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Aerobic Oxidation of α-Pinene Catalyzed by Carbon Nanotubes

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Abstract

Carbon nanotubes (CNTs) and nitrogen-doped CNTs (NCNTs) as metal-free catalysts exhibited excellent activity in the selective oxidation of α-pinene with molecular oxygen as the terminal oxidant. Two distinct pathways, i.e. epoxidation and allylic oxidation, were active in this reaction. An enhancement of epoxidation was observed over CNTs, affording the highest epoxidation/allylic oxidation products ratio. Excellent activity were achieved over NCNTs, displaying 54.5% α-pinene conversion and 272.4 mmol g^{-1} h^{-1} mass-normalized activity, which is competing with the state-of-the-art metal catalysts. The allylic oxidation was enhanced over NCNTs, through which equimolar amounts of epoxide and allylic products are produced. Thus, N-doping boosted the overall conversion and the yields of both of the epoxidation and allylic oxidation products, which are supported by theoretical simulation results.

Keywords: α-Pinene; Carbon catalysis; Nitrogen doping; Epoxidation; Molecular dynamics

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1. **Introduction**

Selective oxidation of hydrocarbons towards oxygenated derivatives is a significant chemical value-chain as the relatively cheap molecules can be converted into value-added products.[1-3] Molecular oxygen is the most promising oxidant from the viewpoint of green chemistry and economy. Most of the aerobic oxidations have been proved to be the radical autoxidation, which can be accelerated by metal catalysts through the Harber-Weiss cycle.[2, 4]

The oxidation of cycloolefins yields the corresponding epoxides and allylic oxidation products.[3, 5] The allylic oxidation is usually dominant for cycloolefins with monocyclic structure, e.g. cyclohexene,[6] in which 2-cyclohexene-1-one and 2-cyclohexene-1-ol are produced through the decomposition of cyclohexene hydroperoxide, an important stable intermedium.[7] Meanwhile, trace amounts of epoxide products may be produced as well.[7] Cycloolefins with complex structure, e.g. terpene substrates, tends to be oxidized to form epoxidation products, which has been revealed in α-pinene oxidation.[3, 8] The oxidation of α-pinene displays complex product distributions, since the oxidation may occur at four possible sites in the molecule as shown in Scheme 1. O_2 addition to allyl radicals will generate peroxyl radicals.[3] After that, peroxyl radical added to the C=C double bond of substrate moleculer was proceeded, yielding a dialkyl peroxide, which can eliminate an alkoxyl radical to favorably form α-pinene oxide, an origin of the epoxidation products.[3]

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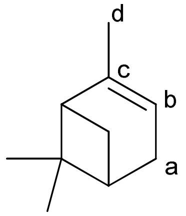

Scheme 1 Molecular structure of α-pinene and its four possible oxidation sites (denoted as a–d).[8]

The aerobic oxidation of α-pinene is of great interest for the research and industrial communities. The allylic oxidation of α-pinene is industrially relevant, because it produces α, β unsaturated alcohol and ketone, i.e. verbenone and verbenol, which are important intermediates in fragrance industry and organic synthesis.[9] The epoxidation product, α-pinene oxide, can be isomerized to campholenic aldehyde, an intermediate in the synthesis of sandalwood-like fragrances, such as Sandalores (Givaudan) or Polysantols (Firmenich).[10] The products can be isolated from the auto-oxidation of α-pinene with air, but the yields are usually low.[11] Numerous studies have revealed that the oxidation of α-pinene can be catalyzed by solid catalysts containing Co, Au, Mn, Rh, Ti, V, etc..[12-21] For example, the silica–titania co-gel catalyst afforded high selectivity (ca. 60%) to verbenone for the allylic oxidation of α-pinene.[21] Timofeeva et al. used vanadium-containing nickel phosphate molecular sieves to catalyze the α-pinene oxidation, giving about 48% allylic oxidation products.[22] Also, molecular sieves are promising solid catalysts for the epoxidation.[23] Trong et al. have utilized modified Ti-MCM-41 for the oxidation of α-pinene to α-pinene oxide with 100% selectivity using *t*-butyl hydroperoxide as oxidant.[23] So far, metal catalysts played central role in the

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catalytic oxidation of α-pinene.

