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# Controllable sulfur, nitrogen co-doped porous carbon for ethylbenzene oxidation: the role of nano-CaCO<sub>3</sub>

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**Abstract:** Heteroatom doped porous carbon materials have exhibited promising applications in various fields. In this work, sulfur, nitrogen co-doped carbon materials (SNCs) with abundant pore structure were prepared by pyrolysis of sulfur, nitrogen-containing porous organic polymers (POPs) mixed with nano-CaCO<sub>3</sub> at high temperature. Among the resultant materials, SNC-Ca-850 possesses a relatively high level of doped heteroatoms and exhibits an excellent catalytic performance for the selective oxidation of benzylic C-H bonds. It is noteworthy that nano-CaCO<sub>3</sub> elevates the doped sulfur content in the synthesized carbon materials to a large extent, and has impact on the existence modes of sulfur. Besides, it enhances the porous structure and specific surface area of resultant SNCs significantly. This work provides a viable strategy to promote the doping of sulfur into carbon materials during pyrolysis process.

#### Introduction

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Owing to the large surface area, abundant pore structure, rich functional sites, as well as excellent thermal and chemical stability, hetero-doped mesoporous carbon materials exhibit promising value as gas adsorbents, supercapacitors and catalysts.<sup>[1]</sup> Among the common hetero elements, N-doped carbons have received extensive study since nitrogen atom has a similar radius with carbon and is easy to be embedded into graphitic lattice. As prior studies reported, the doping of nitrogen is conducive to modifying the electrochemical properties of carbon materials, thus improving their capability in catalysis.<sup>[2]</sup> Recent studies showed the performance of N-doped carbons could be further elevated with secondary doping elements (e.g. boron,<sup>[3]</sup> sulfur,<sup>[4]</sup> or phosphorus<sup>[5]</sup>). For example, the doping of sulfur presents a marked impact on the distribution of charge density and spin density of local carbon atoms, which are highly related to the catalytic activity. Apart from the electronic nature, sulfur atoms are apt to protrude out from the plane of adjacent sp<sup>2</sup> carbon and induce more defects into the skeleton, endowing

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these materials with enhanced specific surface area and active sites, hence, promoting their efficiency in catalysis.<sup>[6]</sup>

Pyrolysis of S-containing precursors under thermal conditions is a practical strategy to produce S-doped carbon materials. Various sulfur sources, like thiourea,[7] elemental sulfur,[8] and potassium thiocyanate,<sup>[9]</sup> as well as resins assembled with S-rich monomers,<sup>[10]</sup> have been employed to the synthesis of S-doped carbon materials. Generally, these S-containing components decompose and release volatile sulfur species (e.g. hydrogen sulfide, sulfur dioxide and elemental sulfur) during pyrolysis, and the generated volatile molecules then interact with carbon at high temperature to form C-S bond, thus realizing the doping of sulfur.<sup>[11]</sup> Nonetheless, only a small fraction of sulfur from precursors could be incorporated to the resultant materials. On the one hand, the low atom utilization ratio of sulfur leads to unnecessary waste; on the other hand, it may cause severe atmospheric contamination.<sup>[12]</sup> Additionally, the formation of C-S bond usually needs high temperature, however, such high temperature may lead to the removal of nitrogen.<sup>[5,13]</sup> Thus, it is particularly important to promote the exploitation of sulfur in the preparation of S, N co-doped materials, making it feasible to achieve a reasonable doping level of sulfur at a relative low temperature, hence, keeping the deprivation of nitrogen within an acceptable degree.

Overall, further research is still in demand on developing a convenient and effective strategy to promote sulfur utilization during pyrolysis. Apart from compounds giving off volatile sulfur at high temperature, thermostable S-containing substitutes, like metal sulfide and sulfate, are also competent as sulfur sources, which provide the opportunity to suppress the loss of volatile sulfur components during pyrolysis.[13a, 14] Limestone, of which the major component is CaCO<sub>3</sub>, has been extensively applied in gas desulfurization.<sup>[15]</sup> As it is capable of capturing acidic sulfur species (H<sub>2</sub>S, SO<sub>2</sub>) to form corresponding sulfide and sulfate (CaS, CaSO<sub>4</sub>), the in situ generated S-containing salts are expected to react with carbon materials at high temperature to achieve the doping of sulfur. Furthermore, nano-CaCO3 has been employed in preparing mesoporous materials to promote their surface area and pore volume, which are salutary for the performance in catalysis.<sup>[16]</sup> Compared with other conventional templates, like mesoporous zeolites and nano-silica,<sup>[17]</sup> whose removal require harsh conditions (i.e. toxic hydrofluoric acid or heated sodium hydroxide solution), nano-CaCO<sub>3</sub>, or its decomposition product CaO, are liable to be etched with diluted acid, thus making it a feasible accessory ingredient to enhance the porous structure of resultant materials. In our previous work, S, N-containing porous organic polymers (POPs) were prepared polymerization of melamine via condensation and terephthalaldehyde in dimethyl sulfoxide (DMSO).[18] During the condensation process, some decomposition products of DMSO (e.g. dimethyl sulfide) interact with POPs to achieve the introduction of sulfur.<sup>[19]</sup> Since sulfur atoms in POPs are bonded to carbon skeleton directly, they are able to in situ dope into

