ACS Catalysis
Research Article
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Selective Allylic Oxidation of Cyclohexene Catalyzed by Nitrogen-Doped Carbon Nanotubes

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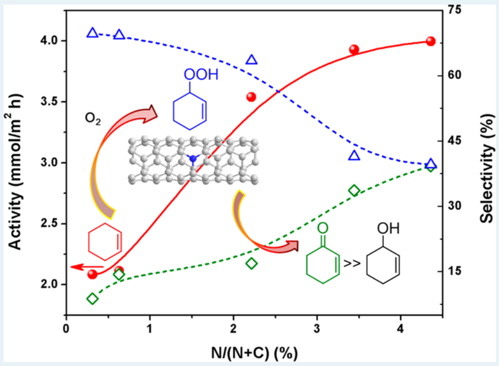
Supporting Information

ABSTRACT: Carbon nanotubes (CNTs) and nitrogen-doped CNTs (NCNTs) were systematically investigated as metal-free catalysts in the selective allylic oxidation of cyclohexene using molecular oxygen as oxidant in the liquid phase. High cyclohexene conversion (up to 59.0%) and 620.1 mmol g^{-1} h^{-1} mass-normalized activity were obtained for NCNTs, competing with the state-of-the-art metal catalysts. The positive effect of nitrogen dopant on the performance of CNTs was demonstrated, with respect to the aspects of enhancing activity and increasing selectivity of 2-cyclohexen-1-one, allowing for a ketone/alcohol ratio of 3.7 at 59% conversion. The unique catalytic role of NCNTs was attributed to their capability to promote the radical chain propagation via stabilizing peroxyl and cycloxyl radicals, which boosted the further conversion of 2-cyclohexen-1-ol toward 2-cyclohexen-1-one as well.



KEYWORDS: *cyclohexene, carbon nanotubes, nitrogen, allylic oxidation, aerobic oxidation*

INTRODUCTION

The interest in nanocarbons as metal-free catalysts has increased rapidly in the past decades due to its high specific surface areas, environmental acceptability, corrosion resistance, thermal stability under nonoxidative conditions, and readily surface modification.[1−3] The defects, structure, and surface chemistry of carbon materials play significant roles in carbon-catalyzed reactions. For instance, the surface defects and carbonyl/quinone groups have been proposed as the active sites for the oxidative dehydrogenation (ODH) of hydrocarbons,[4−6] the activation of methane,[7,8] the hydrogenation of nitrobenzene,[9] and the hydroxylation of benzene to phenol.[10] Carboxylic acid groups on the surfaces of a carbon catalyst were identified as the active sites for the dehydration of alcohols[11,12] and the wet air oxidation of phenols.[13] More remarkably, after it is doped with nitrogen into the carbon skeleton, the catalytic activity might be efficiently enhanced. For instance, N atoms induce more positive charges on the adjacent carbon atoms, thus facilitating oxygen dissociation in the oxygen reduction reaction.[14,15] Recently, we discovered that nitrogen-doped carbon materials have an unexpected activity in the oxidation of hydrocarbons in the liquid phase with oxygen as oxidant.[16−21]

For the oxidative conversion of hydrocarbons toward value-added products, there are two commercial processes (i.e., the noncatalytic autoxidation and the catalytic oxygenation).[22] In autoxidation, peroxide (ROOH) is formed noncatalytically, followed by a subsequent conversion of ROOH to ketone and alcohol. The catalytic process makes use of a radical initiator to accelerate the process via the Harber−Weiss cycle. Carbon nanotubes (CNTs) and their doped derivatives speed up the oxidation of cyclohexane by stabilizing the peroxyl radicals.[18] In this catalysis, the remarkable activity of carbons is due to the charge transfer between CNTs and radicals, facilitated by delocalized electrons in graphene layers.[23] A mechanistic study demonstrated that the role of CNTs is to confine radicals in solvent cages nearby catalyst surfaces, where the αH-abstraction from $C_6H_{11}OOH$ dominates the propagation of a radical chain reaction.[19]

The radical oxidations of hydrocarbons are used not only in the bulk chemical industry but also in the synthesis of value-added fine chemicals.[24,25] The oxidation of cyclic olefin, represented by cyclohexene, produces a variety of oxygen-containing derivatives. Cyclohexene is a promising starting material for one-step production of adipic acid with H_2O_2 as oxidant.[26,27] Cyclohexene can be epoxided to form epoxycyclohexane using hydroperoxide as oxidant.[28,29] The allylic oxidation of cylcohexene is also industrially relevant, because it produces α, β unsaturated alcohol and ketone (i.e., 2-cyclohexene-1-ol and 2-cyclohexene-1-one), which are important intermediates in the fragrance industry and organic synthesis.[25,30] Numerous studies have revealed that the epoxidation of cyclohexene is catalyzed by homogeneous Fe, Mn, Cu, Cr catalysts or their immobilized versions.[31,32] Titanosilicate molecular sieves and metal−organic frameworks are promising solid catalysts for the epoxidation.[33−36] Supported Fe, Co, and Au catalysts have been reported as active for the aerobic oxidation of cyclohexene.[37,38] Recently,

Received: February 12, 2014
Revised: April 4, 2014
Published: April 9, 2014

metal−organic frameworks containing transition metals (e.g., Fe, Cr, Cu, V, etc.) are regarded as active catalysts for the aerobic allylic oxidation of cyclohexene.[39−44] CuO nanorods efficiently catalyzed the conversion into 2-cyclohexene-1-one with more than 95% yield using *tert*-butyl hydroperoxide (TBHP) as oxidant.[45] Hitherto, all the catalytic oxidations of cyclohexene are based on metals as active sites.

