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Nitrogen-Doped sp^2-Hybridized Carbon as a Superior Catalyst for Selective Oxidation**

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Current approaches for efficient C–H bond activation are usually mediated by heterogeneous[1] or homogeneous[2] catalysts. The basis is the employment of transition metals or organometallic centers, which is pivotal for the successful attack on the targeted C–H bonds.[3] However, we have reported that it is feasible to use carbon-based nanomaterials to activate short-chain alkanes in catalytic dehydrogenation reactions[4] although relatively high reaction temperatures are required. It is of particular interest to know whether it is possible to activate C–H bonds to get high value-added products at a moderate reaction temperatures by using cheap metal-free catalysts. To this end, an elegant approach using metal- or boron-doped carbon nitrides as catalysts[5] has been developed for the selective oxidation of allylic and benzylic hydrocarbons in organic solvents with moderate conversion. Attempts to achieve higher activity also include the application of N-alkoxysulfonyloxaziridines for the activation of C(sp^3)–H bonds,[6] although a complicated catalytic system for efficient reaction circulation was required.

Layered carbon, that is, highly exfoliated graphitic structures containing one or a few graphene layers,[7] has an unconventional electronic structure,[8] which was speculated to have a high chemical reactivity.[9] Indeed, researchers observed that layered carbon can catalyze hydrogenation,[10] ring-opening polymerization,[11] and C–H oxidation reaction,[12] and that it could serve as a support for metal oxide catalysts.[13] Herein we describe nitrogen-doped graphene materials that can activate the benzylic C–H bond with exceptionally high activity. The nitrogen atoms introduced are preferentially bound at graphitic sites in the carbon framework. This induces high charge and spin density at the adjacent *ortho* carbon, which promotes the formation of reactive oxygen species and the materials display exceptional catalytic activity even at room temperature.

Firstly, we examined the oxidation of ethylbenzene in aqueous phase with *tert*-butyl hydroperoxide (TBHP) as the oxidant and without using catalyst. However, no obvious activity was observed by GC after a reaction time of 24 h (Table 1, entry 1). Then we used a graphene sample prepared by the arc-discharge method (referred to as Arc-C)[14] as the catalyst for this reaction. Surprisingly, Arc-C activated ethylbenzene at 353 K to generate acetophenone in 20.7 % yield (Table 1, entry 2). As Arc-C had been prepared by a direct-current arc-discharge method with a pure graphite rod as the electrode in an NH_3/He atmosphere, besides trace nitrogen (0.7 %), no element other than carbon was detected by elemental analysis (EA) (oxygen cannot be detected by this method). The full X-ray photoelectron spectrum showed a C content of 97.9 % and low amounts of nitrogen and oxygen of 0.9 % and 1.1 %, respectively. This promising observation suggests that it is layered carbon material itself that catalyzed the oxyfunctionalization of the hydrocarbon. As Arc-C has a relatively low surface area (61.3 $m^2 g^{-1}$) which is an obvious drawback when it is used as catalyst, we decided to use the highly exfoliated layered carbon (multilayer graphene) with much higher surface area (423.6 $m^2 g^{-1}$) in order to obtain a better catalytic performance. The layered carbon (referred to as LC) was prepared by the pyrolytic method with graphene oxide as the precursor. However, this material showed similar acetophenone yield to that of Arc-C (Table 1, entry 4) although its surface area was around seven times higher than that of Arc-C. This result suggests that the catalytic activity is not directly related to the surface area of the catalysts. It is worth noting that this material also contains trace amount of nitrogen (0.4 %).