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carbon composites at high temperature with less involvement of volatile sulfur intermediates. Herein, S, N co-doped porous carbons (SNCs) were prepared by pyrolyzing the mixture of POPs and nano-CaCO<sub>3</sub>. The synthesized materials exhibited superb catalytic performance for the selective oxidation of benzylic C-H bonds.

#### **Results and Discussion**

The morphology and structure of SNCs were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and nitrogen adsorption-desorption measurements. According to the microscope images, SNC-850 presents irregular non-porous particles (Figure S1), while SNC-Ca-850 and SNC-Si-850 possess unconsolidated structures with abundant meso- and macropores (Figure 1). The approximate pore size in SNC-Si-850 is smaller than SNC-Ca-850, which is consistent with the dimensions of applied SiO<sub>2</sub> and CaCO<sub>3</sub> nanoparticles. In order to further explore the effects of nanoon porosity, nitrogen adsorption-desorption templates measurements were performed (Figure S2) and the specific surface areas of SNCs were obtained by Brunauer-Emmertt-Teller (BET) method (Table 1). Both SNC-Ca-850 and SNC-Si-850 exhibit representative Type IV isotherms with H3 hysteresis loops, corresponding to the presence of meso- and macropores.<sup>[20]</sup> Compared with SNC-850, the specific surface area and pore volume are enhanced greatly by the employment of nano-CaCO<sub>3</sub> or SiO<sub>2</sub>. The specific surface area of SNC-Ca-850 is slightly smaller than that of SNC-Si-850, which is probably attributed to the coarser particle size of nano-CaCO<sub>3</sub>. Furthermore, among the materials pyrolyzed at different temperature, SNC-Ca-850 and SNC-Ca-950 possess relatively large surface area. The CO<sub>2</sub> released by CaCO<sub>3</sub> decomposition may activate carbon material at higher temperature, thus leading to more abundant porous structure.[21]



Figure 1. SEM images of (a) SNC-Ca-850, (b) SNC-Si-850 and TEM images of (c) SNC-Ca-850, (d) SNC-Si-850.

The doping content and existence state of sulfur and nitrogen were examined by X-ray photoelectron spectroscopy (XPS) and elemental analysis (EA) (Table 2, S1). As XPS global spectrum presents, the peaks of C 1s, O 1s, N 1s and S 2p are detected, demonstrating the successful doping of nitrogen and sulfur into carbon materials (Figure S3). Four types of nitrogen, pyridinic N (397.8 eV), pyrrolic N (399.0 eV), graphitic N (400.6 eV) and N-O (402.3 eV) are observed in N 1s high resolution spectra (Figure 2, S4-S11).<sup>[22]</sup> With carbonizing temperature elevating, the content of doped nitrogen decreases considerably. As for graphitic N, which is reported to conduce to the catalytic capability for oxidation reactions *via* radical mechanism,<sup>[23]</sup> its relative fraction (compared with total nitrogen) increases with process temperature rising.

