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Bicontinuous mesoporous Co, N co-doped carbon catalysts with high catalytic performance for ethylbenzene oxidation[†]

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A series of bicontinuous mesoporous Co, N co-doped carbon catalysts (Co–N–C), which have large pore sizes and high specific surface areas with remarkable catalytic activity, were prepared through a method using KIT-6 silica as a hard template, and cobalt porphyrin and sucrose as precursors. And morphological and structural characterizations were performed using N₂ adsorption–desorption isotherm, XRD, Raman, TEM and XPS techniques. The results showed that the ethylbenzene oxidation with TBHP as an oxidant over the bicontinuous mesoporous Co, N co-doped carbon catalysts achieved 93% of ethylbenzene conversion with about 99% of selectivity to acetophenone. The superior catalytic performance of the catalysts was attributed to the synergistic effect of factors such as high surface area and well-dispersed metal active sites.

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1. Introduction

Recently, diverse types of carbon-based materials have been actively pursued due to their sustainability and remarkable physiochemical properties, such as ultrahigh surface areas, large pore volumes and tunable pore sizes.¹ Common strategies used for the synthesis of ordered mesoporous carbon are the hard-templating method and the soft-templating method. The hard-templating method usually employs mesoporous silica as a template and carbon materials with controllable structure and good shape can be obtained through a simple acid/base etching process.² Nanoporous silica materials (KIT-6) with three-dimensional (3D) ordered porous structures are widely used as hard templates. Hereafter, the mesoporous carbon materials derived from KIT-6 by a hard-template method have received great attention in recent years due to their advantages of easy mass transfer and avoiding the pore blockage, compared to materials with one-dimensional or layered nanostructures.³

Previous research studies have shown that the incorporation of heteroatoms (B, N, P, and S) into many carbon materials can enhance their catalytic activity by modulating the physicochemical properties.⁴ Among the doping atoms, nitrogen (N) has been used most frequently so far due to the fact that N-doping will enhance π -bonding networks in carbon materials, improving electron

donor ability, and increasing active sites.⁵ Additionally, the use of doped metal nanoparticles, such as Pt, Pd, Rh, Ru and Au, emerges as an innovative tool in catalysis.⁶ Similar to molecularly-defined complexes, the activity and selectivity of such nanoparticles can be fine-tuned by means of their chemical surrounding. It has been shown that carbonizing organometallic complexes enables strong metal-support interactions, thereby influencing the electron density and the steric environment of the active sites.⁷ Metalloporphyrins, with a unique carbon-rich macrocycle and inherent metal-nitrogen coordination, especially transition metalloporphyrins (Co, Fe, and Mn), are attractive precursors for synthesis of M-N-C catalysts.8 Following this concept, earth-abundant-metal porphyrins embedded in nitrogendoped carbon materials have been employed in catalytic reactions.9 Recently, Wu Li et al. have manufactured catalysts for highly selective hydrogenation of nitroarenes with Co nanoparticles supported on ordered mesoporous carbon CMK-3.10

Herein, as illustrated in Scheme 1, we prepared a series of Co/N co-doped ordered mesoporous carbon catalysts (Co–N–C), which have large specific surface areas, well-dispersed metal active sites and high catalytic activity. Briefly, KIT-6 silica, cobalt porphyrin and sucrose were employed as a structural model, a metal precursor and a carbon source, respectively. Metalloporphyrins contain alternating N-containing ligands and Co ions, which could efficiently control the dispersion of active sites at the atomic level.¹¹ The selective oxidation of ethylbenzene under mild conditions with TBHP as an oxidant was carried out to investigate the catalytic performance of the as-prepared catalysts. And a series of morphological and structural characterizations were performed using N₂ adsorption–desorption isotherm, XRD, Raman, TEM and XPS techniques.



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[†] Electronic supplementary information (ESI) available: Experimental details, graphics (Fig. S1–S4) and tables (Tables S1–S3). See DOI: 10.1039/c9nj00453j



Scheme 1 Schematic illustration of the synthesis process of the representative Co-N-C-X catalysts and the catalytic reaction for ethylbenzene.

