthesis,<sup>11</sup> we began to explore metal-free catalytic aerobic oxidation of primary amines bearing that the starting materials are also readily available. Herein, surprisingly, we develop a carbocatalytic system furnishes switchable selectivity in aerobic oxidation of primary amines to nitrile or imines by varying precursor pyrolysis temperature, which is a facile and powerful means to tune heteroatom doping degree as well as configuration environment.

The used precursor bidppz ligand (11,11'-bis(dipyrido[3,2- $\alpha$ :2,3- $c'$ ]phenaziny)) was pyrolyzed at varied high temperature (600-900 °C) under nitrogen atmosphere and suffered subsequent NaOH etch to achieve mesoporous N,O-doped carbons (denoted as m-NOC-x, x = 600, 700, 800, 900). To study their activity, benzylamine (**1a**) was employed as the model substrate. The reaction conditions were 60 mg catalyst, 0.5 mmol **1a**, 200  $\mu$ L aq. NH<sub>3</sub>, 2 bar O<sub>2</sub>, 110 °C. Blank experiment displayed that 5.1% N-benzylidene benzylamine (**2a**) and no benzonitrile (**3a**) was produced (Table 1, entry 1). Surprisingly, m-NOC-600 yielded 77.7% **2a**, however others achieved more and more **3a** at similar total conversion as the pyrolysis

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**Table 1** Aerobic oxidation of benzylamine catalysed by different carbocatalysts<sup>a</sup>


Entry	Catalyst	T (h)	Conv. (%)	Yield (%)		
				2a	3a	4a
1	-	16	34.8	5.1	-	2.8
2	m-NOC-600	4	95.3	<b>77.7</b>	<b>0.7</b>	<b>8.4</b>
3	m-NOC-700	4	99.0	<b>30.3</b>	<b>39.4</b>	<b>10.7</b>
4	m-NOC-800	4	96.5	<b>10.9</b>	<b>61.2</b>	<b>10.6</b>
5	m-NOC-900	4	96.8	<b>5.0</b>	<b>64.9</b>	<b>11.4</b>
6	NOC-900 <sup>b</sup>	16	48.6	39.2	5.6	3.8
7	m-NOC-800	16	99.4	0	83.6	13.7
8	m-NOC-900	16	99.5	0	76.3	14.3
9	m-NOC-800 <sup>c</sup>	16	23.2	23.2	0	0
10	m-NOC-H <sub>2</sub>	4	99.3	16.7	35.3	13.6
11	m-OC <sup>d</sup>	16	92.9	36.3	0.5	7.9
12	m-NOC-NaBH <sub>4</sub>	16	99.5	0	74.2	12.8

<sup>a</sup> Reaction condition: 60mg catalyst, 0.5mmol **1a**, 200μL aq. NH<sub>3</sub>, 2 bar O<sub>2</sub>, 110 °C, naphthalene as internal standard. benzaldehyde (<4.6%) as the by-product. <sup>b</sup> without any templates. <sup>c</sup> N<sub>2</sub>. <sup>d</sup> 20.6 % benzaldehyde.

temperature increased from 700 to 900 °C, the yield 39.4%, 61.2% and 64.9%, respectively (Table 1, entries 2-5). Such a selectivity-tunable results aroused our great interest, which will offer convenience to identify specific active site, and further guide catalysts design. Subsequently, the polypyridine ligand was directly pyrolyzed at 900 °C and the obtained NOC-900 gave 48.6% **1a** conversion and 39.2% **2a** yield (Table 1, entry 6), indicating the indispensability of mesoporous structure and thus exposed active sites. By prolonged reaction time to 16h, m-NOC-800 and -900 gained 83.8% and 76.3% **3a** yield, respectively (Table 1, entries 7-8). In the reusability test, 75.4-85.6% **3a** were obtained during nine tests, which demonstrated the excellent thermal and chemical stability of m-NOC-800 catalyst (Fig. S1). Once it was performed under nitrogen, the reaction delivered only 23.2% **2a** yield and no **3a** (Table 1, entry 9), ensuring that O<sub>2</sub> as oxidant was essential for the reaction.