Table 1. Porous properties of SNC materials.					
Sample	Surface area (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)			
SNC-Ca-850	704	0.88			
SNC-Si-850	942	1.09			
SNC-850	257	0.27			
SNC-Ca-650	402	0.58			
SNC-Ca-750	472	0.61			
SNC-Ca-950	639	0.83			
NC-Ca-850	783	0.94			

In the case of sulfur, it is remarkable that the total doped content in SNC-Ca-850 (2.7 wt% by XPS) is more than 3 times of that in SNC-Si-850 (0.8 wt% by XPS) and SNC-850 (0.6 wt% by XPS). Besides, there are three peaks observed in the high resolution S 2p spectra (Figure 2, S4-S8). The dual peaks at 163.2 and 164.4 eV are attributed to 2p<sub>1/2</sub> and 2p<sub>3/2</sub> orbits of aromatic S (typically thiophenic S and aryl S), while the broad peak ranging from 166.0 eV to 169.5 eV indicates the presence of oxidized S.<sup>[24]</sup> Compared with SNC-Si-850 and SNC-850, SNC-Ca-850 possesses a higher ratio of aromatic S species. These results illustrate that nano-CaCO<sub>3</sub>, to a great extent, enhances the doping level of sulfur, especially aromatic S. It has been proposed that CO<sub>2</sub>, generated from thermal decomposition of CaCO<sub>3</sub>, may react with carbon at high temperature, thus reducing the content of carbon and increasing the relative percentage of sulfur.<sup>[25]</sup> As SNC-Ca-850 was obtained with a moderate yield (0.24 g derived from 1.00 g POPs), just a bit lower than SNC-Si-850 (0.29 g derived from 1.00 g POPs) and SNC-850 (0.30 g derived from 1.00 g POPs), the reaction between carbon and CO<sub>2</sub> may be not the predominant cause for the enhancement of sulfur content. In this case, it is intriguing how CaCO<sub>3</sub> benefits the doping of sulfur into carbon structure. Generally, organic sulfur may exist in four types: aliphatic S (mercaptan, thioether, and disulfide), thiophenic S, aryl S (thiophenol and diaryl sulfide) and oxidized S (sulfone and sulfoxide).<sup>[26]</sup> Among these types, aliphatic and oxidized S are

less stable under heat treatment. Aliphatic S may undergo two competitive transformations, either transforming to more stable aromatic S (thiophenic and aryl S) or degrading to H<sub>2</sub>S. Otherwise, oxidized S is liable to decompose and escape as SO<sub>2</sub>.<sup>[27]</sup> Since CaO derived from the decomposition of CaCO<sub>3</sub>, is of strong Brønsted basicity, it may prevent the efflux of H<sub>2</sub>S and SO<sub>2</sub> *via* following reactions:

$$CaO + H_2S \rightarrow CaS + H_2O$$

$$4 CaO + 4 SO_2 \rightarrow CaS + 3 CaSO_4$$

Because CaSO<sub>3</sub> is of poor thermal stability, the products of reaction between CaO and SO<sub>2</sub> are CaS and CaSO<sub>4</sub> instead of CaSO3.[28] The in situ formed sulfide and sulfate may react smoothly with the carbon materials, thereby elevating the content of doped sulfur.<sup>[13a,29]</sup> According to the X-ray diffraction (XRD) pattern of as-pyrolyzed material before acid etching (Figure S12), the presence of CaS is confirmed.<sup>[30]</sup> However, no peaks attributed to CaSO4 is found, which is probably due to its complete reaction with carbon or other reductive components (e.g. carbon monoxide and hydrogen) generated during pyrolysis.<sup>[29b]</sup> Besides, the surface sulfur content (determined by XPS) is higher than that in bulk (determined by EA), which implies the promoted sulfur doping by the interaction between carbon and CaS/CaSO<sub>4</sub> mainly occurs at the interfaces.<sup>[24a]</sup> Moreover, in such a process, a portion of sulfur in oxidized state (+4) is transformed into lower valence state (-2 in sulfide), which may be contributive to the larger proportion of aromatic S in SNC-Ca-850. The sulfur content rises as pyrolysis temperature elevates from 650 °C to 850 °C, indicating the doping of sulfur via carbon-CaS/CaSO<sub>4</sub> solid reaction is relatively hard to proceed and requires high temperature. Whereas, a slight decrease of sulfur content occurs when the pyrolysis temperature further increases to 950 °C, which may be attributed to the loss of aryl S, as it is unstable over 900 °C and tends to decompose to H<sub>2</sub>S and CS<sub>2</sub>.<sup>[31]</sup> Furthermore, with an increasing pyrolysis temperature, the ratio of aromatic S elevates from 69.3 % (SNC-Ca-650) to 91.5 % (SNC-Ca-950), which corresponds to the higher thermal stability of aromatic S compared with oxidized S.<sup>[27,31]</sup> In addition, no distinct diffraction peaks assigning to inorganic sulfide or sulfate are observed in the S 2p spectra, indicating the residual calcium species are Inductively coupled plasma optical emission minuscule. spectrometry (ICP-OES) test was performed to further determine the residue of calcium. The content of remnant calcium in SNC-Ca-850 is only 0.12 wt%, confirming a nearly complete removal of calcium species via acid etching.