In the next phase, we investigated the relationship between the nitrogen content of the catalyst and its catalytic activity. We prepared nitrogen-modified layered carbon with different nitrogen loadings by a gas-phase CVD method using acetonitrile as the nitrogen source. The nitrogen introduced

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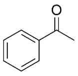
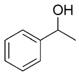
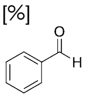
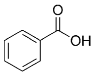
Table 1: Catalytic activity of different carbon materials for the oxidation of ethylbenzene in the aqueous phase.[a]

Entry	Catalyst	N [%] EA	C [%] XPS	N [%] XPS	O [%] XPS	Surf. area [m^2 g^{-1}]	Conv. [%]	Yield [%] 			
1	–	–	–	–	–	–	2.7	1.9	–	–	–
2	Arc-C	0.7	97.9	0.9	1.1	61.3	45.9	20.7	1.8	3.8	1.4
3	Arc-C-N	1.5	94.2	3.9	1.9	38.3	87.8	75.5	0.3	3.2	1.5
4	LC	0.4	98.2	0	1.8	423.6	56.0	27.3	3.1	2.9	1.4
5	LC-N-1.1	1.1	96.4	1.4	2.2	447.1	63.7	36.0	2.4	3.3	1.4
6	LC-N-3.6	3.6	94.5	3.4	2.1	437.3	95.4	84.4	0.1	1.6	–
7	LC-N-4.6	4.6	93.0	4.9	2.1	232.4	97.9	86.4	–	–	5.2
8	LC-N-8.9	8.9	90.8	7.8	1.4	83.7	98.6	91.3	–	–	5.0
9[b]	LC-N-8.9	8.9	90.8	7.8	1.4	83.7	94.0	80.4	–	2.6	1.4

[a] Reaction conditions: substrate (1.0 mmol), TBHP (3.0 mmol, 65 wt% in water), catalyst (0.01 g), H_2O (3 mL), 353 K, 24 h; the conversion and yield were determined by GC. [b] Reaction temperature: 303 K; reaction time: 96 h.

into the system was homogenously distributed in the sample on the nanometer scale (Figure S1). As shown in Table 1 (entries 5–8), the nitrogen-doped catalysts (referred to as LC-N-*x*) exhibited remarkably improved catalytic activity as well as a greatly increased acetophenone selectivity. This indicates the effectiveness of nitrogen doping in tuning the reactivity. Moreover, the data did not display a direct correlation between activity and surface area. Instead, the activity and yield of the targeted product appear to be more in line with the nitrogen content (Table 1, entries 4–8). Particularly, LC-N-8.9, which contains 8.9% nitrogen, has an ethylbenzene conversion of 98.6% and an acetophenone yield of 91.3% (Table 1, entry 8). This result is comparable to or even better than those of metal or organometallic complex catalysts.[15] More importantly, in contrast to reactions with conventional catalysts, our reactions were conducted in aqueous phase under milder conditions (353 K) and an alkali-free media. In a further study, we conducted the reaction at an even lower temperature (303 K). To our great surprise 94.0% conversion was still achieved (Table 1, entry 9). Significantly, the nitrogen-doped LC catalysts are easily recovered by filtration with little compromise of catalytic performance (Figure 1).

What makes these N-doped carbon catalysts so active in C–H bond activation? In principle, there are at least four types of N atoms in the carbon framework based on their location: graphitic, pyridinic, pyrrolic, and pyridine oxide like.[16] In order to determine which type(s) of nitrogen species contribute to the improved activity, we characterized the samples by energy-dispersive spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS). As EDS can detect only the presence of nitrogen in the sample (Figure S2), the location of nitrogen in the graphene framework was resolved by an N 1s XPS experiment.[17] As shown in Figure 2, nitrogen preferentially stays at pyridinic sites (398.5 eV) for the sample with 1.1% N (LC-N-1.1), which has a low yield of acetophenone (36.0%). At higher nitrogen content (3.6% for LC-N-3.6), the N atoms tend to occupy the graphitic sites (401.2 eV), and a dramatic increase of acetophenone yield was achieved (84.4%, Table 1, entry 6). We observed that the more nitrogen there was at graphitic sites in the catalyst, the higher the catalytic activity. Indeed, the LC-N-8.9 catalyst displayed the highest catalytic activity. This observation indicates that graphitic nitrogen dopant is critical for the remarkably activity in the C–H oxidation reaction. This claim is further verified by the dramatically improved activity of nitrogen-doped Arc-C (referred to as Arc-C-N), where introduced nitrogen is again mainly at graphitic sites (Table 1, entry 3, and Figure S3).