Nanocarbons have attracted great attentions from the research and industrial communities in the past two decades as metal-free catalysts, due to their unique chemical and physical properties.[24-26] It has been proved that the defects and surface functionalities of carbon materials play significant roles in the oxidative dehydrogenation (ODH) of hydrocarbons,[27-29] the activation of methane,[30, 31] the hydrogenation of nitrobenzene,[32] the hydroxylation of benzene to phenol,[33] the oxidation of arylalkanes,[34] the dehydration and oxidation of alcohols,[35-38] the Baeyer−Villiger oxidation[39] and the wet air oxidation of phenol.[40] Our previous works have revealed that carbon materials and its nitrogen-doped derivatives showed unexpected activities in the selective oxidation of hydrocarbons in the liquid-phase with oxygen as oxidant.[41-46] Especially, nitrogen doped CNTs (NCNTs) displayed excellent performances in the allylic oxidation of cyclohexene, resulting in the high 2-cyclohexene-1-none selectivity.[6] The remarkable activity of carbons is due to the charge transfer between CNTs and radicals, facilitated by delocalized electrons in graphene layers.[47] It is believed that they promote the radical chain propagation via stabilizing peroxyl and cycloxyl radicals.[6] Recently, nitrogen doped nanocarbons were discovered as efficient catalysts for the epoxidation of trans-stilbene and styrene using tert-butyl hydroperoxide (TBHP) as oxidant.[48, 49] The quaternary nitrogen species is responsible for the epoxidation. These studies proposed a new approach for the alkene oxidation catalyzed by nanocarbons.

In this work, CNTs and NCNTs were used as metal-free catalysts, which displayed

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excellent activity in the oxidation of α-pinene in the liquid phase using oxygen as oxidant. To our best knowledge, it is the first time to demonstrate the α-pinene oxidation can be metal-free catalyzed by nanocarbons with considerable activity. The carbon skeleton is the key essential for the epoxidation, based on the unique structure of α-pinene molecule. Nitrogen dopants in carbon skeletons can efficiently enhance the allylic oxidation through stabilizing peroxyl and cycloxyl radicals. A plausible mechanism was proposed for the metal-free catalytic oxidation according to catalytic results and theoretical calculation.

2. Experimental

2.1 Preparation of catalysts

CNTs were synthesized according to our previous works.[42, 43] 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.[50] Before the growth of CNTs, the catalyst was activated by a mixture of H_2 and N_2 (25 and 25 Ncm^3 min^{-1}) for 30 min. The growth of CNTs was carried out at 700 ^{o}C for 130 min with 20 Ncm^3 min^{-1} liquefied petroleum gas, 10 Ncm^3 min^{-1} H_2, and 50 Ncm^3 min^{-1} N_2.

N-doped CNTs were synthesized by a similar CVD method using 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 v% 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 ^{o}C. The growth of NCNTs was carried out at 800 ^{o}C in Ar or NH_3 at 500 Ncm^3 min^{-1}. The residual

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$FeMo/Al_2O_3$ catalyst in the as-synthesized CNTs or NCNTs was removed by 12 mol/L concentrated HCl aqueous solution for 4 h before characterizations and catalytic tests.

FeO_x/NCNTs were prepared as follows.[42, 43] $FeSO_4\cdot 7H_2O$ was dissolved into 20 mL distilled water, and then 3 g HCl washed NCNTs were added to form suspension. After ultrasonicated for 5 min, 45 mL hydrogen peroxide (30%) was added dropwise with vigorous stirring. The resulting suspension was refluxed at 80 ^oC for 4 h. The solids were collected by filtration and washed with distilled water, and subsequently dried in air at 120 ^oC for 12 h. After that, the catalyst was treated with N_2 at 450 ^oC for 2 h. The FeN_x/NCNTs was synthesized by the same method but treated in NH_3 at 800 ^oC for 4 h.

To study the effect of Mo impurities, the NCNT was firstly purified in concentrated HCl for 4 h, then impregnated with ammonium molybdate ($(NH_4)_6Mo_7O_{24}\bullet 4H_2O$). The solids were washed and dried at 60 ^oC overnight, then were heated in Ar at 500 ^oC for 3 h and NH_3 at 800 ^oC for 3 h to obtain MoOx/NCNTs and MoNx/NCNTs, respectively.

