Graphical Abstract

**P and S Dual-Doped Graphitic Porous Carbon for Aerobic Oxidation Reactions: Enhanced
Catalytic Activity and Catalytic Sites**

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Abstract:

A highly porous graphitic carbon material, dually-doped with P and S, was studied as a metal free catalyst for aerobic oxidation reactions. Catalytic mechanism studies suggest that the active centers, originated from P-and S-doping, additively/synergistically catalyze the aerobic oxidation of benzylic alcohols but with different pathways. For the first time, catalytic centers stemming from S-doping were experimentally identified to be exocyclic S species (C-S-C, sulfur out of the carbon ring), which are different from those proposed for electrochemical oxygen reduction reactions (ORR) with a $4e^-$ pathway and oxygen evaluation reactions (OER). Notably, all the catalytic sites from both P and S doping share a similar “protruding out” pyramid structure, which is in contrast to the planar structure of the catalytic sites in N- or B-doped graphitic materials. The unique geometric structure of the catalytic sites can minimize substrate steric hindrance effects, endowing the P, S co-doped catalysts with a wide substrate scope and functional group tolerance. Furthermore, the unambiguous distinguishment of the catalytic sites from those in OER and ORR provides valuable guidance for designing and developing carbon materials with controlled active sites to satisfy different catalytic applications.

KEYWORDS: Heteroatom doped carbon, Metal-free catalyst, Aerobic oxidation, Heterocyclic sulfur

1. Introduction

Catalytic oxidation of inexpensive and widely available chemicals to produce high value-added compounds is highly desirable for organic synthesis and in the refinery industry. Molecular oxygen (O_2), which has virtually no cost and generates no environmentally hazardous by-products, is an ideal oxidant for cost effective and eco-friendly production processes. However, its activation is difficult due to its triplet ground state structure which renders it unreactive in oxidation reactions.[1] A wide range of homogeneous and heterogeneous transition metal-based catalysts have been developed to activate O_2 for catalytic oxidation reactions. Unfortunately, many of those metals are rare, expensive and/or toxic, which presents sustainability and environmental challenges. The use of metal free carbon-based materials as eco-friendly, abundant, and readily available heterogeneous catalysts for aerobic oxidation reactions has emerged as a promising alternative, in the drive towards green and sustainable chemistry.[2-11] Among the carbon-based materials, graphene-like porous materials are being actively studied. Compared to carbon nanotubes (CNTs), they have similar or larger surface areas. Their electronic and surface properties, which determine their catalytic performance, can also be fine-tuned via heteroatom doping. More importantly, their large scale production for catalytic applications can be achieved at much lower cost and without involving metal catalysts. Therefore, the potential issues caused by residual metal catalysts, which are difficult to completely remove upon CNT fabrication, are avoided. Since the pioneering work by Bielawski's group using graphene oxide (GO, oxygen doped graphene) as catalysts for chemoselective oxidation of alcohols under mild conditions,[12] other heteroatoms, such as N, B, S-doped and NB, NS co-doped graphitic carbon materials have been exploited for catalytic aerobic oxidation reactions.[8-11,13-15] However, the widespread use of these carbon-based catalysts is largely hindered by the low efficiency compared to the traditional metal-based metallic counterparts. To this end, the development of more efficient carbon based catalysts is urgently needed. A fundamental

understanding of the catalytic sites at the molecular and atomic levels is critical for designing and developing the next generation of efficient catalysts to satisfy practical industrial applications.

Recently, an extremely simple and rapid (seconds) approach was developed to directly synthesize gram quantities of P-doped graphitic porous carbon materials with controlled P bond configuration from a biomass compound, phytic acid.[16] The as-produced P-doped graphitic porous carbon materials (referred as P-Gc) was capable of selectively oxidizing both primary and secondary benzyl alcohols to the corresponding aldehydes or ketones. This is in contrast to N-doped graphitic materials which can oxidize primary benzyl alcohols only to their corresponding aldehydes.[13] This difference was attributed to the unique “protruding out” structure of P in P-Gc, compared to the planar structure of the catalytic centers in N-doped graphitic materials. This unique structure minimized the steric hindrance thus allowing secondary alcohol to access the catalytic centers. Furthermore, the P-Gc also exhibited much higher catalytic efficiency and recyclability, compared to GO based catalysts.[12,17] However, it was found that high catalyst loading is still required to reach the desired high conversion and yield, possibly due to the limited catalytic centers on the P-Gc.

On the other hand, metal free carbon-based catalysts have been extensively studied for electrocatalytic oxygen reduction reactions (ORR).[18-24] Some of the catalysts, especially those co-doped with several different heteroatoms could equal or even outperform the activity of precious metal based catalysts (such as Pt/C).[15,22,23,25-31] The improved catalytic performance was attributed to the additive and/or synergistic effects of the co-doped heteroatoms. Since both ORR and aerobic oxidation require activation of inert molecule O₂, it is natural to assume that the strategy of co-doping different heteroatoms into a carbon matrix could also lead to development of good catalysts for aerobic oxidation reactions.

Compared to ORR, studies with doped and/or co-doped carbon materials are very limited, especially co-doped with P as catalysts for selective organic synthesis.[2,32] This is possibly due to the lack of

access for large scale synthesis of multiple heteroatom-doped carbon materials for developing and testing catalysts for organic synthesis. Recently, we found that by simply mixing the other heteroatom (N, S, B) sources (such as ammonium hydroxide -N source, amorphous sulfur -S source, boric acid -B source) with phytic acid prior to microwave heating, various P co-doped porous carbon materials can be rapidly synthesized in gram scale quantities for organic synthesis studies.[33] The synthesized P co-doped porous carbon materials such as P-N, P-S and P-B co-doped porous carbon materials are denoted as PN-Gc, PS-Gc and PB-Gc, respectively.