However, it is still unclear whether these graphitic-type N atoms act as electronic promoters by stimulating the chemical

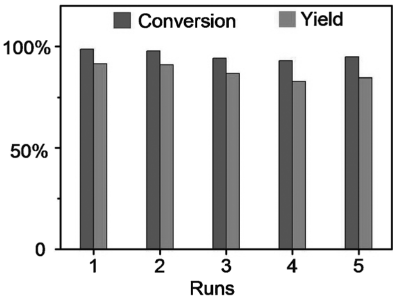


Figure 1. Recovery and reuse of the catalyst LC-N-8.9.

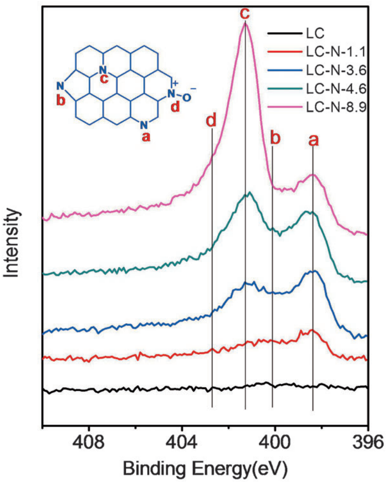


Figure 2. XPS N 1s spectra of LC and LC-N-*x*.

reactivity of adjacent carbon atoms, or whether these atoms themselves participate in the catalytic reaction. To address this issue, we used X-ray absorption spectroscopy (XAS) to study the reaction process (for experimental details see the Supporting Information). Figure 3 shows the C K-edge, and N K-edge XAS spectra of LC, LC-N-8.9, LC treated with the oxidant TBHP (denoted as LC + O), LC-N-8.9 treated with TBHP (LC-N-8.9 + O), and LC-N-8.9 + O reacted with ethylbenzene (LC-N-8.9 + O + EB). It has been reported that some types of imines undergo Ar_2Se_2-mediated oxidation to form the reactive oxaziridines, which then oxidize alkanes to produce desired compounds.[6] In order to find out whether our system also follows a similar mechanism, we investigated the nitrogen species by N K-edge XAS experiments to see whether the reactive oxygen species could be formed on them. As shown in Figure 3 a, almost no signal for nitrogen was detected for LC and LC + O, which is in good agreement with the corresponding N 1s XPS results. For the samples with N dopant, there are peaks at 397.2, 398.3, 400.0, and 405.2 eV, corresponding to the pyridinic C=N π* state, amino-type and C≡N species, graphitic-type N, and the general transition from the N 1s core level to the C−N σ* state (Figure 3 b).[18]

We calculated the theoretical K-edge pattern of the graphitic N site by DFT methods. In Figure 3 b, the dashed blue fitted line shows that a sharp excitonic peak (C−N σ*) appears besides the C=N π* state. Indeed, the experimental curve (blue line) is in good agreement with the simulation, with the other peaks in experimental pattern representing the contributions of other N species. Significantly, the adsorption of the oxidant TBHP and the subsequent reaction with ethylbenzene did not lead to the formation of any new species as there is no evidence of chemical bonding between reactive oxygen and nitrogen. Hence, we concluded that the graphitic-type nitrogen dopant does not directly participate in the activation of C−H bond of the reactant.