In this paper, we present that CNTs and nitrogen-doped CNTs (NCNTs) are active as metal-free catalysts, exhibiting an excellent activity in the allylic oxidation of cyclohexene in the liquid phase using oxygen as oxidant. To the best of our knowledge, it is the first time to demonstrate that the oxidation can be metal-free and catalyzed by nanocarbons with considerable activity, although carbons have been reported as support materials for metal-containing active phases.[46−48] We correlated the catalytic behavior with nitrogen dopant content, defects, and surface functional groups, and we proposed a plausible mechanism for the metal-free catalytic oxidation.

■ EXPERIMENTAL SECTION

Preparation of Catalysts. CNTs were synthesized according to our previous works.[17,18] In brief, CNTs were produced by a chemical vapor deposition (CVD) method with liquefied petroleum gas as carbon source over a FeMo/Al_2O_3 catalyst in a horizontal tubular quartz furnace with 4 cm inner diameter (i.d.). The details of FeMo/Al_2O_3 catalyst can be found in ref 49. Before the growth of CNTs, the catalyst was activated by a mixture of H_2 and N_2 (both at 25 Ncm^3 min^{-1}) for 30 min. The growth of CNTs was carried out at 700 °C for 130 min with 20 Ncm^3 min^{-1} of liquefied petroleum gas, 10 Ncm^3 min^{-1} of H_2, and 50 Ncm^3 min^{-1} of N_2.

The N-doped CNTs were synthesized by a similar CVD method with aniline (AN) and xylene as carbon and nitrogen sources. To grow NCNTs, 10 mL mixtures of AN and xylene, with 0, 10, 50, and 100 vol % AN, were injected by a syringe pump at a rate of 3 mL h^{-1}. The liquid mixtures were vaporized in the quartz tube at about 180 °C. The growth of NCNTs was carried out at 800 °C in Ar or NH_3 at 500 Ncm^3 min^{-1}. The residual FeMo/Al_2O_3 catalyst in the obtained CNTs or NCNTs was removed by 12 mol/L concentrated HCl aqueous solution for 4 h before characterizations and catalytic tests.

The FeO_x/NCNTs were prepared as follows.[17,18] $FeSO_4·7H_2O$ was dissolved into 20 mL of distilled water, and then 3 g of HCl-washed NCNTs were added to form a suspension. After the suspension was ultrasonicated for 5 min, 45 mL of hydrogen peroxide (30%) was added dropwise with vigorous stirring. The resulting suspension was refluxed at 80 °C for 4 h. The solids were collected by filtration, washed with distilled water, and subsequently dried in air at 120 °C for 12 h. The catalyst was then treated with N_2 at 450 °C for 2 h. The FeN_x/NCNTs was synthesized by the same method but treated in NH_3 at 800 °C for 4 h.

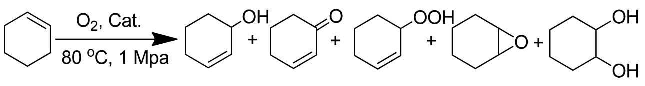
Catalyst Characterization. Brunauer−Emmett−Teller (BET) specific surface areas (SSA) were measured by N_2 adsorption at liquid N_2 temperature in an ASAP 2010 analyzer. Raman spectra were obtained in a LabRAM Aramis micro Raman spectrometer with an excitation wavelength at 633 nm with 2 μm spot size. Transmission electron microscope (TEM) images were obtained with a FEI Tecnai G2 12 microscope operated at 100 kV. The specimens for TEM were prepared by ultrasonically suspending the sample in acetone and depositing a drop of the suspension onto a grid. X-ray photoelectron spectroscopy (XPS) was performed in a Kratos Axis ultra (DLD) spectrometer equipped with an Al Kα X-ray source in ultrahigh vacuum (UHV) (<10^{-10} Torr). Binding energies (±0.2 eV) were referenced to the C_{1s} peak at 284.6 eV as graphite. The concentrations of metal impurities in the catalysts were determined by ICP-AES (Prodigy SPEC Leeman). The surface oxygeneous groups were analyzed by Boehm titration.[50] X-ray diffraction (XRD) patterns were recorded on a Bruker D8 ADVANCE diffractometer equipped with a rotating anode using Cu Kα radiation (40KV, 40 mA).

Cyclohexene Oxidation. The cyclohexene oxidation reaction was carried out in a magnetically stirred 50 mL Teflon-lined autoclave in batch mode. Typically, 10 mL of cyclohexene, 20 mL of acetonitrile, 2 mL of *o*-dichlorobenzene (*o*-DCB) as internal standard, and 50 mg of catalyst were placed into the autoclave. A stirring speed of 1100 rpm was used to minimize the effect of mass transfer[16] and to homogenize the mixture. The amount of catalyst was determined as 50 mg, because an investigation on the effect of catalyst amount shows that there is weak dependence of catalytic results on catalyst amount more than 50 mg, indicating the elimination of liquid−solid contact efficiency (see Figure S1 in Supporting Information). Before the reaction, the reactor was flushed with N_2. Then, the reactor was heated to a stable operational temperature, and subsequently, pure O_2 was fed into the reactor (defining $t = 0$). The oxygen-free cyclohexenyl hydroperoxide decomposition experiment was carried out as follows. After the oxidation was terminated, the reactor was quickly cooled in ice water, and the oxygen was released to ambient pressure. After it was flushed with N_2, the reactor was reheated to 90 °C with 1100 rpm agitation to enable the decomposition of peroxide.[51] The products were analyzed by gas chromatography (GC). To determine the content of cyclohexenyl hydroperoxide, the samples were double analyzed, before and after reducing cyclohexenyl hydroperoxide to 2-cyclohexen-1-ol with triphenyl phosphine (Acros, 99%).[52] Conditions of GC: KB-1701 capillary column (30 m, DF = 0.51 mm, 0.1 μm i.d.), a flame ionization detector (FID). Temperature program was carried out: initial temperature = 120 °C, 4 min; final temperature = 180 °C, heating rate = 10 °C/min, temperature of injector = 280 °C, temperature of detector = 280 °C.