Taking advantage of this simple technique to synthesize these P co-doped carbon materials, in this work, we have compared their catalytic performance for oxidation reactions using molecular oxygen as the sole terminate oxidant. Using aerobic oxidation of benzyl alcohol as an example, we found that the PS-Gc catalyst shows the most improved catalytic performance compared with single doped (S-Gc and P-Gc) and other P co-doped carbon catalysts (PB-Gc and PN-Gc). The PS-Gc catalyst is further characterized by a wide range of substrates. Detailed mechanistic studies suggest that the active centers originating from P doping and S doping additively/synergistically catalyze the aerobic oxidation reaction with different pathways. Most importantly, multiple spectroscopic techniques, especially, Sulfur K-edge X-ray absorption near edge spectroscopy (XANES) were exploited to study the catalytic centers originating from S doping. For the first time, thanks to the high energy resolution of XANES, for the first time, the catalytic sites originating from S doping were experimentally identified to be the exocyclic S species (C-S-C, sulfur out of the carbon member ring), which are different from those proposed for the electrochemical oxygen reduction reactions (ORR) with a $4e^-$ pathway and the oxygen evolution reactions (OER).[34] Notably, all the catalytic sites from both P and S doping share a similar “protruding out” pyramid structure, which is in contrast to the planar structure of the catalytic sites in N- or B-doped graphitic materials. The unique geometric structure of the catalytic sites can minimize substrate steric hindrance effects, endowing the PS-Gc catalysts with a wide substrate scope and functional group tolerance. It preserves the selectivity rule of P-Gc for electron donating and withdrawing properties of the

functional groups on the benzyl alcohols, while still differing from other heteroatom-doped carbon materials.[13,15] It is noteworthy that, without requirement of a co-catalyst,[8] 5-hydroxymethylfurfural (HMF), a biomass molecule from cellulose and cellulose derived carbohydrates, can be catalytically oxidized to 2, 5 diformyl furan (DFF) instead of 2, 5-furan dicarboxylic acid, with almost 100% selectivity, demonstrating great potential for application in the bio-refinery field. The high catalytic activity for a wide range of substrates and excellent chemoselectivity in combination with the rapid, energy saving fabrication approach, suggest that PS co-doped porous carbon materials are promising for “green catalysis” due to their higher theoretical surface area, sustainability, environmental friendliness and low cost.

2. Experimental Section

2.1. Synthesis of Catalysts.

2.1.1. Synthesis of P and other heteroatom (N, B, and S) co-doped catalysts: The P and other heteroatom co-doped porous carbon catalysts were synthesized according to a previously published protocol.[33] Briefly, 1.0 mL of phytic acid (Sigma-Aldrich 50% w/w in water) is mixed with a pre-weighed amount of another heteroatom source (such as amorphous sulfur or ammonium hydroxide or boric acid as S, N and B source, respectively) in a 35 mL Pyrex glass vessel (CEM, #909036) and closed with a Teflon-lined cap (CEM, #909235). The stoichiometry is such that the mole ratio of P and other heteroatom dopants remains 1:1. A uniform dispersion or suspension of the phytic acid and heteroatom source is obtained by bath sonication of the mixture for 15 minutes followed by heating the resultant mixture in a domestic microwave (Sanyo-EM-S9515W, 1100 W, 2.45 GHz) chamber for the desired times to obtain P co-doped carbon material. The microwave heating time is dependent on the microwave absorption capacity of the heteroatom precursor and the resulting mixture. Microwave heating times are 42s, 90s and 150s for the synthesis of PS-Gc, PN-Gc and PB-Gc, respectively. The microwave heating

time is also varied based on the type of domestic microwave, size or physical dimensions of microwave cavity and microwave output power. After microwave heating of the mixture, the resulting product is left to cool in a fume hood and is then filtered, washed and dried as described in the previously.[33]

2.1.2. Synthesis of S-doped carbon material (S-Gc): The S-doped porous carbon catalyst was also synthesized according to a previously published protocol but with slight modifications.[33] Briefly, ~250 mg of myo-Inositol (acting as a C source), ~0.6 mL of concentrated sulfuric acid (acting as a strong dehydrating agent and microwave absorbing agent) and a heteroatom dopant source, which is ~67 mg amorphous sulfur, were mixed by bath sonication for 15 minutes and then heated in a microwave oven for 60 seconds. Mixing of the inositol and amorphous sulfur powder before addition of concentrated H₂SO₄ is very important to get higher atomic doping (~6 atomic % S) into carbon material. The resulting product is left to cool in a fume hood and is then filtered, washed and dried as described in the previously.[33]

2.2. Catalytic oxidation of primary and secondary alcohol reaction.

2.2.1. Materials: The following materials were used as-purchased. Benzyl Alcohol (Millipore, ≥99%), DL-sec-phenyl ethyl alcohol (Acros Organics, ≥97%), cyclohexane methanol (Alfa Aesar, 99%), n-butanol (anhydrous, Sigma-Aldrich, 99.8%), 4-methoxybenzyl alcohol (TCI, >98%), 4-methylbenzyl alcohol (Sigma-Aldrich, 98%), 4-nitrobenzyl alcohol (Alfa Aesar, 99%), 4-fluorobenzyl alcohol (Sigma-Aldrich, ≥97%), cinnamyl alcohol (Sigma-Aldrich, ≥98%), diphenyl methanol (Sigma-Aldrich, 99%), 5-(hydroxymethyl)-2-furaldehyde (Sigma-Aldrich, 99%), Cyclohexanol (Sigma-Aldrich, 99%), Toluene (anhydrous, Sigma-Aldrich, 99.8%).