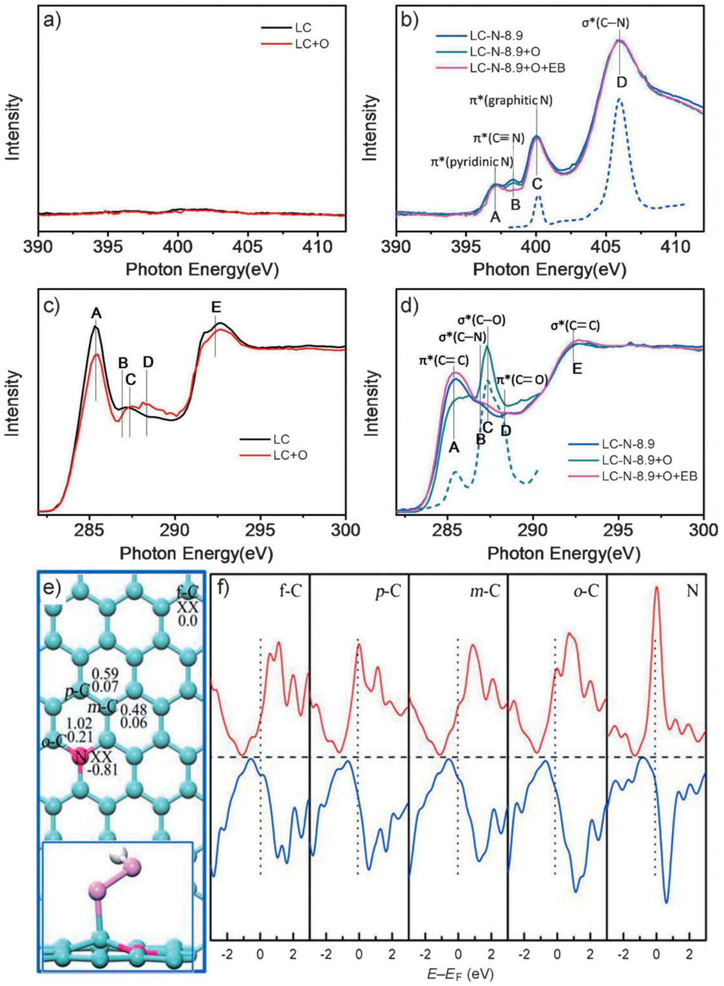


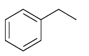
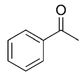
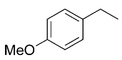
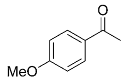
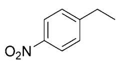
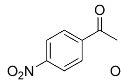
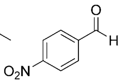
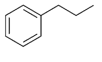
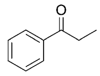
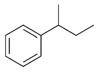
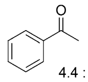
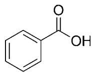
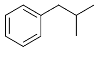
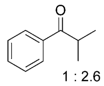
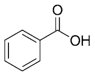
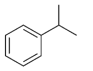
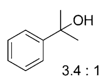
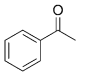
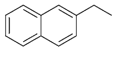
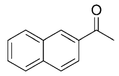
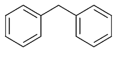
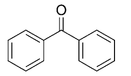
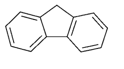
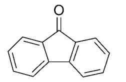
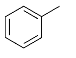
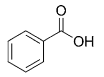
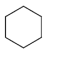
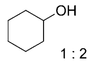
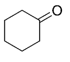
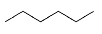
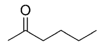
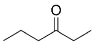
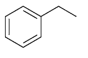
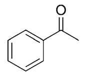
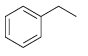
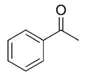
Figure 3. N K-edge (a) and C K-edge XAS spectra (c) of LC and LC + O; N K-edge (b) and C K-edge XAS spectra (d) of LC-N-8.9, LC-N-8.9 + O,and LC-N-8.9 + EB; the blue dashed line in (b) is the DFT-simulated N K-edge XAS spectrum of graphitic N species; the green dashed line in (d) is the DFT-simulated C K-edge XAS spectrum of graphene carbon with a bound peroxo species. e) Schematic representation of different catalytic sites for peroxide adsorption on the N-doped graphene. The adsorption energy is listed in the top line (in eV) beside the corresponding sites; "XX" indicates that peroxide cannot be adsorbed on the site. The charge of different sites before formation of peroxide is shown in the second line (in *e*). The inset at the bottom of (e) shows the local configuration of peroxide on *ortho*-carbon site of N-doped graphene. f) The electronic partial density of states (PDOS) for N and C in different positions of N-doped graphene.