2.2 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. 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.[51] X-ray diffraction (XRD) patterns were recorded on a Bruker D8 ADVANCE diffractometer equipped with a rotating anode using Cu Kα radiation (40KV, 40mA). Raman spectra were obtained in a

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LabRAM Aramis micro Raman spectrometer with an excitation wavelength at 633 nm with 2 μm spot size. X-ray photoelectron spectroscopy (XPS) was performed in a Kratos Axis ultra (DLD) spectrometer equipped with an Al Ka 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. 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.

2.3 α-Pinene oxidation

The α-pinene oxidation reaction was carried out in a magnetically stirred 50 mL Teflon-lined autoclave in batch mode. Typically, 10 mL α-pinene, 20 mL solvent, 2 mL o-dichlorobenzene (o-DCB) as internal standard and 70 mg catalyst were placed into the autoclave. 1100 rpm stirring speed was used to minimize the effect of mass transfer and homogenize the mixture. Before 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). To determine verbenyl-hydroperoxide, the samples were double analyzed, before and after reducing verbenyl-hydroperoxide to verbenol with triphenyl phosphine (Acros, 99%) [52]. Conditions of GC: KB-1701 capillary column (30 m, DF=0.51 mm, 0.1 um i.d.), a flame ionization detector (FID). Temperature program was carried out: initial temperature = 170 ^{o}C, 4 min; final temperature = 250 ^{o}C, heating rate =

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10 °C/min, temperature of injector = 280 °C, temperature of detector = 280 °C.

2.4 Theoretical calculation

Molecular dynamics simulations were performed with Forcite package in Materials Studio. A (5,5) CNT, extended to a supercell of (1*1*20), was employed in three-dimensional period boundary conditions with a size of 30 Å × 30 Å × 49.19 Å. Optimized radical molecules were set into the box, so as to investigate interactions in the system. Graphitic nitrogen doped CNTs (N-CNT) was selected as the comparative material. In details, 15 nitrogen atoms dispersedly in the CNT skeleton, displaying an N atom ratio of 3.75%.

The system was simulated with NVT ensemble at 353 K through Nosé-Hoover-Langevin (NHL)[53-55] thermostat with the decay constant of 1.0 ps. All structures were assigned with COMPASS[56] force field. Simultaneously, for an exception, carbon radical was set to c3 type (generic sp2 hybridization with 3 bonds) to maintain the lone electron. The summation of electrostatic potential and van der Waals potential were both calculated through Ewald method with the accuracy of $1.0*10^{-5}$ kcal/mol. Total simulation time was 400 ps, where 100 ps was used for equilibrium of system and 300 ps for dynamics analysis. The simulation step was 1.0 fs and outputting a trajectory frame at each 2.0 ps.

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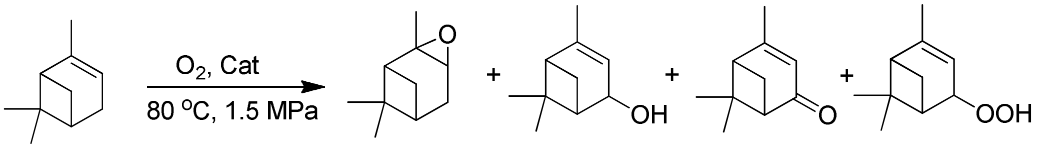
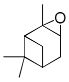
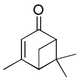
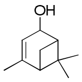
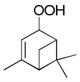
3. Results and discussion

3.1. Oxidation of α-pinene



Scheme 2 Catalytic oxidation of α-pinene.

Table 1 Catalytic performance of the carbons and metal catalysts in the α-pinene oxidation[a]

Catalyst	S_{BET} (m^2/g)	$X^{[b]}$ (%)	r_w[c] (mmol g^{-1} h^{-1})	r_s[d] (mmol m^{-2} h^{-1})	Selectivity [e] (%)				E/A Ratio[f]
									
Blank[g]	—	10.3	—	—	24.5	11.7	15.0	40.4	0.9
AC	731.5	19.1	45.0	0.03	38.2	6.8	5.9	26.7	3.0
CNT	127.8	24.6	43.0	0.34	33.8	7.9	6.1	37.9	2.4
NCNT[h]	155.1	54.5	272.4	1.76	37.8	14.1	17.5	15.3	1.2
Co-HMS[i]	1071	34.2	3.6	0.3	34	22	16	—	0.9
MnAlPO-36[j]	—	59	75.8	—	91	—	—	—	—
Co-POM/MIL-101[k]	2050	45	1.6	0.08	—	27	29	—	—