■ RESULTS AND DISCUSSION

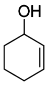
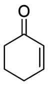
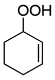
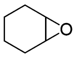
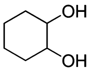
Oxidation of Cyclohexene. Under the reaction conditions investigated, the aerobic oxidation of cyclohexene mainly produced 2-cyclohexen-1-ol, 2-cyclohexen-1-one, cyclohexenyl hydroperoxide, epoxycyclohexane, and 1,2-cyclohexanediol, as summarized by Scheme 1.

Scheme 1. Catalytic Oxidation of Cyclohexene



Catalytic performances of diverse catalysts, including activated carbons (AC), CNTs, and NCNTs are summarized in Table 1. (See Figure S2 in Supporting Information for the TEM images of CNTs and NCNTs.) A blank experiment showed that the noncatalytic autoxidation of cyclohexene gave 13% conversion after 4 h. The addition of undoped CNTs moderately improved the conversion to 21% under the same conditions, slightly higher than AC. Although AC has the larger surface area, the diffusion resistance in micropores might hinder the access to reactants. In addition, the relatively low graphitization degree of AC is adverse to the electron transfer in the radical reaction.[18,19] Significant conversion boosting was observed when NCNTs (with 4.36% N content, see Tables 3 and S1) were used as catalysts. After a 4 h reaction, the conversion was high up to 59%, corresponding to a mass-normalized activity of 620 mmol g^{-1} h^{-1} and a surface area normalized activity of 4 mmol m^{-2} h^{-1}. The activity was comparable with state-of-the-art metal catalysts (see the additional literature survey in Table S2). The oxidation of cyclohenxene over carbons mainly went through allylic oxidation toward 2-cyclohexen-1-ol, 2-cyclohexen-1-one, and cyclohexenyl hydroperoxide, whereas a small portion of epoxidation was observed as well. For example, the epoxidation over NCNTs contributed 5.9% epoxycyclohexane and 0.18%

Table 1. Catalytic Performances of Carbon Materials in Aerobic Cyclohexene Oxidation[a]

Catalyst	BET (m^2/g)	X[b] (%)	r_w[c] (mmol g^{-1} h^{-1})	r_s[d] (mmol m^{-2} h^{-1})	Selectivity [e] (%)					one/ol ratio[f]
										
Blank[g]	—	13.5	—	—	15.5	9.9	67.9	3.0	0.8	0.6
AC	731.5	17.0	99.1	0.1	5.9	7.5	73.0	3.0	2.3	1.3
CNT	127.8	21.0	95.9	0.8	7.1	8.1	62.9	2.2	1.2	1.1
NCNT[h]	155.1	59.0	620.1	4.0	11.2	41.1	27.3	5.9	0.18	3.7
Au/La-OMS[i]	—	48.0	19.7	—	40.3	44.4	—	2.5	—	1.1
Au/Al_2O_3 [j]	258	12.6	16.5	0.06	52.6	32.1	—	—	—	0.61

[a]Conditions: 80 °C, 1 MPa O_2, 8.0 g cyclohexene, 9.6 g acetonitrile, 50 mg catalyst, 2.5 g *o*-DCB as internal standard, 4 h. [b]Conversion. [c]Initial reaction rate of cyclohexene consumption normalized by catalyst mass. [d]Initial reaction rate of cyclohexene consumption normalized by catalyst surface. [e]Selectivity of major products. The byproducts include 2-cyclohexene-1,4-dione, bi-2-cyclohexen-1-yl, adipic acid, and others. [f]The molar ratio of 2-cyclohexen-1-one/2-cyclohexen-1-ol. [g]Without catalyst. [h]The NCNTs were synthesized by 100% AN in NH_3 atmosphere. See Table 3. [I]Conditions: 16.2 g cyclohexene, 20 mg catalyst, 80 °C, and 0.4 MPa O_2, 24 h (ref [63]). [j]Conditions: 16.2 g cyclohexene, 50 mg catalyst, 150 °C, 1.5 MPa O_2, 3 h (ref [64]).

1,2-cyclohexanediol due to hydrolysis.[53] Compared to CNTs, NCNTs displayed the much lower cyclohexenyl hydroperoxide selectivity and a higher selectivity to 2-cyclohexen-1-one, resulting in a higher ketone/alcohol ratio up to 3.7.

The time-dependent formations of the five major products over CNTs and NCNTs are shown in Figure 1. NCNTs displayed an outstanding activity and high yields to allylic oxidation products (e.g., 2-cyclohexen-1-one and cyclohexenyl hydroperoxide). NCNTs have a much higher pseudo-first-order rate constant of 0.19 h^{-1}, 2-fold higher than that of CNTs, 0.075 h^{-1}. The enhancement of nitrogen doping on activity was also evidenced by the Arrhenius plots shown in Figure 2. The apparent activation energy (E_a) was calculated as 32.6 ± 0.03 kJ mol^{-1} for NCNTs, which is much lower than that of CNTs (63.4 ± 0.11 kJ mol^{-1}), indicating the positive effect of NCNTs on reducing the reaction energetic barrier.