2. Experimental section

2.1. Catalyst preparation

2.1.1 Synthesis of Co-N-C-X catalysts. KIT-6, sucrose and cobalt porphyrin (CoTPP) were used to synthesize Co-N-C-X catalysts, which acted as a template, a carbon source and a metal precursor, respectively. Briefly, 0.58 g of sucrose was dissolved in 2.4 g of H₂O containing 0.07 g of H₂SO₄, and then, 0.06 g of CoTPP and 0.6 g of KIT-6 were added successively into the solution to form a transparent mixture. Subsequently, the mixture was transferred to a drying oven at 100 °C for 6 h and 160 °C for 6 h. After cooling to room temperature, 1.9 g of H_2O , 0.035 g of H₂SO₄, 0.31 g of sucrose and 0.03 g of CoTPP were added. After this, the autoclave was heated again at 100 °C and 160 °C for 6 h respectively. Carbonization was completed in a quartz boat at a temperature up to 900 °C under a N2 atmosphere for 4 h. The products were finally obtained by etching the silica templates in 3 M NaOH solution for 4 h, and this process was repeated 3 times. The catalysts were obtained after being filtered, washed and dried at 100 °C overnight under vacuum, namely Co-N-C-10 (0.1:1). A series of controllable Co-N-C-X catalysts were prepared by controlling the mass ratio of CoTPP/sucrose of 0.02:1, 0.05:1, 0.15:1, and 0.2:1, marked as Co-N-C-2, Co-N-C-5, Co-N-C-15, and Co-N-C-20, respectively. For comparison, CoCl₂·6H₂O and tetraphenylporphine as metal or nitrogen precursors were supported on KIT-6 following similar processes as the above mentioned impregnation method, and the final samples were assigned as Co-C and N-C, respectively.

2.1.2 Synthesis of Co–N/C. Briefly, 0.58 g of sucrose was dissolved in 2.4 g of H_2O containing 0.07 g of H_2SO_4 , and then 0.6 g of KIT-6 was added into the solution to form a transparent mixture. Subsequently, hydrothermal, calcination and etching processes the same as above were followed. The template-free carbon product was obtained after being filtered, washed and dried at 100 °C overnight in a vacuum, namely C. Co–N/C catalysts were prepared through an impregnation method, and the typical process is as follows: 0.6 g of C was added

before CoTPP (60 mg) was dissolved in CH_2Cl_2 (10 mL), and then, refluxed at 40 °C for 24 h with constant magnetic stirring. After removing the solvent, the samples were transferred into a quartz boat, and then heated to 900 °C at a rate of 5 °C per minute and kept for 4 h under N₂. The product was denoted as Co–N/C.

2.2. Catalyst characterization

Using a NOVA 1000e from Quantachrome Instruments, N₂ adsorption-desorption analysis of the samples were outgassed at 200 °C for 3 h was conducted at 77 K and a relative pressure range of 0.05 to 0.98. The specific surface areas were calculated using the BET method. The pore size distribution plot was recorded from the desorption branch of the isotherm based on the DFT model. The surface morphology of the samples was investigated and high angle annular dark field scanning TEM images (HAADF-STEM) were obtained using an FEI Talos F200x with an image corrector operating at 300 kV. X-ray powder diffraction (XRD) was performed using a Japan XRD-6100 analyser with Ni-filtered Cu Ka radiation (50 kV, 10 mA). Raman spectroscopy was performed using a Mono Vista 2560 Spectrometer with a laser at 532 nm (2.33 eV). X-ray photoelectron spectra (XPS) measurements were obtained using an Escalab 520Xi system and Al Ka radiation (1486.6 eV).

2.3. Catalyst activity

In an oven-dried reaction tube with 15 mg catalyst, 3 mL H₂O, ethylbenzene (122 μ L, 1 mmol) and TBHP (490 μ L, 3.5 mmol) were added successively. After heating to 80 °C, the mixture was stirred for another 6 h. When the mixture was cooled down to ambient temperature, ethyl acetate and *n*-dodecane were added as an extraction agent and an internal agent, respectively. The organic layer was extracted and analysed by gas chromatography (Shimadzu GC-2014 equipped with a capillary column (RTX-5)). Catalyst recovery experiments were carried out under the same conditions; the Co–N–C-10 catalyst was extracted from the mixture using ethyl acetate after the reaction, centrifuged and washed with alcohol, and then dried at 80 °C in a baking oven overnight before being used again.