To unveil the underlying factors of the catalytic selectivity preference among the m-NOC-x samples, a series of techniques were performed to make a detail comparison so as to identify specific active site. In general, catalysts of high surface area and porous structure are very beneficial for catalysis because of sufficient exposure of active sites. Thus, all the samples were first investigated by the N<sub>2</sub> adsorption-desorption method (Table S2 and Fig. S2). In comparison with NOC-900 obtained by direct pyrolysis without any hard-templates, m-NOC-800 exhibited a typical type-IV isotherms with a distinct hysteresis loop (Fig. S2a), indicating mesoporous structure. The pore size distribution calculated by the Barrett-Joyner-Halenda (BJH) method showed a peak centred at around 12.2 nm owing to the parent SiO<sub>2</sub> nanoparticle (Fig. S2b). As shown by the analysis results in Table S2, m-NOC-600, -700, and -800 owned a similar high BET surface area (655.8, 656.1, and 689.3 m<sup>2</sup>·g<sup>-1</sup>), but differed distinctly on catalytic selectivity (Table 1, entries 2-4). However, of a higher 780.4 m<sup>2</sup>·g<sup>-1</sup> surface area, m-NOC-900

owned similar catalytic activity and selectivity to m-NOC-800. Meanwhile, all the m-NOC-x samples were of similar total pore volume for (Table S2), indicating that other factors dominated its catalytic behaviour. Subsequently, the morphology and microstructure of the samples were displayed by electron microscope.

Scanning electron microscope (SEM) viewed that m-NOC-600 and -800 presented similar irregular bulk morphology (Fig. S3). When further zoomed in, the both presented loosened coral-like structure whereas "sticks" staggered in NOC-900. Transmission electron microscope (TEM) further displayed clearly interconnected vesicle-like pore feature of both m-NOC-600 and -800 after thorough alkaline wash with pore sizes range from several to dozens of nanometre as shown in Fig. 1a, 1b, and S4, which was consistent with N<sub>2</sub> adsorption-desorption analysis results. It seemed the microstructure did not make a difference. Elemental mapping images showed a highly uniform distribution of C, N and O on the surface of nanocarbons (Fig. 1c-1f). From the above analysis results that m-NOC-600 and -800 presented antipodal selectivity in spite of similar surface area, morphology and pores structure, inferences can be made that catalyst components may be the key factor.

To gain more details on dual N, O-doping affected the catalytic selectivity of as-prepared catalysts, the C1s, N1s and O1s X-ray photoemission spectroscopy (XPS) analysis were conducted for each m-NOC-x, respectively as shown in Fig. 2 with detail convolution data listed in Table S3. XPS results indicated that N 1s and O1s for all the m-NOC-x existed in the same configuration, but C 1s in m-NOC-600 differed distinctly from the others. As obtained by deconvoluting C 1s spectra, there were three photoelectron peaks for m-NOC-600, located

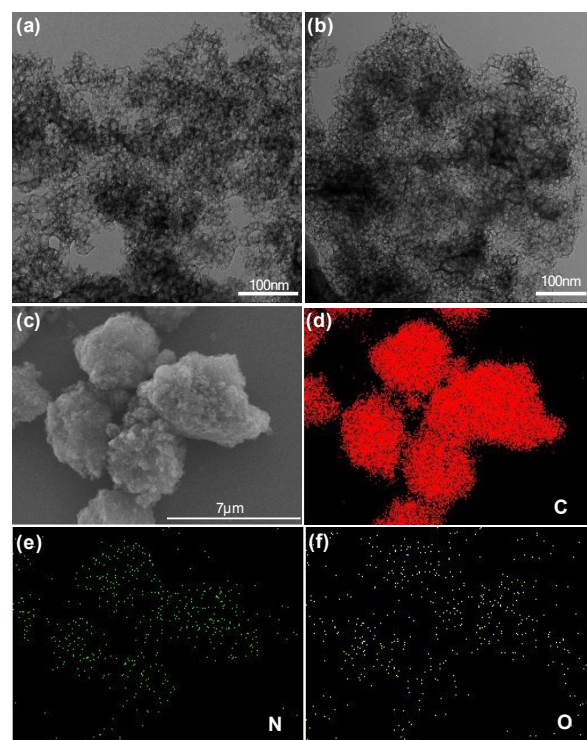


Fig. 1 (a, b) TEM of m-NOC-600 and -800. (c, d, e, f) Elemental mapping of m-NOC-800.

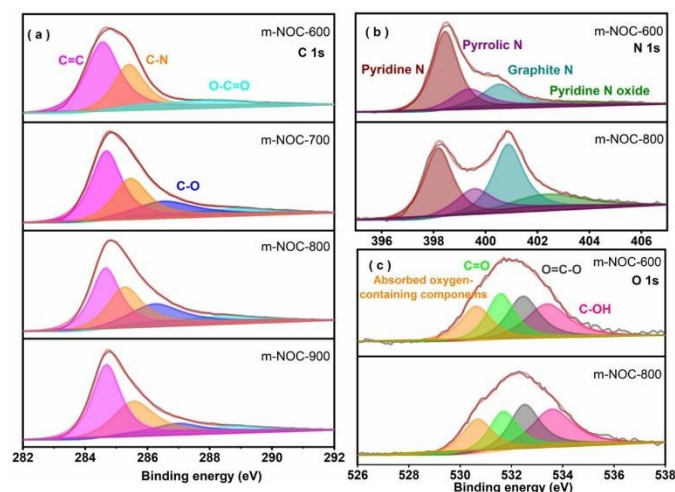


Fig. 2 (a) C 1s, (b) N 1s, (c) O 1s XPS spectra of m-NOC-x.