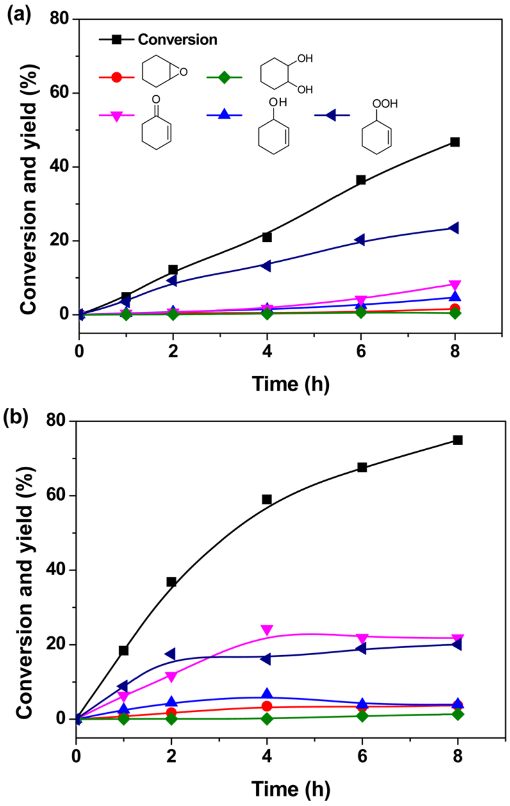


Figure 1. Conversions and product yields for aerobic oxidation of cyclohexene catalyzed by (a) CNT and (b) NCNT (100% AN + NH_3). Conditions: 80 °C, 1 MPa of O_2, 8.0 g of cyclohexene, 9.6 g of acetonitrile, 50 mg of catalyst, 2.5 g of *o*-DCB as internal standard.

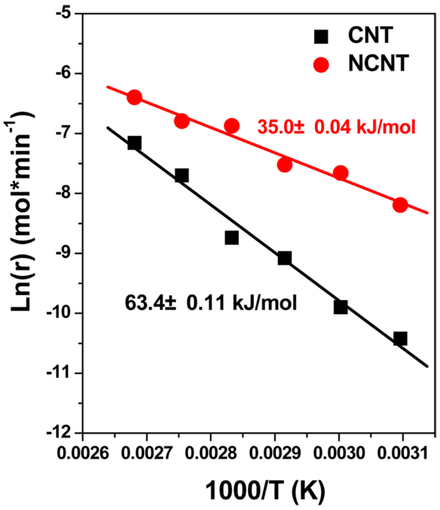


Figure 2. Arrhenius plots of catalytic oxidation of cyclohexene with CNTs or NCNTs (100% AN + NH_3) as catalyst.

On the aspect of selectivity, CNTs and NCNTs showed higher activity toward allylic oxidation than epoxidation. Figure 3 compares the ratio of allylic oxidation products (i.e., 2-cyclohexen-1-ol, 2-cyclohexen-1-one and cyclohexenyl hydroperoxide) to epoxidation products (i.e., epoxide and 1,2-cyclohexanediol). CNTs and NCNTs tend to catalyze cyclohexene to generate allylic products with the maximum allylic/epoxidation ratio up to 20 at about 20% conversion. However, the ratio decreased at high conversions, the decrease is on one hand due to the gradual accumulation of epoxidation products. On the other hand, the allylic products are over oxidized at high conversions to form byproducts, such as 2-cyclohexene-1,4-dione, bi-2-cyclohexen-1-yl, adipic acid, and 7-oxabicyclo-[4,1,0]heptan-2-one,[54,55] which are not included in the calculation of allylic products as indicated by the increased unknown products with conversion in Figure 1.

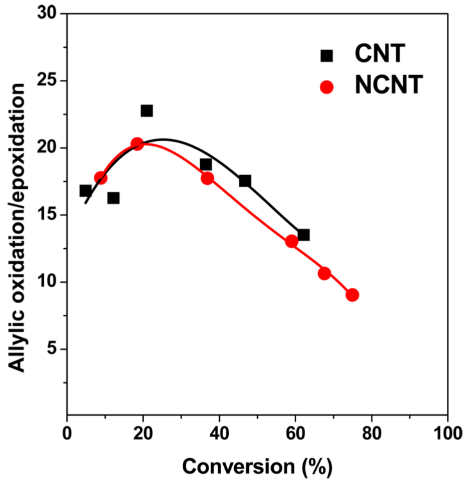


Figure 3. Ratio of allylic oxidation to epoxidation in the oxidation of cylcohexene catalyzed by CNT and NCNT (100% AN + NH_3). The ratio is defined as the molar ratio of allylic products (i.e., 2-cyclohexen-1-one, 2-cyclohexen-1-ol, and cyclohexenyl hydroperoxide) to epoxidation products (i.e., epoxide and 1,2-cyclohexanediol).

Figure 4 shows the dependences of selectivities of allylic products on cyclohexene conversion. When CNTs were used as catalysts, peroxide was the main product. Its highest selectivity was achieved at about 10% conversion, whereas the selectivities of ketone and alcohol maximized at about 55% conversion, displaying a typical characteristic of sequential reaction from cyclohexenyl hydroperoxide to ketone and alcohol. NCNTs showed a quite different product distribution. The highest selectivity of peroxide was achieved at 25% conversion. Under the same conversions, NCNTs provided much higher selectivity to ketone product, meanwhile the selectivity of peroxide was lower than CNTs. As a result, NCNTs offered high ketone/alcohol ratios, indicating the potential selective production of 2-cyclohexen-1-one.

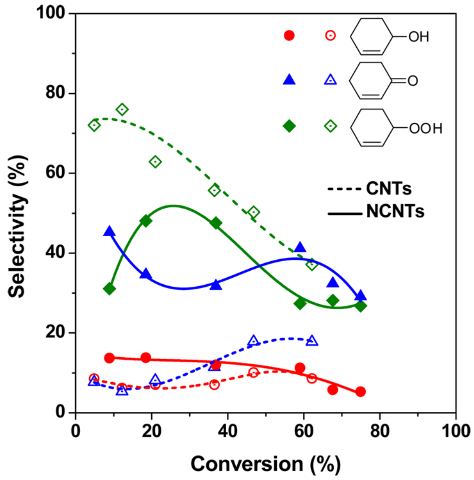
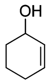
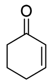
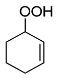
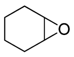
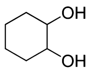


Figure 4. Allylic product distributions of CNTs and NCNTs (100% AN+NH_3) as functions of cyclohexene conversion.