2.2.2. Solvent free alcohol oxidation: A catalytic reaction for benzylic alcohol oxidation was carried out by mixing the predetermined amount of catalyst and benzylic alcohol in a 10 mL microwave reaction vial (VWR 89079-402) and then sealed with a PTFE-faced aluminium cap. After that, the air inside the reaction vessel is removed using a traditional vacuum system and replaced with the desired atmosphere

before heating the reaction vial in an oil bath for specified time and at a specified temperature. For control experiments with a radical inhibitor, a specified amount BHT (butylated hydroxytoluene) and acetonitrile (for maintaining uniform dispersion of BHT) was added to the above-described mixture at the beginning of the reaction. The detailed experimental conditions, the amount of the reactant and catalysts were specified in the footnote of each table. After completion of each reaction, ~0.7 mL of CDCl_3 and 100 μL of anhydrous toluene (internal standard) was mixed with the reaction mixture and filtered with a 0.02 μm syringe filter and analyzed by ^1H NMR spectroscopy (Bruker Avalanche 500 MHz). % conversions, % selectivity, % yield and turn over number (TON) were calculated according to the previously published methods.[12,16] In brief, % conversion of the benzyl alcohol were calculated by integration of the benzaldehyde PhCHO peak (1H) and the ortho aromatic protons of benzoic acid (2H), versus the benzyl alcohol PhCH_2OH (2H) peak. % yield of the products (benzaldehyde and benzoic acid) were calculated by integration of the benzaldehyde PhCHO peak (1H) or the ortho aromatic protons of benzoic acid (2H), versus the internal standard toluene peak (3H peak of PhCH_3). % selectivity for benzaldehyde was calculated as the ratio of moles of benzaldehyde *100 / total moles of the products (benzaldehyde + benzoic acid). TON was calculated by calculating the ratio of (moles of oxidized benzyl alcohols that converted to the products) / (mass of the catalysts in grams), due to non-Bertholloid nature of the carbon based catalyst. We have repeated the benzyl alcohol oxidation experiments multiple times ($n = 3$) and found that the % conversion value of benzyl alcohol can be obtained within $\pm 7\%$ of standard error.

2.2.3. Kinetic studies of an alcohol oxidation in water: Kinetic studies for aerobic oxidation reactions at different reaction temperatures were carried out in 20 mL microwave reaction vials sealed with a PTFE-faced aluminium cap. 5 mg of PS-Gc and 10 μL of benzyl alcohol are added to 10 mL of oxygen saturated deionized (DI) water as the solvent in a reaction vial and the reaction is carried out in a 1 atm O_2 environment. During the experiments, ~0.3 mL aliquots were withdrawn at a regular interval of 15 minutes, filtered via 0.02 μm syringe filter and analyzed by HPLC (Varian Pro-Star and Phenomenex C18

column, mobile phase 50:50 ratio of Methanol: 0.44% Acetic acid in DI water) to monitor the amount of benzaldehyde produced.

2.3. Material characterization.

The morphology of PS-Gc materials was studied with scanning electron microscopy (SEM, Hitachi S-4800). The SEM samples were prepared by sprinkling the dried PS-Gc powder on a piece of carbon tape. The heteroatom doping and atomic % of all elements in the porous graphitic carbon were analyzed by Energy Dispersive X-ray Spectroscopy (EDS) characterization. The sample for EDS characterization was prepared by drop casting of the slurry of a sample (PS-Gc dispersed in ethanol by short bath sonication) on to a piece of copper tape and allowing it to air dry. The X-ray photoelectron spectroscopy (XPS) characterization was performed after drop casting the catalyst onto a Si substrate. The thickness of the catalyst film on the Si substrates was roughly 30–50 nm. XPS spectra were acquired using a Thermo Scientific K-Alpha system with a monochromatic Al K α X-ray source ($h\nu = 1486.7$ eV). For data analysis, Smart Background subtraction was performed, and spectra were fit with Gaussian/Lorentzian peaks using a minimum deviation curve fitting method (part of the Advantage software package). The surface composition of each species was determined by the integrated peak areas and the Scofield sensitivity factor provided by the Advantage software. FT-IR spectra of PS-Gc samples (thin films deposited on ZnSe windows) were acquired with a Thermo-Nicolet 6700 spectrometer (Thermo-Electron Corp., Madison, WI), using a sample shuttle and a mercury-cadmium-telluride (MCT) detector. Four blocks of 128 scans were co-added. Spectral resolution was 4 cm^{-1} and two levels of zero-filling were incorporated so that data were encoded every 1 cm^{-1} . Raman spectra of the PS-Gc material (deposited on Anodisc membrane) was collected using a Confocal Raman Microscope (Wi-Tec, Alpha 3000R) with an excitation laser at 785 nm. The surface area of PS-Gc material was measured using Brunauer–Emmett–Teller (BET) and Methylene blue (MB) adsorption method, as described in the previous report.[35] The porosity of the PS-Gc was measured using Barrett-Joyner-Halenda (BJH) adsorption-desorption isotherm

(see supporting information for more detail). The S K-edge (2472.02 eV) XANES spectra were recorded at APS at 9-BM beamline in fluorescence mode at room temperature. The X-ray energy from the Si (111) monochromator was calibrated relative to the 3% sodium thiosulfate standard. Three scans were collected in order to confirm the absence of X-ray damage and improve the signal-to-noise ratio. The spectra were processed and averaged in the Athena XAS analysis program.[36] All the spectra were deconvoluted using Gaussians and 2 arctangent functions using Athena.[36]

3. Results and Discussion

For large scale synthesis of valuable chemicals in industry, solvent free reactions are highly preferred for cost reduction. Therefore, our catalytic studies of these P co-doped carbon materials were performed in solvent-free reaction conditions. First, we have compared the catalytic efficiency of the various as synthesized P co-doped porous carbon catalysts for selective oxidation of benzyl alcohol to benzaldehyde at 80°C for 48 hours. As shown in Table 1, benzyl alcohol oxidation cannot proceed efficiently in the absence of a catalyst (entry 1). The reaction cannot proceed either in the presence of carbon based catalysts, which do not have heteroatom doping (such as rGO or non-doped porous carbon, entry 2 and 3), or with amorphous sulfur (resource for S doping). These results demonstrate that heteroatom doping is important for enabling a carbon material to be catalytically active.