[a] Conditions: 80 °C, 1.5 MPa O_2, 10 mL α-pinene, 20 mL CH_3CN, 2 mL o-DCB, 70 mg catalyst, 4 h. [b] Conversion. [c] Initial reaction rate of α-pinene consumption normalized by catalyst mass. [d] Initial reaction rate of α-pinene consumption normalized by catalyst surface. [e] Selectivity of major products. The by-products include pinocarveol, pinenol, myrtenal and others. [f] E/A ratio means the

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molar ratio of epoxidation products, i.e. α-pinene oxide, to allylic oxidation products, i.e. verbenol and verbenone. [g] Without catalyst. [h] The NCNTs were synthesized by 100% AN in NH_3 atmosphere. [i] Ref. [57]. Conditions: 3.97 mL α-pinene, 100 mg catalyst, 40 mL 1,4-dioxane, 80 ^{o}C, atmospheric pressure, 24 h. [j] Ref. [58]. Conditions: 40 mL α-pinene, 250 mg catalyst, 50 ^{o}C, 3 MPa O_2, 8 h. [k] Ref. [59]. Conditions: 0.016 mL α-pinene, 14 mg catalyst, 1 mL CH_3CN, 50 ^{o}C, 0.1 MPa O_2, 2 h.

Activated carbons (AC), CNTs and NCNTs (see Fig. S1) were evaluated in the α-pinene oxidation, as summarized in Table 1. The main products, such as α-pinene oxide, verbenol, verbenone and verbenyl-hydroperoxide, were produced through the aerobic oxidation of α-pinene (Scheme 2). 10.3% α-pinene conversion was obtained after 4 h without any catalysts, which can be attributed to the radical autoxidation process.[3] The selectivity pattern may be obviously influenced by the oxygen pressure in the case of autoxidation.[8] However, no obvious difference was observed on the selectivity pattern in our study from 0.5 to 2.5 MPa O_2 in the presence of carbon catalysts (Fig. S2). Utilizing AC and CNTs as catalysts, the conversions were significantly improved to 19.1% and 24.6% under the same conditions, respectively. The activity of CNTs was higher than AC, probably due to the diffusion resistance in micropores and relatively low graphitization degree of AC.[6, 43, 44] When NCNTs (with 4.36% N content, see Table S1) were used as catalysts, the conversion was improved by about two-folds compared with CNTs, affording high up to 54.5% conversion, corresponding to a mass normalized activity of 272.4 mmol g^{-1} h^{-1} and a surface area normalized activity of 1.76 mmol m^{-2} h^{-1}. This result was even higher than typical state-of-the-art metallic solid catalysts as listed in

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Table 1, indicating NCNTs is promising for the α-pinene oxidation. The influence of residual metals in NCNTs was ruled out by washing with 12 mol/L HCl, post-loading metal oxides and nitrides over NCNTs. The results showed that the effect of metal was negligible and NCNTs were intrinsically a metal-free catalyst. (see Supporting Information, Fig. S3, S4 and Table S2)

Two types of products can be generated by the oxidation of α-pinene through two distinct pathways, i.e. epoxidation and allylic oxidation.[3, 8] Compared with the blank experiment, the introduction of AC or CNTs significantly improved the epoxidation, resulting in 38.2% and 33.8% α-pinene oxide selectivity, respectively. Accordingly, the epoxidation/allylic oxidation (E/A) ratios were 3.0 and 2.4, indicating the selective production of α-pinene oxide. In this work, the E/A ratio was calculated from the molar ratio of α-pinene oxide to the sum of verbenol and verbenone, and verbenyl-hydroperoxide was not counted in the allylic products, because the epoxide comes from it, as discussed below. When NCNTs were used as catalysts, the selectivity of α-pinene oxide remained high at 37.8%, meanwhile the selectivities to verbenone and verbenol were enhanced, resulting in the lower E/A ratio of 1.2.