at around 284.6, 285.4, and 288.0 eV respectively, which are specified as C=C, C-N and O=C-O groups in Fig. 2a<sup>12</sup>. However, another peak positioned at 286.5 eV for others appeared at higher pyrolysis temperature, which is assigned to C-O group. As shown in Fig. 3, benzonitrile yield exhibited a positive dependence on the C-O content and no obvious correlation on any N and O configurations (Fig. S5). Although the C-O content in m-NOC-900 was lower, its comparative activity with m-NOC-800 may ascribe to the higher BET surface area, which can act as a supplementary to expose more active sites. It was conceivable to infer that the C-O group may be the active site for nitriles synthesis. The intensity ratio  $I_D/I_G$  in the Raman spectra, usually used to indicate the density of defects,<sup>13</sup> decreased slightly at higher temperatures (Fig. S6), which eliminated the possibility of defects as active site. The N 1s spectra displayed four peaks at 398.1, 399.6, 400.7 and 403.2 eV for all the m-NOC samples (Fig. 2b and S7a), which is in line with pyridinic N, pyrrolic N, graphitic N, and pyridinic N-oxide. Pyridinic N, pyrrolic N, graphitic N content decreased as increasing pyrolysis temperature with a concomitant decrease in total N content, but graphitic N percent increased, which was in accordance to Raman results.

To identify as-supposed active sites, hydrogen reduction was employed for further treatment of the mesoporous carbon material, denoted as m-NOC-H<sub>2</sub>.<sup>14</sup> With hydrogen reduction,

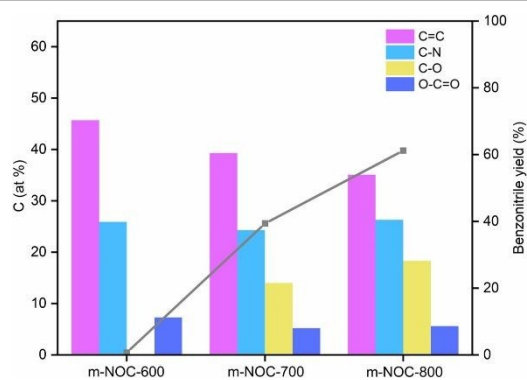


Fig. 3 The content of surface C 1s species and the benzonitrile yield over the m-NOC catalysts at different pyrolysis temperatures.

Table 2 C 1s of the m-NOC-800, m-NOC-H<sub>2</sub> and m-OC<sup>a</sup>

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m-NOC	Total C	C=C	C-N	C-O	O=C-O
800	85.3	35.1	26.3	18.3	5.6
-H <sub>2</sub>	85.4	39.9	24.3	16.4	4.8
m-OC	89.0	61.0	-	18.7	9.2

<sup>a</sup> Calculated by XPS convolution

C-O content was decreased from 18.3% to 16.4% (Table 2) displayed by C1s XPS comparison in Table S2 and thus, m-NOC-H<sub>2</sub> gave more imines (16.7% vs 10.9%) but less nitriles (35.3% vs 61.2%) than the fresh m-NOC-800 (Table 1, entry 4 vs 10), which further supported our hypothesis on C-O active sites. To make clear whether elemental N play an important role or not, control experiment with sole O-doped mesoporous carbon as catalyst was performed. The as-obtained m-OC-800 derived from sucrose delivered 36.3% N-benzylidene benzylamine, proving the essentiality of N dopants (Table 1, entry 11; Table 2). Thermogravimetric analysis demonstrated that mass loss occurred at around 550 °C (Fig. S8) and the active sites may begin to form after 600 °C, which was consistent with XPS results. Total O content increased from 4.8 to 5.6 for m-NOC-600 and -700, indicating that more O-containing components formed after 600 °C, in accordance with our hypothesis about active sites formation. The O 1s spectrum was deconvoluted into four components with binding energy peaks centered at 533.6, 532.5, 531.8 and 530.8 eV (Fig. 2c and S7b). The first three peaks are specified as C-OH, O=C-O and C=O groups, respectively.<sup>15</sup> The remaining peak at 530.8 eV corresponds to the absorbed oxygen-containing components (for example, CO<sub>2</sub>, H<sub>2</sub>O, et al.). Noteworthy, the carboxylic acid groups in graphene oxide were well regarded as the active site in oxidation.<sup>16</sup> In order to evaluate the possible effects of these carboxylic acid groups, after suffered from NaOH, the m-NOC-800 was further treated with NaBH<sub>4</sub>. However, we did not observe any appreciable change in both activity and selectivity compared with the fresh m-NOC-800 (Table 1, entry 12).