Figure 2. High resolution (a) N 1s and (b) S 2p XPS spectra of SNC-Ca-850.

Cample	Composition (wt%)			
Sample	N by XPS	N by EA	S by XPS	S by EA
SNC-Ca-650	17.1	12.6	1.3	0.8
SNC-Ca-750	14.1	9.0	1.6	1.1
SNC-Ca-850	9.7	6.2	2.7	1.6
SNC-Ca-950	1.9	1.6	2.4	1.3
SNC-Si-850	10.7	6.8	0.8	0.6
SNC-850	9.8	6.0	0.6	0.5

6.4

6.1

5.3

1.8

2.5

1.0

1.3

Table 2. Composition of nitrogen and sulfur of SNC materials

10.3

9.3

84

NC-Ca-850

SNC-Ca-850c

SNC-Ca-850

(recycled)

Figure 3a shows the XRD patterns of SNC materials. Two broad peaks at  $2\theta = 24^{\circ}$  and  $43^{\circ}$  are assigned to the (002) and (100) lattice planes of carbon, respectively.[32] It is conspicuous that the peak near 24° is asymmetric, which could be deemed to be the combination of disordered (22°) and graphitic carbon (26.5°).[21] Compared with SNC-Si-850 and SNC-850, the diffraction angle corresponding to maximum intensity of SNC-Ca-850 is closer to 22°, indicating it possesses a lower degree of graphitization. Besides, Raman spectra were depicted in order to further probe the defective nature of materials (Figure 3b). The bands at 1352 and 1533 cm<sup>-1</sup> are ascribed to disordered carbon (D band) and graphitic carbon (G band), respectively.[33] The intensity ratio between D band and G band of SNC-Ca-850  $(I_D/I_G = 1.09)$  is slightly larger than that of SNC-Si-850  $(I_D/I_G =$ 1.02) and SNC-850 ( $I_D/I_G = 1.01$ ), revealing SNC-Ca-850 a more defective structure, which is consistent with the results of XRD. It has been proposed that the existence of nano-CaCO3 may be liable to create edge sites and crystal boundaries, thus preventing the formation of highly-ordered carbon.<sup>[21]</sup> Besides, the more disordered structure in SNC-Ca-850 is also probably related to its higher content of doped sulfur. Since the size of sulfur atom is much bigger than carbon, it tends to form a bulge at the layer of local sp<sup>2</sup> carbon, thus breaking the regular graphitic structure and generating defects.[34]





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Selective oxidation of aromatic alkanes with benzylic C-H bonds is one primary approach to producing corresponding ketones.[33b] Generally, this reaction can be accelerated by catalysts based on transition metal (e.g. cobalt,<sup>[35]</sup> iron,<sup>[36]</sup> manganese,<sup>[37]</sup> and nickel<sup>[38]</sup>). Nevertheless, these catalysts are at risk of metal leaching, which limits their application in food and pharmaceutical industries. The development of metal-free catalysts, typically based on carbon, makes it possible to avoid this problem from the origin. Herein, SNC materials were applied as heterogeneous catalysts for the selective oxidation of C-H bonds. Using tert-butyl hydrogen peroxide (TBHP) as oxidant, ethylbenzene was transformed to acetophenone with benzaldehyde and 1-phenylethanol as byproducts. Ethylbenzene was barely converted without catalyst or simply adding activated carbon (AC) to the reaction system (Table 3, entry 1-2). An excellent catalytic capacity was presented by SNC-Ca-850. Under the optimized reaction conditions, high ethylbenzene conversion (92.4 %) and acetophenone selectivity (97.4 %) were achieved in 4 h (Table 3, entry 3). Otherwise, moderate conversion and selectivity were acquired over SNC-Si-850, while only a modicum of acetophenone was afforded over SNC-850 (Table 3, entry 4-5). Besides, SNC-Ca-850 exhibited the best catalytic performance among all SNC-Ca materials pyrolyzed at different temperatures (Table 3, entry 6-8). Furthermore, SNC-Ca-850 showed good reusability since a satisfactory activity was retained after 4 cycles (Table 3, entry 9; Figure S14).