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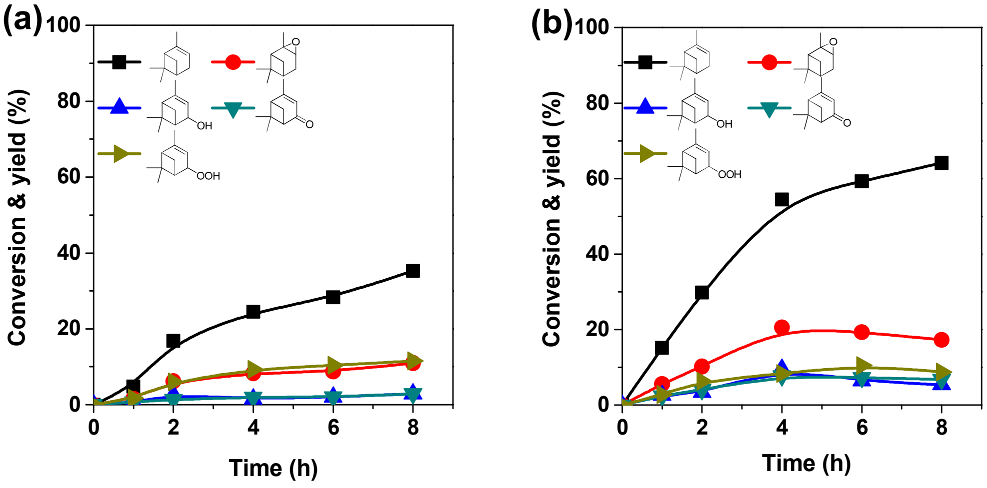

Fig. 2 Conversions and product yields of (a) CNT- and (b) NCNT (100%AN+NH$_3$) -catalyzed aerobic oxidation of α-pinene. Conditions: 80 ^{o}C, 1.5 MPa O$_2$, 10 mL α-Pinene, 20 mL CH$_3$CN, 2 mL o-DCB, 70 mg catalyst.

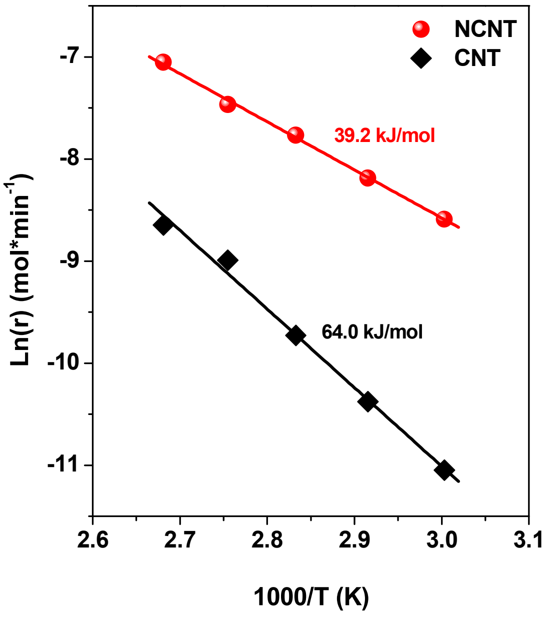

Fig. 3 Arrhenius plots of catalytic oxidation of α-pinene with CNTs or NCNTs (100%AN+NH$_3$) as catalyst.

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Fig. 2 shows the time courses of α-pinene oxidation catalyzed by CNTs and NCNTs. In the presence of CNTs or NCNTs, the reaction starts up rapidly without induction period. NCNTs displayed the higher pseudo first-order reaction rate constant of 0.149 h^{-1} than that of CNTs, 0.0592 h^{-1}, indicating the much higher activity than CNTs. The improvement of activity was also evidenced by the Arrhenius plots shown in Fig. 3. The apparent activation energy (E_a) was calculated as 39.2 kJ mol^{-1} for NCNTs, which is much lower than that of CNTs (64.0 kJ mol^{-1}), indicating the positive effect of NCNTs on reducing the reaction energetic barrier.

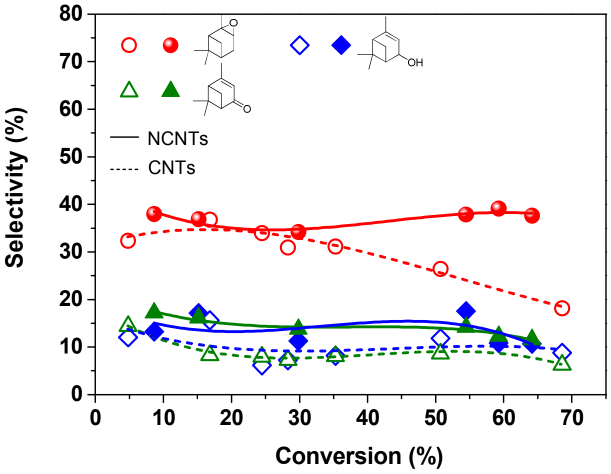

Fig. 4 Product distributions of CNTs and NCNTs (100%AN+NH_3) as functions of α-pinene conversion.