Recently, PN co-doped carbon materials were shown to have excellent catalytic efficiency for both ORR and OER, thereby demonstrating potential for replacement of precious metal catalysts for fuel cell and metal air battery applications.[19, 37, 38] As expected, the PN-Gc catalyst exhibited improved catalytic efficiency (~35% conversion) for aerobic oxidation of benzyl alcohol compared to that of P-only doped carbon materials (P-Gc, 21% conversion). Surprisingly, we found that the PS-Gc catalyst (~54% conversion) has even higher catalytic efficiency than PN-Gc. On the other hand, co-doping of B with P (PB-Gc) diminishes the catalytic activity of P-Gc to ~4% conversion for benzyl alcohol oxidation. This

may arise from the formation of P-B type functionalities, which deactivate the catalytic sites originated from P-doping alone. A similar scenario occurred in NB co-doped carbon catalysts.[11]

Table 1. Comparison of various P co-doped porous carbon catalysts for its catalytic efficiency towards selective benzylic alcohol oxidation.^a

Entry	Catalysts	% Conversion	% Yield	% Selectivity	TON ($\times 10^{-2}$)
1	--	ND	ND	ND	ND
2	Non doped carbon	4.2	ND	97.0	0.08
3	rGO	3.7	ND	96.0	0.08
4	Amorphous sulfur ^b	3.5	3.29	51.4	0.07
5	P-Gc[16]	21.2	20.8	95.6	0.43
6	S-Gc	18.3	14.5	86.8	0.37
7	PS-Gc	53.8	47.6	87.7	1.09
8	PN-Gc	35.4	35.5	97.2	0.72
9	PB-Gc	3.8	3.9	94.7	0.08

Reaction conditions: ^a0.1 mL benzyl alcohol (~1 mmol), 50 mg catalyst, 1 atm O₂, 80 °C, 48 hours. ^b8 mg of amorphous sulfur was taken as a catalyst. “ND” = not detectable (conversion or yield value < 1%).

To understand whether the improved catalytic performance of PS-Gc arises from a synergistic and/or an addition effect of the two different heteroatoms (P and S), we synthesized a S-only (S-Gc) doped carbon material and tested its catalytic performance toward benzyl alcohol oxidation. From the results listed in Table 1, it is clear that PS-Gc catalyst shows higher conversion (~54%) than the total of the conversion from P-doped and S-doped carbon catalysts (P-Gc (~21%) and S-Gc (18%)), which suggests that the P and S heteroatom doping in PS-Gc imparts synergistic effects. We have also calculated and compared the turnover number (TON; expressed as a ratio of mol of oxidized substrate/mass of catalyst)

of PS-Gc with other catalysts. It was found that PS-Gc (1.09) showed higher TON than P or S-doped and other P co-doped carbon catalysts at similar reaction conditions. Based on the above results it was concluded that PS-Gc was the most improved catalytic performance toward benzyl alcohol oxidation among all P co-doped carbon catalysts.

Due to the improved catalytic efficiency of the PS-Gc catalyst, we performed more detailed studies of its structure and catalytic performance in various alcohol oxidations to understand the catalytic mechanism and to identify the catalytic sites. First, the physical and chemical properties of PS-Gc were extensively characterized by scanning electron microscope (SEM), Energy Dispersive X-ray Spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS), Fourier Transform Infrared spectroscopy (FT-IR) and Raman spectroscopy. As shown in Figure 1, PS-Gc has a geometric structure similar to the P-Gc materials, i.e. two highly wrinkled graphene like sheets sandwiched a porous carbon monolith. The wrinkled structures possibly result from P and S doping and their larger atomic size compared to C atoms, which induces local geometrical distortion in the carbon network. XPS and EDS analysis demonstrated that both P (~2.5 atomic %) and S (~6.0 atomic %) were incorporated in the PS-Gc carbon matrix (Figure 1A-inset, Figure S1 and Table S1). The porous structure both in the carbon monolith and in the highly wrinkled skin-like graphene would enlarge the surface area of the PS-Gc material. The methylene blue dye adsorption method and Brunauer–Emmett–Teller (BET) method (Figure S2) were used to measure its surface area, which was calculated to be $\sim 900 \text{ m}^2/\text{g}$. The average diameters of the pores in the PS-Gc catalyst are 7.73 and 6.76 nm calculated from the BJH adsorption and desorption, respectively. A high surface area of the PS-Gc catalyst and the existence of the nanopores are beneficial for effective mass transfer as well as for facile access of catalytic centers by reactants.

Figure 1. Scanning electron microscopic (SEM) images of PS-Gc. (A) top view and (B) Side view. Inset of (A) is Energy Dispersive X-ray Spectra (EDS) of PS-Gc.

Raman spectroscopy was also used to characterize the PS Gc material. As shown in Figure S3, the Raman spectra of the PS-Gc shows the G band ($\sim 1594 \text{ cm}^{-1}$) and the D band ($\sim 1312 \text{ cm}^{-1}$). The presence of the G band (1594 cm^{-1}) confirms the presence of graphitic sp^2 carbon. The intensity of the D band (1312 cm^{-1}) and the intensity ratio (ID/IG) of D and G band are very similar to those of P-Gc, GO and reduced GO (rGO).[16] These results are consistent with previous reports that incorporation of heterogeneous dopants breaks the hexagonal symmetry of the graphene plane, which leads to the high intensity of D band in their Raman spectra.[15,35,39]

It is commonly accepted that the bonding configuration of the doped heteroatom controls the catalytic behavior of a heteroatom-doped carbon catalyst. To study the bond configurations of S and P in the PS-Gc catalyst, the C1s, P2p, S2p, and O1s XPS peaks were carefully deconvoluted as shown in Figure 2A, B and S4, and the results summarized in Table S2 and S3. Based on the P2p peak deconvolution, it was found that PS-Gc contains 2.76% of P doping, mainly in the form of P-O ($\sim 135.11 \text{ eV}$, 1.72%) and P-C ($\sim 133.25 \text{ eV}$, 1.02%) type of bonding configuration. The increased percentage of P-O bond may be

beneficial for catalytic activity of the PS-Gc catalyst as it was demonstrated previously that the P-O functionality in P-Gc plays a crucial role in the catalytic oxidation of benzyl alcohols.[16]