Effects of Metal Oxides and Nitrides. Because there are residual metal catalysts, mainly Fe, in CNTs and NCNTs, their effects should be considered to verify if the catalysis is intrinsically metal-free. To this end, NCNT catalysts with a small amount of iron oxides or iron nitrides were prepared. In addition, the effect of washing with concentrated HCl on the performance of NCNTs was also investigated to directly evaluate the role of residual iron species. As summarized in Table 2, there is no evident difference on the aspects of both conversion and selectivity of products between the as-prepared and HCl-washed NCNTs, indicating a negligible contribution from residual catalysts in NCNTs. In the cases with postloaded iron oxide or iron nitride, (see Figures S3 for their XRD patterns and TEM images) about 3 wt % foreign Fe compounds resulted in a slight decrease of conversion, probably due to the occupation of carbon surfaces by iron species. The above results demonstrated that metals in NCNTs are not the active phase for cyclohexene oxidation; therefore, NCNTs are intrinsically a metal-free catalyst for the oxidation of cyclohexene.

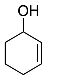
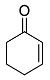
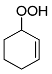
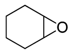
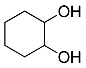
Effect of Nitrogen Content. As mentioned above, NCNTs displayed high activity for the allylic oxidation of cyclohexene. We further investigated the role of nitrogen content on catalytic performance to achieve an optimal catalyst. The nitrogen content in NCNTs can be tuned by the composition of precursor and reaction atmosphere, as reported by our previous work.[17] Table 3 shows the catalytic performances of the NCNTs with different nitrogen content. The doping of nitrogen heteroatoms effectively increased the conversion of cyclohexene. For the N-CNTs synthesized with aniline as the sole nitrogen source, the conversion of cyclohexene gradually increased with the content of aniline in the precursor. The selectivity of peroxide varied in the range of 62−70%, and the ketone/alcohol ratio increased from 0.9 to 1.9. The introduction of NH_3 significantly boosted the cyclohexene oxidation. The conversion increased by 2-fold when switching the nitrogen source from aniline to gaseous ammonia, due to the remarkably increased SSA. Meanwhile, the selectivity of

Table 2. Effect of Metal Residuals on Cyclohexene Oxidation Catalyzed by NCNTs[a]

Catalyst	Fe amount[b] (wt%)	X (%)	Selectivity[c] (%)				
							
NCNT-p[d]	0.263	55.2	10.2	36.1	32.4	4.2	1.7
NCNT-w[e]	0.015	54.4	11.4	38.8	35.2	4.5	1.3
FeOx/NCNT	3.284	53.2	11.0	35.2	36.3	3.9	1.2
FeNx/NCNT	3.682	49.2	12.1	39.0	29.6	4.4	1.0

[a] Conditions: 80 °C, 1 MPa of O_2, 8.0 g of cyclohexene, 9.6 g of acetonitrile, 50 mg of catalyst, 2.5 g of *o*-DCB as internal standard, 4 h. The NCNTs were synthesized by xylene in the NH_3 atmosphere. See Tables 3 and S1. [b] Measured by ICP-AES. [c] Selectivity of major products. The byproducts include 2-cyclohexene-1,4-dione, bi-2-cyclohexen-1-yl, adipic acid, and others. [d] As-prepared NCNTs. [e] HCl-washed NCNTs.

Table 3. Effect of Nitrogen Content of NCNTs on the Aerobic Oxidation of Cyclohexene[a]

Synthesis condition [b]	SSA (m^2/g)	X[c] (%)	r_w[d] (mmol g^{-1} h^{-1})	r_s[e] (mmol m^{-2} h^{-1})	Selectivity[f] (%)					one/ol ratio[g]
										
0%AN+Ar	27.0	15.9	84.8	3.1	18.5	9.7	66.1	2.7	1.4	0.5
10%AN+Ar	48.5	17.6	101.0	2.1	10.0	8.7	70.1	2.6	0.9	0.9
50%AN+Ar	71.2	21.9	150.4	2.1	10.1	15.4	69.2	2.9	1.2	1.5
100%AN+Ar	49.3	25.4	174.4	3.5	8.8	16.9	62.9	2.8	1.1	1.9
0%AN+NH_3	129.3	54.4	508.1	3.9	11.4	38.8	35.2	4.5	1.3	3.4
100%AN+NH_3	155.1	59.0	620.1	4.0	11.2	41.1	27.3	5.9	1.6	3.7

[a] Conditions: 80 °C, 1 MPa of O_2, 8.0 g of cyclohexene, 9.6 g of acetonitrile, 50 mg of catalyst, 2.5 g of *o*-DCB as internal standard, 4 h. [b] The volume fraction of aniline in precursor + reaction atmosphere. [c] Cyclohexene conversion. [d] Initial reaction rate of cyclohexene consumption normalized by catalyst mass. [e] Initial reaction rate of cyclohexene consumption normalized by catalyst surface. [f] Selectivity of major products. The byproducts include 2-cyclohexene-1,4-dione, bi-2-cyclohexen-1-yl, adipic acid, and others. [g] The molar ratio of 2-cyclohexen-1-one/2-cyclohexen-1-ol.

peroxide decreased to 35%, and the selectivity of 2-cyclohexen-1-one increased to 39%, resulting in the higher ketone/alcohol ratio of 3.4. The highest reaction rate per gram of catalyst, 620.1 mmol g^{-1} h^{-1}, was achieved over the sample synthesized with aniline in NH_3. These results evidently showed that the performances of NCNTs can be tuned by the synthesis conditions.