We then examined the C K-edge XAS spectra. As shown in Figure 3 c,d, LC and LC-N-8.9 have at least five peaks. Peak A around 285.4 eV and peak E around 292.5 eV can be assigned to the unoccupied π* and excited σ* states, respectively, in the C_6 cell of graphene, while peaks B and D around 286.9 eV and 288.3 eV are attributed to C−N bonding and the C=O group (π*) in COOH, respectively.[19] Clearly, the reaction with oxidant decreases the intensities of peaks A and E of LC-N-8.9, which indicates the partial breakdown of the π-electron system (sp^2 hybridization). Importantly, we noticed that a sharp peak (peak C) at about 287.2 eV, which was assigned to epoxide or peroxide species in two previous studies,[20] appeared after N-doped layered carbon reacted with the oxidant (LC-N + O). In contrast, for LC + O this peak was rather insignificant and after the reaction with ethylbenzene (LC-N + O + EB), the prominent peak decreased to its original intensity. In the simulated *ortho*-carbon K-edge spectra with or without the adsorption of peroxide, one new sharp peak appears besides the well-known π* peak of graphene (green dashed line in Figure 3 d). Therefore, peak C can be assigned to peroxide-like species. We thus conclude that the difference in the catalytic activities of LC and N- doped LC are due to their different capabilities to promote the formation of reactive oxygen species, peroxide-like species in this case, which is the actual contributing factor for the C−H bond activation.

Therefore, it is clear that the excellent performance of our catalysts is due to the ability of carbon to host the reactive oxygen species with the introduction of nitrogen. But how does carbon gain this property? Is it due to the modulated electronic structure after the introduction of nitrogen dopant? In order to answer these questions, we investigated the electronic partial density of states (PDOS) and the charge of nitrogen and carbon in different positions. The study includes *ortho*-, *meta*-, and *para*-carbon atoms and carbon atoms far away from the doped nitrogen (referred to as *f*-carbon). One obvious difference is identified by the density of states (DOS) near the Fermi level (Figure 3 f). The DOS intensities near the Fermi level for *ortho*-carbon are much stronger than those for the *f*-carbon, which confers the carbon a metal-like d band electronic structure, and therefore, a metal-like catalytic performance. The spin difference of the *ortho*-carbon is also much more pronounced than that of other carbon species. Indeed, it was observed by STM that the local electronic structure around an N dopant in nitrogen-doped graphene is strongly modified, which is in good agreement with our current observations.[21] Moreover, the incorporation of the nitrogen dopant will induce the charge redistribution. Nitrogen has one more electron than carbon and bears a negative charge of 0.81 e. The *ortho*-carbon (average 0.21 e) has much larger compensating positive charge than the *meta*- (0.06 e), *para*- (0.007 e), and *f*-carbons (0.0 e). The spin density due to the unpaired electron is also delocalized mainly onto the *ortho*-carbon (0.17), but other carbon atoms have much smaller spin densities (*m*-C: 0.03; *p*-C: 0.08; *f*-C: 0.0). The unique electronic properties of *o*-carbon modified by the nitrogen dopant make it a superior position for the adsorption of reactive oxygen species such as peroxide. Significantly, peroxide was less likely to be adsorbed on the pristine graphene sheet and the carbon atoms distant from the nitrogen dopant. Meanwhile, the nitrogen atom is also not able to host the peroxide species because of the high negative charge of nitrogen. Instead, peroxide can be adsorbed on the *o*-carbon next to the nitrogen dopant; the adsorption energy is 1.02 eV. After the formation of the peroxide species, the *ortho*-carbon atom moves out of the graphene plane by about 0.42 Å and form a tetrahedral structure, with the distance between the *o*-carbon and the oxygen atom of 1.60 Å. This result is consistent with the experimental results, where, after the formation of the reaction oxygen species, the π^* absorption (285.4 eV) decreased, indicating the partially breakdown of the extended π-electron system. On the *meta*- and *para*-carbon positions, the adsorption energy of peroxide is much weaker than that on *o*-carbon. This demonstrates that *o*-carbon has superior chemical reactivity. The results of O K-edge absorption and FTIR spectroscopy (Figures S4 and S5) support our conclusion based on C K-edge XAS observation and also further support the proposal that the peroxide groups generated on the surface of the catalyst are the active oxygen species on the surface of the nitrogen-doped layered carbon catalyst.