For S doping, the S2p peak deconvolution analysis shows that the PS-Gc contains mainly the C-S-C (~163.7 eV, 4.09%) type of S (such as exocyclic/epoxide S and/or heterocyclic thiophenic S) and small amounts of oxidized S (~167.9 eV, 1.32%) such as SO_x (x= 1-3). Deconvolution of the O1s peak demonstrated that PS-Gc contains carbonyl (~530.9 eV, 3.83%, C/P/S=O), epoxide/ether (~532.5 eV, 7.09%, C-O-C/P/S), hydroxyl (~533.2 eV, 5.61%, C/P/S-OH) and carboxyl/adsorbed water (~535.1 eV, 1.48%) type of oxygen functionalities (Figure S4). However, from XPS O1s peak deconvolution, it is difficult to differentiate whether these oxygen functionalities are directly attached with heteroatoms (P and S) or to carbon atoms. To better understand these oxygen containing functional groups, the PS-Gc catalyst was further studied by FT-IR spectroscopy (Figure 2C). For comparison, P-Gc, S-Gc, and GO (also known as O doped graphene) were also measured with FT-IR and their spectra were displayed together with the spectra of PS-Gc. As shown in Figure 2C, unlike GO, P-Gc, S-Gc and PS-Gc show a stronger peak at 1155 cm⁻¹, which can be assigned to P=O and/or C-S-C/C-S functional groups. These FT-IR results further confirm that S is successfully doped in the PS-Gc and S-Gc materials. On the other hand, GO shows strong peaks due to the presence of different types of C-O functionalities at 1354 cm⁻¹ (-OH or C-O stretching vibrations), 1412 cm⁻¹ (C-O in COOH), 1712 cm⁻¹ (C=O), 1816 cm⁻¹ (-CO-O-CO-), and 833 cm⁻¹ (C-H/C-O), which are absent in P-Gc and PS-Gc. These results suggested that the majority of the O containing functional groups are anchored on heteroatoms (P and S) rather than on C atoms, similar to previous results for P-doped carbon materials.[16]

Figure 2. (A) P2p and (B) S2p XPS peak deconvolution of the PS-Gc catalyst. (C) is the FT-IR spectra comparison of GO, P-Gc, S-Gc and PS-Gc catalysts.

The selective oxidation of benzyl alcohol to benzaldehyde in solvent-free conditions with the PS-Gc catalyst was further optimized. Reactions with varied temperature (40 to 100 °C), time (4 to 48 hours) and catalyst loading (10 to 100 wt %) were performed to optimize the reaction conditions (Table 2). As shown in Table 2 (entries 1 to 4), as the reaction time is increased from 4 to 48 hours (at 50 wt% catalyst and 80 °C), the conversion of benzyl alcohol increased from 6 to 50%. However, the selectivity to benzaldehyde drops below 90% when the reaction runs for more than 24 hours, suggesting that the longer reaction time affects the selectivity to the aldehyde product. The conversion of benzyl alcohol increased from 2 to 68 % (Table 2, entry 3, 5 to 7) as the reaction temperature was raised from 40 to 100 °C (50 wt% catalyst, 24

hours) with high aldehyde selectivity (> 90%). Furthermore, the conversion of benzyl alcohol increased from 17 to >90 % (Table 2, entry 3, 8 to 10) as the catalyst loading increased from 10 to 100 wt% (100 °C, 24 hours) with good aldehyde selectivity (> 90%). We also compared the catalytic efficiency of PS-Gc with GO at lower catalyst loading (20 wt %), the point at which the active sites for GO were at their optimum efficiency.[12] The PS-Gc catalysts still shows better alcohol conversion (34.5%) than GO (24% conversion, Table 2, entry 9 and 12), suggests that the PS-Gc has much higher catalytic activity for benzylic alcohol oxidations than GO.

Table 2. Optimization experiments for solvent free alcohol oxidation catalyzed by PS-Gc at 1atm O₂.

Entry	PS-Gc catalyst (mg)	Temperature (°C)	Time (hours)	% Conversion	% Yield	%Selectivity	TON (× 10-2)
1	50	80	4	5.8	4.1	96.8	0.12
2	50	80	8	10.1	7.8	94.9	0.21
3	50	80	24	25.5	25.7	91.7	0.46
4	50	80	48	50.4	42.8	87.3	1.03
5	50	40	24	2.2	2.2	98.5	0.04
6	50	60	24	10.7	9.7	96.5	0.22
7	50	100	24	67.6	53.6	91.0	1.38
8	10	100	24	17.2	16.6	93.5	1.75
9	20	100	24	34.5	30.7	92.0	1.75
10	75	100	24	85.5	54.0	87.2	1.16
11	100	100	24	93.3	70.8	96.5	0.95
12[12]	20 (GO)	100	24	24.0	--	100	1.1

All reactions were performed with 100 µL of benzyl alcohol.

These results encouraged us to probe the scope of the PS-Gc catalyst for different types of alcohols. As shown in Table 3, it was feasible to catalyze the aerobic oxidation of both primary and secondary benzyl alcohols to their corresponding aldehydes/ketones (entry 8 and 9). In fact, a similar catalytic efficiency was observed for the secondary alcohol and the primary ones, suggesting that the PS-Gc catalyst has good tolerance to the steric hindrance of substrates. This property was not observed for N-doped graphitic materials,[13] while it was well demonstrated in P-Gc.[16] This difference has been attributed to the planar structure of the catalytic centers in N-doped graphitic materials vs. the “protruding out” structure of P in P-Gc, which minimized the steric hindrance for secondary alcohol to access the catalytic centers. It has been reported that due to the larger diameter of S compared to C, the S-C bond is much longer than those C-C bonds, which can introduce much more defects and local geometrical distortion in the S-doped carbon materials.[40] The conversion for secondary alcohol by the PS-Gc catalyst was also much higher than that achieved when P-Gc was used as the catalyst, indicating that the active centers from S-doping should also have similar geometric structures as those catalytic centers from P-doping, so that the secondary alcohol can still be easily access the catalytic sites.