Figure 5 shows the dependences of surface-area-normalized activity and selectivities of allylic products on the nitrogen content in NCNTs. The nitrogen contents were measured by XPS, as reported elsewhere (ref 17, see also Table S1 for quantitative XPS results). It is clearly shown that the nitrogen content is beneficial for the specific activity of NCNTs, demonstrating the positive effect of nitrogen heteroatoms. Meanwhile, the selectivity of 2-cyclohexen-1-one, at 20% conversion, increased with nitrogen content from 9% to 40% as the nitrogen content changed from 0.3% to 4.36%, evidencing the improved production of the ketone product. It is interesting to investigate the dependence of catalytic performances on specific type of the nitrogen functionalities (e.g., pyridinic and quaternary nitrogens), which are commonly regarded as active sites for nitrogen-doped carbon materials.[56,57] However, on the current stage, we have not drawn any conclusion about the separate role of the specific functionality yet (see Figure S4), because all nitrogen functionalities simultaneously increased with the gross nitrogen content in the NCNTs synthesized by the CVD method described here. To this end, the controllable synthesis of NCNTs with a specific type of nitrogen group is desirable in the future.

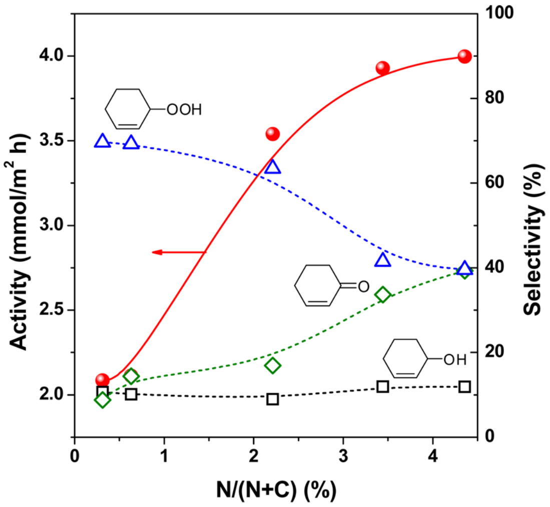


Figure 5. Dependences of activity and selectivities of allylic products on the gross nitrogen content in NCNTs. The selectivities were obtained at similar cyclohexene conversion of about 20%.

Effects of Defects and Oxygen Functional Groups. The oxygen functional groups, such as Lewis basic C═O sites, on carbon surfaces have been proved responsible for activating hydrocarbons in the ODH of aromatic hydrocarbons[58] and alkanes[5] in the gas phase. It is interesting to investigate if the performance of NCNTs in the cyclohexene oxidation can be improved by introducing oxygen-containing groups. As shown in Table 4, a negative effect of oxygen functionalities on the cyclohexene conversion were observed, although the HNO_3 treatment significantly increased the SSA and defectiveness indicated by Raman I_D/I_G values. Annealing NCNTs at above 600 °C decomposes the oxygenous groups and repairs the defects, indicated by the decrease of I_D/I_G ratios with elevating annealing temperature.[18] The conversion of cyclohexene increased with annealing temperature, suggesting that defects are not the active sites of the oxidation of cyclohexene, agreeing with the previous observation in the oxidations of cyclohexane and ethylbenzene.[18,21] Hence, it may be expected that the electronic interaction between reactive intermediates (e.g., radicals) and graphene planes with high electron conduction plays a critical role,[16−18] as further discussed in the following subsection.

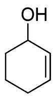
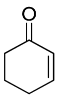
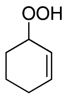
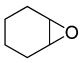
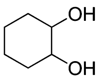
Reusability of NCNTs. The stability of a catalyst is an important consideration for its commercialization. We selected NCNTs to evaluate the reusability for five runs. After each run, the recycled catalyst was repeatedly washed by deionized water and acetone, then dried at 110 °C overnight. The catalytic results are shown in Figure 6. Obviously, NCNTs showed outstanding recyclability. After five recycles, there was no noticeable decrease in both the conversion of cyclohexnene and selectivities of allylic oxidation products, demonstrating their stability under the reaction conditions.

Reaction Mechanism. It is widely accepted that the oxidation of alkene in the liquid phase is a radical reaction, which is summarized by eqs 1−9 as follows.[24,25,59−61]

$$\text{Initiation: RH} + \text{initiator} \rightarrow \text{R}^{\bullet} + \text{H} - \text{initiator} \tag{1}$$

$$\text{Propagation: R}^{\bullet} + \text{O}_2 \rightarrow \text{ROO}^{\bullet} \tag{2}$$

Table 4. Properties and Performances of NCNTs in the Aerobic Oxidation of Cyclohexene with Different HNO_3 Oxidation Durations and Annealing Temperatures[a]

HNO_3 reflux[b] (h)	Annealing[c] (K)	SSA (m^2/g)	Raman I_D/I_G	Boehm titration (mmol g^{-1})			X (%)	Selectivity (%)				
				-OH	-C=O	-COOH						
0	333[d]	88.3	1.32	0.26	0.19	0.10	59.0	11.2	41.1	27.3	5.9	1.3
0.5	333[d]	153.9	1.63	0.47	0.69	0.34	52.6	9.0	31.6	31.1	5.0	0.7
4	333[d]	176.8	1.64	0.73	1.15	0.65	44.9	8.1	32.1	45.5	4.8	1.5
7	333[d]	179.7	1.67	0.74	1.22	1.03	35.6	7.8	30.0	43.1	4.6	1.5
7	873	196.6	1.58	n.d.[e]	n.d.	n.d.	48.2	6.7	32.7	44.2	6.0	1.1
7	1173	207.1	1.48	n.d.	n.d.	n.d.	52.1	7.3	34.2	36.2	6.1	1.6
7	1373	248.7	1.43	n.d.	n.d.	n.d.	55.6	6.6	36.8	37.8	5.8	1.6