3. Results and discussion

3.1. BET

The porous texture was characterized by N₂ adsorptiondesorption measurements. Fig. 1A and B show the resulting isotherms and the pore size distribution of Co–N–C-*X* and KIT-6. The isotherm of KIT-6 was type IV with an H4 hysteresis loop in $P/P_0 = 0.5-0.8$, from which the specific surface area is estimated to be 880 m² g⁻¹ (Fig. 1A). And the pore diameter of KIT-6 derived from the desorption branch of the isotherm is calculated using the DFT mode and it is hierarchically mesoporous with a pore size distribution of 5–6 nm(Fig. 1B). All Co–N–C-*X* samples were different from KIT-6 which showed a typical type IV curve according to the IUPAC nomenclature, indicating the presence of micropores and mesopores with a narrow pore size



Fig. 1 (A) Nitrogen adsorption-desorption isotherms at 77 K, and (B) the corresponding DFT mesopore size distribution curves of KIT-6, and Co-N-C-X.

distribution.¹² The reported microporous materials showed that micropores have no facilitation effects on diffusion and mass transfer due to their small pore sizes. But the mesopores could improve the performance very well.¹³ Therefore, the mesoporous structure had an overwhelming effect on the excellent performance of the mesoporous catalyst. This could be attributed to the fact that the mesoporous structure allowed the reactants to easily enter the active part, which improved the performance of the mass transport. The porous properties of the samples are summarized in Table 1. The specific surface area, average pore sizes and pore volume first increased with the increase in mass ratio of CoTPP/sucrose from 0.02:1 to 0.1:1, and then declined with a further increase in mass ratio from 0.1:1 to 0.3:1. CoTPP served not only as metal and nitrogen precursors, but also as partial carbon sources. When the content of CoTPP was low, the pores of KIT-6 were not fully filled. In contrast, when the content was high, the pores were blocked. Co--N--C-10 exhibited higher values of 423 m²/ g⁻¹, 0.81 cm³/ g^{-1} and 5.78 nm for the specific surface area, pore volume and average pore size (Table S1, ESI[†]), respectively. So the Co-N-C-2, Co-N-C-5, Co-N-C-15 and Co-N-C-20 samples had a lower specific surface area, a smaller pore volume, and a narrower pore size, which might lead to reaction defects entering into the hole of these catalysts and disable contacts with the active site. The specific surface area and average pore size of Co-N/C was 481 m² g⁻¹ and 4.70 nm, respectively (Table S1, ESI[†]). Typically, Co-N-C-10 catalysts with a higher surface area and a uniform distribution of pore size could provide more active sites and be more efficient for diffusion of substrates. It was worth noting that the Co-N/C had a higher specific

Table 1 The results of N₂ adsorption-desorption measurements

Sample	D _p (nm)	$S_{\rm BET} \left({ m m}^2 { m g}^{-1} ight)$			$V_{\rm p}~({\rm cm}^3~{\rm g}^{-1})$		
		$S_{\rm total}$	$S_{ m micro}$	S _{meso}	V _{total}	V _{micro}	V _{meso}
KIT-6	4.95	880	143	737	1.09	0.09	1.00
Co-N-C-2	4.85	629	253	376	0.76	0.15	0.61
Co-N-C-5	4.93	765	347	418	0.96	0.18	0.78
Co-N-C-10	5.78	645	222	423	0.93	0.12	0.81
Co-N-C-15	5.52	581	212	369	0.80	0.12	0.68
Co-N-C-20	5.14	458	188	270	0.59	0.11	0.48

 S_{BET} : BET surface area; S_{total} : BET surface area; S_{micro} : micropore surface area; S_{meso} : mesopore surface area; $S_{\text{meso}} = S_{\text{total}} - S_{\text{micro}}$; V_p : pore volume; V_{total} : total pore volume; V_{micro} : micropore volume; V_{meso} : mesopore volume; $V_{\text{meso}} = V_{\text{total}} - V_{\text{micro}}$; D_p : average pore diameter.

surface area, a larger pore volume and an average pore size than any other samples, which could provide more opportunities for the substrates to participate in the reaction.