We further found that the catalytic efficiency of the PS-Gc catalyst is strongly dependent on the electronic properties of the substituent groups attached to the para- position of benzyl alcohols. Similar to P-Gc[16] and some metal based catalysts,[41,42] electron donating groups favour the selective oxidation of benzylic alcohol to its corresponding aldehyde (Table 3, entry 1 to 4). For example, 4-methoxy (electron-donating) substituted benzyl alcohol reached >90% conversion with excellent selectivity (>99%) to its respective benzaldehyde. In contrast, 4-nitro (electron withdrawing) substituted benzyl alcohol showed poor conversion (~10%) with moderate selectivity (~51%) towards its respective aldehyde. This substituent effect for benzyl alcohol oxidation was not observed in N- doped carbon materials,[13] but was observed in N, O, S-triple doped carbon catalyst (the reaction was performed using TBHP as an oxidant, instead of O₂),[15] however, the trend was opposite. In this case, benzyl alcohols

with the electron-withdrawing $-\text{NO}_2$ group gave higher alcohol conversion compared to the molecules with the electron-donating group ($-\text{OMe}$).

In addition, similar to the majority of carbon based metal free catalysts,[13,16,43] the PS-Gc catalyst was also found to be inactive ($< 5\%$ conversion) for aerobic oxidation of aliphatic alcohols (Table 3, entry 10 to 12), a consequence of their lower reactivity compared to those aromatic ones. Moreover, for alcohol substrates with aromatic structure, an adjacent π -conjugated structure to the alcohol group is required for catalytic oxidation. The π -conjugated structure possibly makes the adjacent C more active. In addition, it possibly promotes better substrate-catalyst interaction via π - π interaction compared to those alcohol molecules which contain aromatic rings but with aliphatic alcohol chain. For example, PS-Gc is incapable of catalyzing 3-phenyl-1-propanol, but efficient in promoting the oxidation of cinnamyl alcohol (79 %conversion, with excellent selectivity $>90\%$) (Table 3, entry 5 and 6).

Finally, it is noteworthy that 5-hydroxymethylfurfural (HMF), a biomass molecule from cellulose and cellulose derived carbohydrates, can be catalytically oxidized to 2, 5 diformyl furan (DFF) with almost 100% selectivity without requirement of a co-catalyst, demonstrating its great potential application in the bio-refinery field (Table 3, entry 7). Recently, several metal based catalysts decorated on various solid supports have been developed, but most of their catalytic reaction leads to the generation of 2, 5-furandicarboxylic acid instead of DFF.[44,45] GO and N-doped active carbon were also explored as metal free catalysts to promote its conversion to DFF.[43] For comparison, the PS-Gc catalyst demonstrated 5 times higher conversion efficiency than N-doped active carbon under similar reaction conditions, while GO needs a co-catalyst to reach the desired conversion.[8]

Table 3. The scope of PS-Gc in the oxidation of different alcohols^a

Entry	Alcohols	% Conversion	% Selectivity
1 ^b		92.3	100
2		89.9	100
3		69.2	91.6
4		9.9	51
5		79.0	90.5
6		< 1	100
7 ^c		50.8	100
8		67.2	100
9 ^d		88.4	97.2
10		< 1	100
11		< 1	41
12		4.1	100

Reaction conditions: ^a25mg PS-Gc catalyst, 0.5mmol alcohol, 1atm O₂, 100°C, 24 hours. ^b20mg catalyst was used. ^c50mg PS-Gc catalyst, 0.5mmol alcohol, 1atm O₂, 80°C, 24 hours. ^dReaction was performed at 80 °C to avoid decomposition of substrate alcohol.

In general, a catalyst facilitates a reaction by lowering the activation energy (E_a), the energy needed to proceed a reaction via forming an intermediate and/or the desired product. For P-doped carbon (P-Gc) catalyst,[16] the calculated activation energy is 49.6 kJ.mol^{-1} , which is similar to Ru metal based heterogeneous catalysts (51.4 kJ.mol^{-1} for Ru/ Al_2O_3 catalyst[46] and 47.8 for Ru/TEMPO catalyst[47]) but lower than that reported for N-doped carbon catalysts[13] (56.1 kJ.mol^{-1}). To know whether the presence of two heteroatom dopant (P and S) in PS-Gc is responsible for further lowering the activation energy for alcohol oxidation reaction and thus enhancing the catalytic efficiency of the catalyst, the kinetic studies of PS-Gc were undertaken. For that, the selective oxidation of benzyl alcohol to benzaldehyde by PS-Gc catalyst was performed in aqueous solution at different reaction temperatures. Samples were collected from the reaction mixture at a different reaction time (interval of 15 minutes) for each reaction temperature. A plot (Figure 3) of the concentration of benzaldehyde produced as a function of the reaction time at different temperatures (40 to 100°C) was drawn and from these linear plots, the apparent reaction rates (k_{obs}) for different reaction temperatures were calculated. The apparent activation energy (E_a) for PS-Gc is calculated from the slope of the linear plot ($\ln k_{\text{obs}}$ versus $1/T$, Figure 3B) using the Arrhenius equation. The E_a value ($32.02 \text{ kJ.mol}^{-1}$) of PS-Gc for benzyl alcohol oxidation is found to be much lower than P-Gc, N-doped carbon catalysts, and Ru metal based catalysts, suggesting that P and S heteroatom co-doping lowers the activation energy for the benzyl alcohol oxidation reaction and so shows better catalytic performance than the P-doped carbon catalyst.

Figure 3. (A) The plot of different reaction temperatures versus benzaldehyde molar concentration. Reaction conditions: 10 mg benzyl alcohol, 5 mg PS-Gc catalyst, 10 mL water, 1 atm O_2 . (B) Arrhenius plot for the benzyl alcohol oxidation. The rate constant (k) values at different temperature were regarded as the pseudo-zero-order rate constants (k_{obs}) because the plot of the molarity of benzaldehyde versus reaction time is linear.