[a] Conditions: 80 °C, 1 MPa of O_2, 8.0 g of cyclohexene, 9.6 g of acetonitrile, 50 mg of catalyst, 2.5 g of *o*-DCB as internal standard, 4 h. The NCNTs synthesized with 100% AN in NH_3 were used as the base case. [b] 9 M HNO_3, 110 °C. [c] In Ar gas for 4 h. [d] Vacuum drying at 60 °C overnight. [e] Not detected.

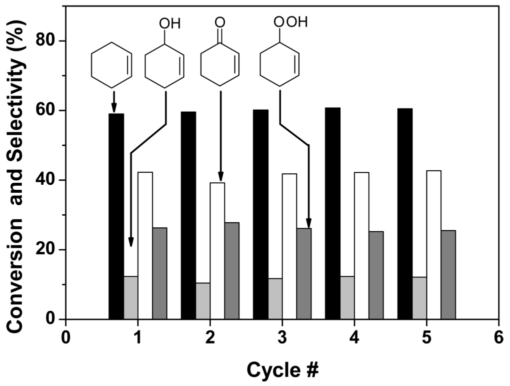


Figure 6. Recyclability of NCNTs (100% AN + NH_3) in the liquid-phase allylic oxidation of cyclohexene.

$$ROO^{\bullet} + RH \rightarrow ROOH + R^{\bullet} \tag{3}$$

$$ROOH \rightarrow RO^{\bullet} + {}^{\bullet}OH \tag{4}$$

$$RO^{\bullet} + RH \rightarrow ROH + R^{\bullet} \tag{5}$$

$${}^{\bullet}OH + RH \rightarrow H_2O + R^{\bullet} \tag{6}$$

$$\text{Termination: } R^{\bullet} + R^{\bullet} \rightarrow R - R \tag{7}$$

$$ROO^{\bullet} + ROO^{\bullet} \rightarrow ROH + R = O + O_2 \tag{8}$$

$$ROO^{\bullet} + R^{\bullet} \rightarrow ROOR \tag{9}$$

Among these elementary steps, the propagation steps are rate-determining. Increasing the stability of peroxyl radicals usually favors the overall rate.

The radical nature of the carbon-catalyzed oxidation of cyclohexene was verified by testing the effect of the radical scavenger. As shown in Table 5, the addition of *p*-benzoquinone, a typical radical scavenger, dramatically suppressed the conversion of cyclohexene from 59% to 2.2%, even lower than that of the blank experiment in Table 1. It strongly indicates the dominant role of radical reactions in this oxidation. We also compared the performances of oxidations started from various products to determine how carbon was involved in this reaction. It has been reported that the 2-cyclohexen-1-ol can be oxidized to 2-cyclohexen-1-one with proper catalysts.[62] However, in our reaction, activity was observed neither in the cases from 2-cyclohexen-1-ol nor 2-cyclohexen-1-one and epoxycyclohexane as substrate, indicating that the participation of reactive radicals is prerequisite of the catalytic role of NCNTs, which should be derived from cyclohexene or its peroxide. Thus, the carbon−radical interaction should be essential for this process, as revealed in the oxidation of cyclohexane.[16−20]

Table 5. Catalytic Activities of Oxidations of Various Substrates Catalyzed by NCNTs (100% AN + NH_3)[a]

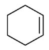
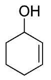
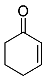
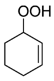
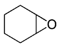
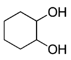
substrate	additive	%
cyclohexene[b]	——	59.0
cyclohexene[b]	*p*-benzoquinone	2.2
2-cyclohexen-1-ol	——	<1
2-cyclohexen-1-one	——	<1
epoxycyclohexane	——	<1

[a] Conditions: 80 °C, 1 MPa of O_2, 10 mmol of substrates, 9.6 g of acetonitrile, 50 mg of catalyst, 2.5 g of *o*-DCB as internal standard. [b] 8.0 g of cyclohexene.

It is known that sp^2 carbons catalyze the decomposition of peroxides via an electron-transfer catalysis process,[16] which has been proposed to be responsible for the formation of alcohol and ketone from cyclohexyl hydroperoxide in the oxidation of cyclohexane.[19] The decomposition reaction of cyclohexenyl hydroperoxide stoichiometrically produces equimolecular alcohol and ketone. Usually, the noncatalytic autoxidation offers an one/ol ratio in the range from about 0.77 to 1.1.[51] As shown in Table 3, the one/ol ratio in the NCNT-catalyzed oxidation of cyclohexene can reach 3.7 in the case of high nitrogen content.