As shown in Fig. 2, when the nanocarbons were used as catalysts, epoxide was the main product. It should be noted that NCNTs afforded the obviously higher yields to verbenone and verbenol in equimolarity than CNTs. Fig. 4 shows the dependences of selectivity of oxygenated derivatives on α-pinene conversion. Three main products were

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selected, α-pinene oxide, verbenone and verbenol, representing epoxide and allylic oxides, respectively. Compared with CNTs, NCNTs provided much higher selectivity to allylic oxides and almost constant selectivity of epoxide. Although the relatively high epoxide selectivity can be reached at low conversions on CNTs, the epoxide selectivity decreased significantly at high conversions. Benefiting from the reduced selectivity of verbenyl-hydroperoxide, NCNTs afforded the higher selectivity of allylic oxides, because the decomposition of verbenyl-hydroperoxide generates verbenone and verbenol. To summarize, NCNTs selectively oxidize α-pinene to produce α-pinene oxide at about 37% selectivity even at high conversion level up to 65% (Fig. 4), while CNTs cannot achieve a balance of selectivity and conversion, due to the over-oxidation in the prolonged reaction duration.

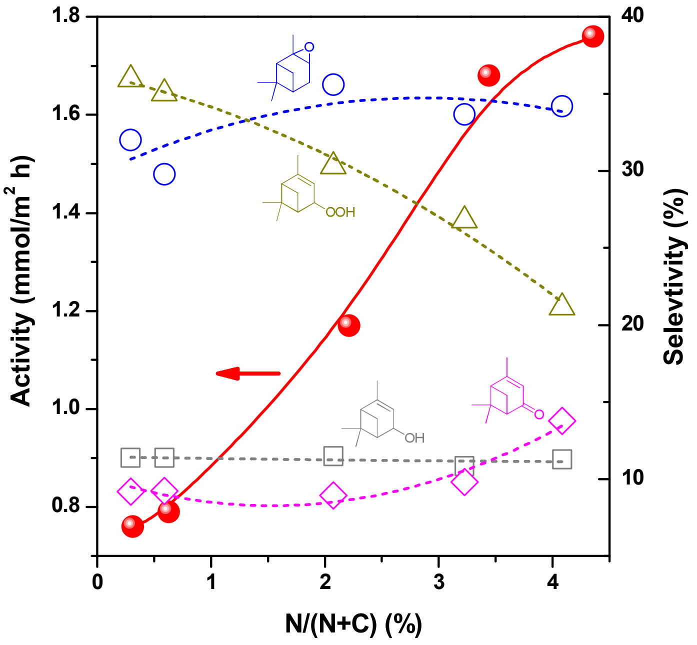

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Fig. 5 Dependences of activity and selectivities of four main products on the gross nitrogen content in NCNTs. The selectivities were obtained at similar α-pinene conversion of about 30%.

To further understand the impact of nitrogen doping on catalytic performance, NCNTs with different nitrogen contents were synthesized by tuning the composition of precursor and reaction atmosphere. In this work, the nitrogen contents were in the range from 0.3% to 4.36%, measured by XPS, as reported by our previous work.[42] (see also Table S1 for quantitative XPS results) The introduction of nitrogen heteroatoms effectively enhanced the catalytic activity of the NCNTs and had the significant influence on the product distribution as well (Table S3). Fig. 5 shows the dependences of specific activity and selectivity of oxygenated derivates on the nitrogen content on NCNTs. It is clearly shown that the nitrogen dopant is beneficial for the specific activity of NCNTs, demonstrating the positive effect of nitrogen heteroatoms. On the aspect of selectivity, the most apparent impact of N-doping was the decrease of verbenyl-hydroperoxide selectivity with the increase of nitrogen content, attributed to the decomposition of peroxide over carbons and nitrogen dopants.[6, 41] A slight increase of the selectivity of epoxide by about 8 percent was observed as the nitrogen content changed from 0.3% to 4.36%. It was worth noting that the selectivity of verbenone considerably increased, indicating the selective production of ketone products by NCNTs.[6]