It is noteworthy that S-doped and N, S co-doped materials have recently been studied for ORR and OER.[24,34,48-50] However, studies aimed at using them as catalysts for organic synthesis are sparse.[9,15] The catalytic mechanism in the organic synthesis was not studied and the bond configuration of S, which plays the essential catalytic role during oxidation events has not been identified. To shed light on the mechanism of catalytic oxidation of benzylic alcohols with the PS-Gc catalyst, several control experiments were performed. In our previous study of P-Gc, we found that no free radical was involved during the catalytic reaction, a result which is different from that for GO[12] and N-doped carbon catalyst.[13,43] To understand whether free radical intermediates are involved in the PS-Gc catalyzed reaction, we performed the benzyl alcohol oxidation (100 °C, 24 hours, 1atm O_2) in the presence of butylated hydroxytoluene (BHT, 50 wt %), a known free radical quencher in acetonitrile solvent (to dissolve BHT). As shown in Table 4, the conversion of benzyl alcohol **was** barely influenced

by the addition of BHT in the reaction system, suggesting a radical, which can be quenched by BHT, was not involved during the catalytic reaction.

In our previous work, we also demonstrated that P-Gc was able to initiate the oxidation of benzylic alcohol in the absence of oxygen because oxygen containing functionalities on P-Gc (P-OH and P=O) were directly involved in the oxidation of benzyl alcohol in first step of catalysis.[16] To determine whether activation of oxygen is required for the first step of the oxidation, we have performed the benzyl alcohol oxidation reaction in the presence of O₂ (1atm), air and inert environment (N₂). As shown in Table 5, we found that the conversion of benzyl alcohol decreased from ~71% to 31% if the reaction was run in the presence of air instead of pure O₂. It further decreased to 14% if the same reaction was run in presence of N₂. But if the PS-Gc catalyst was recovered from the reaction run under 1 atm N₂, and reused under 1atm O₂, the alcohol conversion increased to ~54%. These results clearly indicate that the activation of oxygen is important in the first step of the catalysis. The moderate conversion (14%) achieved in N₂ environment is possibly due to the active sites from P-doping (especially P-OH and P=O functionalities) in PS-Gc. To support this conclusion, we have tested and compared the catalytic performance of S-Gc in the presence of 1 atm N₂ and O₂ environments, respectively. As shown in Table 5 (entry 5 and 6), S-Gc was able to catalyse the benzyl alcohol oxidation in the presence of O₂ (18% conversion) but not in the presence of N₂ (< 4% conversion). These results suggest that the PS-Gc and S-Gc are very different from P-Gc, i.e. the first step of catalysis for the active sites from S doping is oxygen activation. Altogether these results suggest that PS-Gc has two different kinds of active centers, one coming from S-doping, and the other one from P-doping. These two types of catalytic centers facilitate the oxidation of benzylic alcohol. It appears that the catalytic centers from P-doping and their catalytic mechanism toward aerobic oxidation largely remain unchanged from those in the P-only doped carbon materials (P-Gc).

Table 4. The benzyl alcohol oxidation in presence of BHT (radical quencher)^a

Entry	Catalyst (~50 wt %)	% Conversion	% Yield	% Selectivity
1	PS-Gc + BHT	28.01	26.54	97.24
2	PS-Gc	34.23	32.59	96.59

Reaction conditions: 25mg PS-Gc catalyst, 0.5 mmol of benzyl alcohol, 0.3mL acetonitrile, 1atm O₂, 100°C, 24 hours. 0.125 mmol (or 50 wt% of benzyl alcohol) of butylated hydroxytoluene (BHT) is added in entry 1 for controlled reaction.

To identify the catalytic centers that derived from S-doping in the PS-Gc catalyst, we further characterized the PS-Gc catalysts before and after the catalytic reactions, which are referred as to fresh and used catalysts in the following section. As shown in Table S1, both EDX and XPS analysis showed that certain S species were lost during the catalytic reaction, consistent with the observed activity decrease in the used catalyst (Table S5). However, due to the limited energy resolution of XPS, it is still not clear which S species were lost, and if they possibly serve as the catalytic centers for the aerobic oxidation.

Sulfur K-edge X-ray absorption near edge spectroscopy (XANES) is a powerful analytic technique for studying sulfur speciation in different S containing materials.[34,51,52] Sulfur species with different oxidation states have been precisely identified based on the edge shift, which spans up to 12 eV over a -2 to +6 sulfur oxidation state range. To determine which S species bonded to carbon materials were lost during the reaction, and therefore to identify the possible catalytic centers from S-doping on PS-Gc, we used sulfur K-edge XANES to further study the PS-Gc catalyst before and after the catalytic reaction. As shown in Figure 4, the fresh PS-Gc catalyst shows two separate and broad groups of peaks. The one at higher energy range is from the oxidized S species (2478.5~ 2483 eV) and the other one at lower energy range is from the reduced S species (2473~2479.5 eV). Based on the literature assigned energy values,[34] the peak in the oxidized S region can be deconvoluted into two peaks at ~2481.5 and 2483.2

eV, which are assigned to sulfonate (-SO₂-) and sulfate (-SO₃-) species, respectively. While the peak for the reduced S group can be deconvoluted into four different peaks at 2470.4, 2472.7, 2474.3 and 2476.2 eV, which are assigned to inorganic sulfide, exocyclic sulfur (C-S-C, sulfur out of the carbon member ring), heterocyclic sulfur (sulfur in the ring), and sulfoxide(-SO-), respectively. The relative quantities of each S species were summarized in Table S4.