The oxidation of 2-cyclohexen-1-ol has demonstrated that the higher ketone selectivity was not caused by the direct oxidation of alcohol toward ketone (see Table 5). To further verify if the higher ketone selectivity was caused by NCNT-catalyzed decomposition of cyclohexenyl hydroperoxide, an anaerobic decomposition of the peroxide was conducted. As shown in Table 6, the 24 h postdecomposition of cyclohexenyl hydroperoxide caused an obvious decrease of peroxide concentration and increased concentrations of alcohol and ketone, whereas the epoxidation products remained unchanged. The ratio of their generated amounts was 0.86, which is around 1 and much lower than the one/ol ratio from the oxidation reaction. It indicates that the high one/ol ratio was an intrinsic feature of NCNT-catalyzed oxidation of cyclohexene. This result also proves that the epoxide was not formed directly through the peroxide as described in the previous report[63] but rather through the direct oxidation of cyclohexene by molecular oxygen.[62]

Table 6. Decomposition of Cyclohexenyl Hydroperoxide in the Product of the Oxidation of Cyclohexene Catalyzed by NCNTs (100% AN + NH_3)[a]

Time (h)	Concentration (mol/L)						Δone/Δol[b]
							
$t = 0$ [c]	1.27	0.202	0.774	0.507	0.136	0.029	--
$t = 24$ [c]	1.04	0.438	0.977	0.193	0.090	0.030	0.86

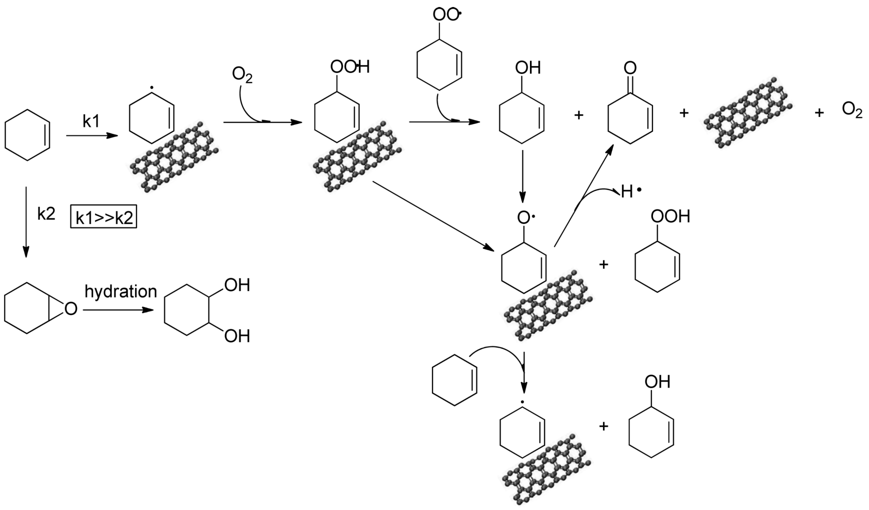
[a]Conditions: 80 °C, 1 MPa of O_2, 8.0 g of cyclohexene, 9.6 g of acetonitrile, 50 mg of catalyst, 2.5 g of *o*-DCB as internal standard. After reaction, the mixture was cooled quickly in the ice water, and the oxygen was released to ambient pressure. After it was flushed with N_2, the reactor was reheated to 90 °C with 1100 rpm agitation to enable the decomposition of hydroperoxide. [b]The molar ratio of 2-cyclohexen-1-one/2-cyclohexen-1-ol. [c]The time for the decomposition of cyclohexenyl hydroperoxide.

A plausible mechanism was proposed to elucidate the observed selectivity pattern. As shown in Scheme 2, cyclohexene is oxidized by molecular oxygen via allylic oxidation and epoxidation routes. However, with CNTs/NCNTs as catalysts, the former is much faster, allowing for a selective allylic oxidation of substrate. The cyclohexenyl radical formed due to pyrolysis may be stabilized by CNTs/NCNTs, then the formation of peroxyl radicals is facilitated by the insertion of oxygen. The chain reaction propagates via the reactions shown in eqs 2–6. The termination of two peroxyl radicals on the surfaces of CNTs allows for the formation of alcohol and ketone. Due to the stabilization effect of CNTs and NCNTs on the radicals, the probability of forming alcohol and ketone is enhanced, thus the overall reaction rate is improved. On the other hand, the stabilized peroxyl radicals may react with alcohol products to generate alkoxyl radicals, due to their strong ability to abstract α-hydrogen. The alkoxyl radicals undergo further propagation by abstracting a hydrogen atom from cyclohexene substrate, as eq 5. Meanwhile, the alkoxyl radicals may be converted to ketone product through the abstraction of the weakly bonded αH atom by O_2.[24] This reaction consumes alcohol product and results in the higher one/ol ratio. In this process, the consumption of alcohol is obviously determined by the extent to which peroxyl and alkoxyl radicals are stabilized and their sequential reactions are improved. Hence, doping CNTs with nitrogen facilitates the formation of 2-cyclohexen-1-one, because it may enhance the interaction between radicals and carbons.

■ CONCLUSIONS

We demonstrated that CNTs and NCNTs are efficient metal-free catalysts for the aerobic allylic oxidation of cyclohexene toward the production of corresponding unsaturated ketone and alcohol. Pristine CNTs produce cyclohexenyl hydroperoxide as the major product with 60–66% selectivity at about 20% conversion. Nitrogen dopant significantly enhances the mass specific activity by up to 6-fold. The selectivity pattern of allylic products is altered by nitrogen dopant as well, featured by the considerably improved ketone/alcohol ratio. A systematic investigation on the effects of nitrogen content, residual metals, defects, and oxygenous groups indicated that the electronic interaction between radicals and carbon catalysts plays a central role in this reaction. The excellent activity and reusability of NCNTs suggest a promising new catalyst for the selective production of unsaturated ketone via allylic oxidation by using molecular oxygen as ultimate oxidant.

Scheme 2. Proposed Reaction Pathways of the NCNT-Catalyzed Oxidation of Cyclohexene



■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Effect of the catalyst amount, XPS, TEM, and XRD results for CNTs, NCNTs and metal-loaded NCNTs. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the National Science Foundation of China (nos. 21133010, 21273079), the Guangdong Provincial National Science Foundation of China (nos. 9251064101000020, S20120011275), Program for New Century Excellent Talents in University (NCET-12-0190), and the Fundamental Research Funds for the Central Universities of China (no. 2014ZG0005).

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