3.2. TEM

The morphologies and structures of the KIT-6 and the carbon materials were studied by TEM. A typical regular threedimensional (3D) ordered porous structure about 5 nm could be observed in KIT-6 (Fig. S1A and B, ESI[†]). Significantly, there was a very big change in the morphological features of KIT-6, which was clearly observed in Co-N-C-10 (Fig. 2A-C). However, we hardly observed any metal-containing nanoparticles in the high resolution transmission electron microscopy (HRTEM) image because the leaching process removed most of the unstable cobalt particles and a small amount of cobalt species might be incorporated into the carbon framework in disordered forms (Fig. 2D). Meanwhile, from the HAADF-STEM images and the corresponding elemental maps of Co-N-C-10, it can be seen that the Co species were mostly bound to O species uniformly covering the entire carbon materials (Fig. 2E and F), which demonstrated that the cobalt species were uniformly bound with O and N within the carbon materials. However, there were large amounts of Co species deposited and well-distinguished pores as revealed by the TEM analysis of different regions within Co-N/C (Fig. 2G-I), indicating that the Co of Co-N/C was not evenly distributed as in Co-N-C-10. In addition, Co-C was similar to Co-N/C (Fig. S2C and D, ESI†), which suggested that the use of CoTPP contributed to the dispersibility of Co species.

3.3. XRD and Raman spectroscopy

Fig. 3A shows the XRD diffraction patterns of the as-prepared samples. All samples showed two broad peaks located at



Fig. 2 (A–D) TEM analysis of different regions within Co–N–C-10, (E and F) HAADF-STEM and the corresponding elemental maps of the Co–N–C-10 catalyst, (G–I) TEM analysis of different regions within Co–N/C.



 24.7° and 43.4° , which could be assigned to the (002) and (101) diffraction peaks of graphitic carbon, respectively.¹⁴ The XRD pattern of the Co-N-C-10 composite showed weak peaks at around 39.5°, which were in good agreement with JCPDS card 43-1300 (Fig. 3A), implying the presence of CoO in the Co-N-C-10 composite. No other detectable peaks appeared in the XRD pattern of Co-N-C-10, which could be due to the cobalt atoms being incorporated into the carbon framework in disordered forms, which was consistent with the TEM image. However, with the increasing amount of CoTPP, the peaks matched Co₃O₄, CoO and some remaining cobalt metals, indicating partial oxidization of the metallic cobalt in Co-N-C-15 and Co-N-C-20. The results suggested that there was a deposit of cobalt particles in these composites. The same conclusion applied to Co-C (Fig. S3, ESI⁺). The pattern of Co-N/C showed a good matching with the metal cobalt peaks, which again proves the deposit of cobalt metal in the TEM image (Fig. S3, ESI⁺).¹⁵ This result was in good agreement with the TEM observations (Fig. 2G-I).

Raman spectra have been widely used to investigate the degree of graphitization and defect of catalysts.¹⁶ Fig. 3B shows the Raman spectra of Co–N–C-X. All of them showed a similar pattern with a D band at 1330 cm⁻¹ (related to the defects) and a G band at 1590 cm⁻¹ (related to the crystalline graphite).¹⁷ The values of the I_D/I_G ratio, reflecting the defect and disorder level in the graphitic carbon layers, for Co–N–C-5, Co–N–C-10, Co–N–C-15 and Co–N–C-20 were 1.03, 1.07, 1.03 and 1.02, respectively. A higher I_D/I_G value for Co–N–C-10 was due to the incorporation of heterogeneous atoms into the matrix.¹⁸