To make clear the nature of selectivity preference, real-time monitoring of the reaction procedure catalysed by m-NOC-600 and -800 was conducted and the results were shown in Fig. 3. m-NOC-600 could catalyze **1a** to transform smoothly to **2a** giving up to 85.8% yield at 5.3h (Fig. 4a) and even after 16h, only 6.5% **3a** was obtained (Scheme S1a). Distinctly differently, when it came to m-NOC-800, there appears a crest that once **2a** was formed, it immediately converted to the desired product **3a** (Fig. 4b), indicating that **2a** was the possible reactive intermediates

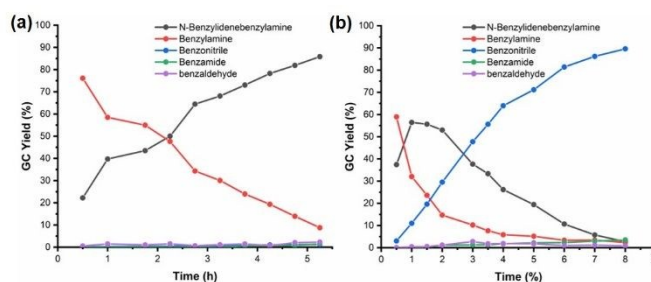


Fig. 4 Reaction time course of the selective aerobic oxidation of benzylamine over (a) m-NOC-600 and (b) m-NOC-800. (c) imine as substrate catalysed by m-NOC-800.



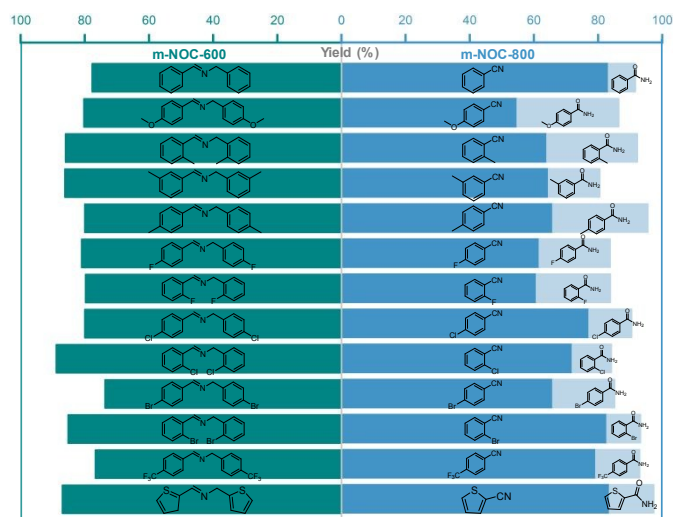


Fig. 5 Imines and nitriles synthesis over m-NOC-600 and m-NOC-800. Reaction conditions: 0.5 mmol benzylamine, 60mg catalyst, 2 bar O<sub>2</sub>.

and Scheme S2 displayed possible reaction pathway. The reaction course with **2a** used as substrate in Fig. S9 further confirmed **2a** intermediates and finally, 89.1% yield of **3a** was obtained under the standard conditions (Scheme S1b).

Fig. 5 showed data for aerobic oxidation of various substituted benzylamines (see Table S2 and S3 for detailed data) on m-NOC-600 and m-NOC-800 catalysts, respectively. In the presence of m-NOC-600 catalyst, it was highly selective for the imines, whereas it swung to the corresponding nitriles with amides as another aldehyde ammoxidation product over m-NOC-800 catalyst. In detail, benzylamine derivatives bearing electron-donating groups gave the corresponding nitriles in moderate to high yields as well as those bearing electron-withdrawing groups. Even for heterocyclic aromatic amines such as thiophen-3-ylmethanamine, m-NOC-600 and m-NOC-800 successfully achieved 87% imines and 83.3% nitriles separately. Unfortunately, aliphatic amines such as octylamine could not be converted accordingly.

In summary, we have succeeded in employing a N, O-doped mesoporous carbon as the first efficient metal-free catalyst for the aerobic selective oxidation of primary amines to nitriles under molecular oxygen. Beyond that, the m-NOC at 600 °C and 800 °C can achieve successfully the switch between imine and nitrile products. The transformation of imine intermediate to nitriles stems from the C-O group with neighbouring N environment on the surface. More attempts to explore the application of carbocatalysts in synthetic transformation is on the way, broadening the field of metal-free catalysis.

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## Conflicts of interest

There are no conflicts to declare.

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