Table 3. Catalytic evaluation for ethylbenzene oxidation. <sup>[a]</sup>					
$\bigcirc$	Catalyst, TBHP 80 °C, 4 h		н + СНО		
Entry	Catalyst	Conv. (%)	Sel. (%)		
1	Blank	6.7	51.8		
2	AC	24.5	60.5		
3	SNC-Ca-850	92.4	97.4		
4	SNC-Si-850	86.3	92.5		
5	SNC-850	31.6	68.0		
6	SNC-Ca-650	51.3	59.2		
7	SNC-Ca-750	73.9	80.2		
8	SNC-Ca-950	60.4	75.1		
9 <sup>[b]</sup>	SNC-Ca-850	80.1	87.9		
10	NC-Ca-850	75.2	94.0		
11	SNC-Ca-850c	72.8	92.3		

[a] Reaction conditions: catalyst (10 mg), ethylbenzene (0.5 mmol), TBHP (2 mmol, 70 wt% solution in water), water (2 mL), 80 °C, 4 h. [b] reused for 4 times.

Compared with SNC-850, the considerably high catalytic capabilities of SNC-Ca-850 and SNC-Si-850 may be due to their larger surface area and higher pore volume, which are preferable to the mass transfer of reactants and products. According to prior studies, the presence of graphitic N is conducive to enhance the catalytic activity.<sup>[23,39]</sup> Although both surface area and graphitic N content of SNC-Ca-850 are slightly lower than that of SNC-Si-850, the former material shows better catalytic performance, which is probably related to its higher content of sulfur. In addition, the S, N co-doped carbon material exhibits higher effect than the N single doped one (Table 3, entry 10). Because of the mismatch of outermost orbitals of carbon and sulfur atoms, the sulfur atom possesses a higher density of positive charge, thus being feasible to adsorb reactive oxygen species (ROS).<sup>[24b,40]</sup> Furthermore, there exists a synergetic effect between co-doped sulfur and nitrogen, which endows the adjacent carbon atoms with elevated spin density, hence further promoting the capability of adsorbing ROS.<sup>[40b]</sup> The relatively high sulfur content provides SNC-Ca-850 with enhanced ability to enrich ROS. Besides, the hydrophobic surface of SNC-Ca-850 renders it affinitive to low-polarity substrates (i.e. aromatic alkanes). The condensed ROS and substrates near the surface of catalyst, thereby, accelerate oxidation reactions effectively. In this case, the superior catalytic performance of SNC-Ca-850 could be attributed to its higher content of doped hetero elements, especially sulfur. Moreover, after being calcinated at 250 °C under aerobic conditions (SNC-Ca-850c), the content of aromatic S decreases from 2.3 wt% to 1.0 wt%, while oxidized S increases from 0.4 wt% to 0.8 wt%. The calcinated material shows relatively poor catalytic performance (Table 3, entry 11). Similar change of sulfur existing modes and catalytic effect are observed in the recycled catalyst (Table 3, entry 10), implying aromatic S may be the contributive species to the selective oxidation of benzyl C-H.

Table 4. Selective evidetion of substituted gramatic alkanes <sup>[a]</sup>				
Entry	Substrate	Conv. (%)	Sel. (%)	
1	$\bigcirc$	99.4	97.1	
2	Мео	93.0	96.7	
3	O <sub>2</sub> N	85.3	87.7	
4	Me	89.5	79.0	
5	Br	91.5	89.2	
6		97.4	98.7	

[a] Reaction conditions: SNC-Ca-850 (10 mg), substrate (0.5 mmol), TBHP (2 mmol, 70 wt% solution in water), water (2 mL),  $80 \degree C$ , 6 h.

In addition, a number of substrates were tested under the modified conditions with SNC-Ca-850. Aromatic ketones with

strong electron donating (methoxyl) or withdrawing (nitro) groups were afforded with satisfactory yields (Table 4, entry 2-3). Besides, alkyl and halide substituted substrates were converted with high efficiency (Table 4, entry 4-5). Furthermore, the catalytic system was also effective to the substrate with bulky group (Table 4, entry 6).

#### Conclusions

In summary, S, N co-doped porous carbon materials were developed by pyrolyzing the homogeneous mixture of S, N-containing polymers and nano-CaCO<sub>3</sub> under inert atmosphere. The adscititious nano-CaCO<sub>3</sub> not only enhances the formation of porous structure, but also has a remarkably enhancive impact on the content of doped sulfur. The modified porosity and doping effect endow the materials with superior catalytic performance for the selective oxidation of aryl alkanes with TBHP as oxidant. Hence, this strategy is feasible to improve the utilization of sulfur in pyrolysis process, thus promoting the sulfur doping content of carbon materials.