We also investigated the catalytic performance of the N-doped LC materials with different benzylic substrates (Table 2). Significantly, in preliminary experiments (entries 12 and 13) cyclohexane oxidation proceeds with 24.7 % yield while for hexane oxidation, the yield of the products is 7.2 %. This demonstrates that our new metal-free catalysts are not only active for benzylic substrates, but also potentially active for the catalytic oxidation of cyclic paraffins and linear hydrocarbons. Moreover, this catalytic system can also use dioxygen (Table 2, entries 14 and 15) as the oxidant (with a small amount of TBHP as the initiator). In an experiment with 10 mmol ethylbenzene and 10 mL water and a catalyst loading of only 0.01 g, the yield of acetophenone reached around 70 % under 4 MPa O_2 pressure.

Table 2: Oxidation of arylalkanes in the aqueous phase.

Entry	Substrate	Product[a]	Conv. [%]	Yield [%]
1			98.6	91.3
2			85.8	70.7
3		  8.5 : 1	94.1	94.0
4			94.6	77.0
5		  4.4 : 1	92.4	68.9
6		  1 : 2.6	92.1	90
7		  3.4 : 1	97.0	90.9
8			> 99	95.9
9			> 99	> 99
10			97.6	97.5
11			67.5	67.0
12		  1 : 2.7	–	24.7
13[b]		  1 : 1.1	–	7.2
14[c]			78.9	68.3
15[d]			89.6	75.6

[a] Values listed with product mixtures refer to molar ratios. [b] Reaction temperature: 373 K. [c] Reaction conditions: TBHP (3.0 mmol, 65 wt % in water) as initiator, ethylbenzene (10.0 mmol), LC-N-8.9 (0.010 g), H_2O (10 mL), O_2 (4.0 MPa), 373 K, 48 h. [d] TBHP (6 mmol, 65 wt % in water), O_2 (5.0 MPa), the other reaction conditions are same to [c].

Based on these results and discussions, we conclude that the incorporated nitrogen (mostly at graphitic-type sites) in layered carbon catalysts is pivotal for the C−H bond activation reaction. The nitrogen dopant did not participant in the activation of reactant, but instead changed the electronic structure of the adjacent carbon atoms and promoted/stimulated their chemical reactivity. This is the key factor for the success of our metal-free C—H activation catalysts.

Experimental Section

Catalyst preparation: Graphene oxide was generated from natural flake graphite according to a modified Hummers method.[22] Graphene oxide was rapidly heated (20 K min^{-1}) in a quartz tube (under hydrogen flow, 30 mL min^{-1}) and it was transformed into a sootlike carbon material at about 473 K. This material was heated to 1173 K (20 K min^{-1}) under hydrogen flow (30 mL min^{-1}) and kept at that temperature for 10 min. The final product was referred to as layered carbon (LC). Nitrogen was introduced into the framework of LC through a CVD process (1073 K) by using a N_2 stream (40 mL min^{-1}) saturated with acetonitrile vapor (as the nitrogen source, at 293 K). The content of nitrogen in the product can be adjusted by varying the time of the exposure to the acetonitrile/N_2 stream (from 30 min to 900 min). The sample obtained was referred to as LC-N-*x*. For example, the product with 8.9 wt % of nitrogen was denoted as LC-N-8.9. Arc-C-N was prepared by a similar CVD process at 1073 K, although the treatment time is 600 min. Before CVD, Arc-C was heated at reflux in 65 % HNO_3 solution (413 K) for 12 h.

Catalytic reaction: Substrate (1.0 mmol), catalyst (0.01 g), TBHP (3.0 mmol, 65 wt % in water), and water (3 mL) were introduced into a 35 mL glass reactor sealed with Teflon lid (Beijing Synthware Glass, Inc. Pressure Vessel, Heavy Wall). The reaction mixture was heated to the designated temperature in an oil bath and kept at that temperature for a period of time. After that, 0.05 g *n*-dodecane was added to the system as an internal standard and then 10 mL CH_2Cl_2 was added to extract organic compounds in the reaction system. The organic phase was analyzed by Agilent 6820 GC with a HP-5 capillary column and an Agilent GC-MS. For details on the reactions with dioxygen as the oxidant, see the footnotes of Table 2.

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