3.4. XPS

The surface compositions and chemical states of Co–N–C-10 were further determined by X-ray photoelectron spectroscopy (XPS). As shown in Fig. 4A, a set of peaks corresponding to C 1s (284.8 eV), N 1s (401.0 eV), O 1s (531.6 eV) and Co 2p (780.0 eV) were observed.¹⁹ The ratio of C, O, N and Co was 79.24%, 18.80%, 1.52% and 0.44%, respectively (Table S2, ESI†). The peaks of the C 1s spectrum showed the following types of C species: C—C, C–N, C–O, and C—O, indicating the existence of carbon atoms connected to N and O heteroatoms (Fig. 4B). The corresponding N 1s XPS spectra could be well-fitted with four peaks at \approx 398.5, 400.5, and 401.3 eV, assigned to pyridinic, pyrrolic and graphitic N species, respectively (Fig. 4C).²⁰ The peak at a binding energy of 398.5 eV could be attributed to pyridinic N, which should also include the contribution from nitrogen bound to the metal (M–N), due to the small difference



Fig. 4 XPS spectra of the as-prepared catalysts. (A) Survey, (B) C 1s, (C) N 1s, (D) Co 2p spectra of Co–N–C-10 and Co–N/C.

between the binding energies of M-N and pyridinic N.21 Notably, the pyridinic and pyrrolic N sites were the most and second most abundant ones, which were highly demanded because they could provide strong N coordination and act as good anchoring sites for deposition and stabilization of Co.²² At the same time, there were relatively lower contents of pyridinic N in the Co-N/C (Table S2, ESI⁺). Moreover, some previous studies have reported that a larger amount of pyridinic species bound to cobalt was considered indispensable for the high catalytic performance.²³ For the Co 2p XPS data, the signals were relatively weak because most Co species were located inside the N-doped carbon matrix. The Co 2p_{3/2} high-resolution spectra were fitted with three components corresponding to metal Co (778.5 eV), Co-O (780.0 eV) and Co-N (781.7 eV) (Fig. 4D).²⁴ The ratio of Co, Co-O and Co-N was 6.9%, 40.6% and 52.5%, respectively (Table S2, ESI⁺). The dominant existence of Co-O and Co-N in the XPS analysis indicated that the Co of the Co-N-C-10 composite was partly oxidized and partly combined with N species. XPS analysis reflected that the N sites can act as coordination and anchoring sites for Co of the Co-N-C-10 catalyst, which agrees well with the results of XRD, TEM and STEM-HAADF.

3.5. Catalyst performance

In order to identify the performance of catalysts, we conducted experiments at 80 °C using TBHP as the oxidant and water as the solvent. It was found that the blank experiment gave a very low yield under the reaction conditions (Table 2, entry 1). To our delight, the desired acetophenone was obtained in 93% yield at full conversion with the Co–N–C-10 catalyst (Table 2, entry 4). Other samples with different contents of CoTPP exhibited a lower conversion than Co–N–C-10 (Table 2, entries 2, 3, 5 and 6), because the lower specific surface area, the smaller pore volume, and the narrower pore radius might lead to reaction defects entering into the mesopores of these catalysts and disable contacts with the active site. Meanwhile, compared with Co–N–C-10, the Co–N/C was found to exhibit

Table 2 Results of different catalysts for the oxidation of ethylbenzene

Entry	Catalyst	Conv./%	Yield(Sel.)/%	
1	_	<5		
2	Co-N-C-2	82	77(94)	
3	Co-N-C-5	87	84(97)	
4	Co-N-C-10	93	93(100)	
5	Co-N-C-15	91	90(99)	
6	Co-N-C-20	89	88(99)	
7	Co-N/C	78	75(96)	
8	Co-C	55	42(77)	
9	N-C	52	40(76)	
10	С	45	33(73)	

Reaction conditions: substrate (1.0 mmol), TBHP (3.5 mmol, 75 wt% in water), catalyst (0.015 g), H_2O (3.0 mL), 353 K, 6 h; the conversion and yield were determined by GC.