#### **Experimental Section**

**Characterization:** XRD patterns were measured with Bruker D8 Focus equipped with a Cu Kα X-ray source. Raman spectra were recorded by Thermo Scientific DXR Microscope. ICP-OES measurements were performed on Varian VISTA-MPX. SEM images were obtained using Hitachi S-4800 microscope. TEM images were obtained using JEOL JEM-2100F field emission electron microscope. Nitrogen sorption isotherms were obtained using Quantachrome Autosorb iQ analyzer at 77 K. EA were performed on Vario EL Cube. XPS measurements were carried out with Thermo Fisher Scientific X-ray ESCALAB 250Xi.

**Preparation of POPs:** POPs were synthesized according to our previous work.<sup>[18]</sup> Melamine (1.26 g) and terephthalaldehyde (2.00 g) were dissolved into 62 mL DMSO. The solution was transferred into a 100 mL polyphenylene oxide (PPO) lined autoclave, heated to 180 °C and kept for 10 h. After cooling down to ambient temperature, 100 mL water was added to the mixture to afford light brown precipitate. The resultant solid was washed with water and dried at 80 °C under vacuum. EA found: C, 51.60 %; H, 4.37 %; O, 9.22 %; N, 33.77 %; S, 1.04 %. For comparison, sulfur-free POPs (SFPOPs) were synthesized by replace DMSO with N, N-dimethyl acetamide as solvent.

**Preparation of SNCs:** The as-synthesized POPs (1.00 g) and hydrophobic nano-CaCO<sub>3</sub> (1.00 g, average particle size 50 nm) were mixed in a flask containing 20 mL ethanol and stirred for 12 h. After solvent evaporation, the remaining mixture was placed in a quartz container and pyrolyzed under argon atmosphere at specific temperature for 2 h. The obtained solid was etched with diluted hydrochloric acid (3 mol/L), thoroughly washed with water, and dried at 60 °C under vacuum to afford porous S, N co-doped carbon materials, denoted as SNC-Ca-*t* (*t* stands for the pyrolysis temperature), respectively. For comparison, SNC-Si-*t* was prepared by replacing nano-CaCO<sub>3</sub> with nano-SiO<sub>2</sub> (average particle size 20 nm) as template, which was removed by hydrofluoric acid (3 mol/L) in the following etching procedure. SNC-*t* was prepared by direct pyrolysis of POPs with no additional ingredients. SNC-Ca-850c was obtained by calcinating as-prepared SNC-Ca-850 under air atmosphere at 250 °C for 30 min. Besides, sulfur-free nitrogen-doped porous carbon (NC-Ca-*t*) was prepared by employing SFPOPs in place of POPs as precursor.

**Catalytic tests:** The selective oxidation of aromatic alkanes with TBHP was adopted as a model reaction to evaluate the catalytic performance of synthesized SNCs. In a typical procedure, substrate (0.5 mmol), TBHP (2 mmol) and water (2 mL) were introduced into a 15 mL sealed tube containing catalyst (10 mg). The mixture was placed in an 80 °C oil bath with magnetic stirring and kept for 4 h. After reaction, 10 mL ethanol was added and the suspension was stirred for a while to ensure the system homogeneous. Finally, the mixture was analyzed by EWAI GC-4000A gas chromatograph with a PEG-20M column.

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**Keywords:** Carbon • Doping • Heterogeneous catalysis • Mesoporous materials

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# FULL PAPER Sulfur, nitrogen co-doped porous Yutian Qin,# Haotian Guo,# Bowei carbon materials were synthesized by Wang,\* Jiayi Li, Ruixiao Gao, Pengzhi pyrolyzing porous organic polymers Qiu, Mingming Sun, and Ligong Chen\* mixed with nano-CaCO₃. The Page No. - Page No. employment of nano-CaCO3 not only enhances the forming of porous Controllable sulfur, nitrogen costructure, but also promotes the doped porous carbon for doping of sulfur into carbon skeleton. ethylbenzene oxidation: the role of The resultant materials exhibit nano-CaCO<sub>3</sub> excellent catalytic performance for the selective oxidation of benzylic C-H bonds.

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