Table 5. The catalytic performance of the PS-Gc and S-Gc in benzyl alcohol oxidation in presence of different environments^a

Entry	Catalyst (~50wt %)	Oxidant (1 atm)	% Conversion	% Yield	% Selectivity
1	PS-Gc	O ₂	71.11	52.87	90.73
2	PS-Gc	air	31.65	30.62	97.4
3	PS-Gc	N ₂	14.04	11.82	99.08
4 ^b	PS-Gc	N ₂ to O ₂	53.80	46.26	93.6
5	S-Gc	O ₂	18.28	14.51	86.75
6	S-Gc	N ₂	3.62	ND	94.3

Reaction conditions: ^a25mg catalyst, 0.5 mmol of benzyl alcohol, 1atm oxidant, 100°C, 24 hours. ^bPS-Gc catalyst was recovered from entry 3. “ND” = not detectable (conversion or yield value < 1%).

Comparing the XANES spectra of the fresh and the used PS-Gc catalysts, it is obvious that the peak intensity for exocyclic sulfur (C-S-C, sulfur out of the carbon member ring) and SO_x largely decreased and at the same time sulfoxide (-SO-) peak increased in the PS-Gc-used catalyst. This suggests that exocyclic sulfur and SO_x groups are the primary active centers that resulted from S doping in the PS-Gc. Initially, we assumed that the SO_x groups might behave similarly as the PO_x groups in P-Gc, where they are directly involved in the oxidation of alcohol resulting in the reduction to sulfoxide (-SO-) functionalities. If this was the case, the first step of oxidation reaction should not require molecular

oxygen as oxidant. However, considering the fact that molecular oxygen was required for the first step of reaction, we excluded this possibility and concluded that the exocyclic S species (which is similar to epoxides in GO,[17] playing a major role in aerobic catalysis) were the catalytic centers in activating molecular oxygen and catalyzing the benzyl alcohol oxidation reaction. Further, considering that the exocyclic S species indeed have a “protruding out” kind of geometry structure, this conclusion is also supported by the excellent tolerance of the PS-Gc catalyst to steric hindrance of substrates.

Figure 4. The deconvolution of normalized S K-edge XANES spectra of fresh and used PS-Gc catalysts.

Recently, heterocyclic-S species have been experimentally identified as the OER catalytic centers.[34] These species have also been proposed and widely accepted as the catalytic centers for ORR with the $4e^-$ pathway.[48-50,53] Even though charge polarization stemming from the difference in electronegativity

between C and S is almost negligible, S-doping introduces high spin density on neighbouring (or nearby) carbon atoms, which are the atomic active sites for O₂ surface adsorption in a parallel diatomic configuration, thereby facilitating the direct reduction of O₂ to OH⁻ or H₂O via a four electron process. On the other hand, the mismatch of the outermost orbitals of S and C induces positive charges on S atoms, which could adsorb two OOH groups, promoting ORR via a 2e⁻ pathway.[48,53]

Based on the results and discussion presented above, we propose the following mechanism for the catalytic aerobic oxidation (Figure 5), where a secondary benzyl alcohol is used as an example. In the first step of catalysis, molecular oxygen was first activated on exocyclic S forming a reactive oxygen species (ROS). Since the presence of a radical quencher (BHT) did not influence the catalytic reactions, we assume that a non-radical ROS species, such as peroxo like species (OOH) were formed during the oxygen activation step, which oxidized the alcohol to its corresponding aldehyde/ketone. At the same time, some of them were reduced back to exocyclic S, thereby completing the catalytic reaction cycle. On the other hand, some were converted to sulfoxide type of S, which deactivated the catalytic centers. This hypothesis is consistent with the observed gradually decreasing the catalytic efficiency of the catalysts. It is also supported by the increased intensity of sulfoxide (-SO-) peak in the XANES spectrum and the appearance of a new peak at ~1225cm⁻¹ in the FT-IR spectrum of the PS-Gc-used catalyst (Figure S6), which is assigned to S=O type functional groups.

Figure 5. The proposed mechanism for benzylic alcohol oxidation by exocyclic S active centers.

4. Conclusions

This work demonstrated that P and S dual-doped porous carbon (PS-Gc) material largely improved catalytic activity with excellent selectivity in aerobic alcohol oxidation reactions compared to those single heteroatom-doped carbon catalysts (N, P, S, and GO) and P co-doped with other heteroatoms (PB-Gc and PN-Gc). The PS-Gc catalyst can selectively oxidize a variety of primary and secondary benzylic alcohols to their respective aldehydes/ketones with an excellent tolerance for substrates with steric hindrance. The electronic properties of the substituted groups influence the catalytic conversion, with electron rich ones favoring the conversion and selectivity. This rule was observed in P-only doped carbon materials, but not in N-doped carbon materials. A similar electronic dependence was observed in N, S, O triple doped carbon materials, but with an opposite trend. The calculated activation energy of benzyl alcohol oxidation is $\sim 32 \text{ kJ}\cdot\text{mol}^{-1}$ for the PS-Gc, which is much lower than the P-doped and N-doped carbon catalysts. From the various control experiments and the detailed characterization of the fresh and used PS-Gc catalysts, the following conclusion were reached: 1) The PS-Gc catalyst probably contains two distinct types of catalytic centers from P and S-doping. 2) The PS-Gc catalyst requires oxygen activation in the first step

of oxidation, which is different from that of P-only doped graphitic carbon materials. 3) S is doped in the PS-Gc catalyst with multiple bonding configurations (exocyclic, heterocyclic, sulfoxide, sulfonate, sulfate etc.) but only the exocyclic-S (C-S-C) species appears to play the catalytic role in activating the oxygen molecule for selective aerobic oxidation of alcohols. It is noteworthy that these S species have been theoretically predicted as the catalytic centers for ORR with $2e^-$ pathway, different from those catalytic centers for ORR with $4e^-$ pathway. 4) The S containing active sites (exocyclic-S) are not stable during the catalytic oxidation reaction and are partially converted to sulfoxide type of S species, which cannot be reduced back into exocyclic-S during the catalytic reaction. It is noteworthy that 5-hydroxymethylfurfural (HMF), a biomass molecule from cellulose and cellulose derived carbohydrates, can be catalytically oxidized to 2, 5 diformyl furan (DFF) with almost 100% selectivity without requirement of a co-catalyst, demonstrating its great potential application in the bio-refinery field.

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