a relatively lower conversion and yield (Table 2, entry 7). The XRD and TEM images showed that there was aggregation of cobalt species in the preparation process which resulted in reactive Co not being well exposed and not being in good contact with the reactants like Co-N-C-10. Thereafter the key factors of the catalytic effect were not only specific area, pore volume and average pore size, but also the dispersion of Co species. In order to verify the unique catalytic performance, a series of control experiments were conducted to show that the high activity for selective oxidation of ethylbenzene took place only in the presence of Co and N. As shown in Table 2 (entries 8-10), the catalysts N-C, Co-C and C only afforded ethylbenzene conversion of 55%, 52%, and 45%, respectively. The catalytic effect of catalysts Co-C and N-C was higher than that of C, so both cobalt and nitrogen could improve the catalytic activity. However, since Co and N existed together in the catalyst Co-N-C-10, its catalytic performance was much higher than that of Co-C and N-C. Hence, the presence of Co-N could improve the catalytic activity more significantly, which confirmed that the Co-N sites also played a vital role in providing the conversion and selectivity for ethylbenzene oxidation under the investigated conditions.²⁵ In an earlier report, it has been proven that Co-N sites were typically responsible for the high catalytic activity in ethylbenzene oxidation.⁹ Hence, there existed a synergistic effect of three factors affected the catalytic activity of the catalyst.

Here, the stability and reusability of the Co–N–C-10 catalyst were studied for the application of selective oxidation of ethylbenzene catalysts. As depicted in Fig. 5A, after five successive cycles the conversion obtained was 89%. It could be seen that the activity was well-retained after five consecutive circles, demonstrating its excellent stability. Interestingly, as shown in Table S1 (ESI[†]), after the Co–N–C-10 was reused 5 times, the specific surface area and pore volume both decreased, while the pore diameter increased, about 347 m² g⁻¹, 0.75 cm³ g⁻¹ and 8.66 nm, respectively. The reason for this phenomenon could be that there were collapse and blocking of micropores partly. From the TEM images (Fig. S4, ESI[†]) and the XPS analysis (Table S2, ESI[†]) of the recycled catalyst, there existed partial collapse and blocking of pore and partial leaching of cobalt. Furthermore, from the analysis of XPS, the contents of



Fig. 5 (A) The results of Co–N–C-10 recycling experiments, (B) N₂ adsorption–desorption isotherm plot of Co–N–C-10-R. The inset on top left: BJH pore size distribution of Co–N–C-10-R, (C and D) XRD patterns and Raman spectra analysis of the reused catalyst, (E and F) high-resolution XPS spectra of the reused Co–N–C-10-R catalyst.

pyridinic N and Co-N changed from 1.52% to 0.94% and 52.9% to 39.0%, respectively, which were lower than those of the fresh ones. And then the content of Co-N decreased. So the activity of the used catalyst showed a little change after several recycling. The results further illustrated that the structure was well maintained and the stable Co-N species were indispensable in the reaction. The embedment of the active sites as well as the bicontinuous structure of carbon materials provided a stabilizing effect during catalysis and therefore preserves the nanoparticles from further agglomeration, leaching and subsequent deactivation. Using Co-N-C-10 as the catalyst, we further investigated the oxidation of a wide range of substituted arylalkanes with TBHP. A good yield was observed for other arylalkanes such as isopropylbenzene, tetrahydronaphthalene, diphenylmethane, indan and fluorine (Table S3, entries 1-9, ESI[†]), and a moderate yield in the oxidation of toluene to benzoic acid (Table S3, entry 10, ESI[†]), indicating that the catalyst showed general applicability for the selective oxidation of arylalkanes to ketones.

4. Conclusion

To sum up, we prepared a highly active Co, N co-doped carbon catalyst *via* structuring of sucrose and cobalt porphyrin upon impregnation into KIT-6 and then removing the template by etching with NaOH. The results revealed that the desired

catalysts possessed high surface area and well-dispersed metal active sites. Compared to the two-step method, Co–N/C catalysts supported on mesoporous carbon, hard-templating enabled the synthesis of well-structured Co–N–C-10 catalysts significantly enhancing the activity due to improved dispersibility of the Co–N active sites. The mass ratio of sucrose to CoTPP influenced the resulting catalyst performance significantly. In this respect, the ratio of sucrose to CoTPP is 1:0.1 the best result, which was attributed to the large mesopores derived from improved KIT-6 replication and high surface areas, thus facilitating the dispersibility of the active sites within the catalyst. Applying the optimal Co–N–C-10 catalyst, a wide range of arylalkane compounds were oxidized to the corresponding ketone in excellent yields. This strategy could be extended to immobilize other metal or metal composite active sites into mesoporous silica structures.

Conflicts of interest

There are no conflicts to declare.

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