Table 2 Properties and performances of NCNTs (AN+NH_3) in the aerobic oxidation of α-pinene with different HNO_3 oxidation durations and annealing temperatures.[a]

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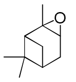
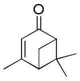
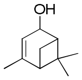
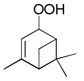
HNO_3 reflux[b] (h)	Annealing [c] (K)	S_{BET} (m^2/g)	Raman I_D/I_G	Boehm titration (mmol g^{-1})			X (%)	Selectivity (%)			
				-OH	-C=O	-COOH					
0	333[d]	88.3	0.93	0.26	0.19	0.10	54.5	37.8	14.2	17.5	15.3
7	333[d]	179.7	1.67	0.74	1.22	1.03	51.0	40.6	17.1	13.8	16.4
7	1173	207.1	1.48	n.a.	n.a.	n.a.	61.4	41.1	18.7	13.4	15.9

[a] The NCNTs synthesized with 100% AN in NH_3 were used as the base case. Conditions: 80 °C, 1.5 MPa O_2, 10 mL α-Pinene, 20 mL CH_3CN, 2 mL o-DCB, 70 mg catalyst, 4 h. [b] 9 M HNO_3, 110 °C. [c] In Ar gas for 4 h. [d] Vacuum drying at 333 K overnight. [e] Not applied.

To further tune the selectivity, oxygen-containing groups were introduced on the carbon catalysts by treating with HNO_3. A negative effect of oxygen functionalities on catalytic performance was observed over CNTs (Table S4). It is consistent with the previous works concerning the oxidations of cyclohexane,[43] cyclohexene,[6] ethylbenzene[46] and cumene[60] catalyzed by carbons, indicating that the oxygen functional groups and defects are unfavorable for the radical oxidation of hydrocarbon in the liquid phase.[6, 43, 46] As shown in Table 2, after treated by HNO_3 for 7 h, abundant oxygen-containing groups were introduced on NCNTs, meanwhile the conversion slightly decreased from 54.5% to 51.0%. This result indicated that the oxygen groups were unfavorable the specific activity, taking into consideration the significantly improved specific surface area of NCNTs after HNO_3 treatment. After removed the groups by annealing at 900 °C,[43] the conversion was further elevated to 61.4%, while the selectivity of epoxide increased from 37.8% to

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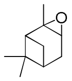
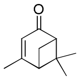
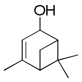
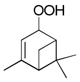
41.1%. Hence, by the oxidation-annealing process, the performance of NCNTs was improved, because of either the improved surface area or the unique interaction between NCNTs and α-pinene.

Table 3 Effect of solvents on α-pinene oxidation catalyzed by NCNTs[a]

Solvent	Polarity[b] (kcal/mol)	X[c] (%)	Selectivity[d] (%)			
						
Acetonitrile	0.46	54.5	37.8	14.1	17.5	15.3
Acetone	0.355	28.6	29.2	11.4	10.3	23.2
1,4-Dioxane	0.164	26.7	23.0	13.1	14.8	12.4
Toluene	0.099	13.9	35.6	16.5	16.1	18.9
n-Hexane	0.009	21.9	26.9	15.9	11.6	18.4

[a] Reaction Conditions: 80 °C, 1.5 MPa O_2, 10 mL α-pinene, 20 mL CH_3CN, 2 mL o-DCB, 70 mg catalyst, 4 h. The NCNTs were synthesized by xylene in the NH_3 atmosphere. [b] The measure of polarity used is the empirical solvent parameter E_T^N, derived from the solvatochromism of a pyridinium N-phenolate betaine. The polarity data of solvents were obtained from reference [61]. [c] Conversion. [d] Selectivity of major products. The by-products include pinocarveol, pinenol, myrtenal and others.

Solvent has significant influences on the outcome of organic reaction. In this study, five solvents with different polarity were selected to investigate the solvent effect. As summarized in Table 3, the conversion of α-pinene increased with the solvent polarity

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ascending. The highest conversion, 54.5%, was obtained when acetonitrile was used as solvent, which has the strongest polarity among the solvents tested. It is probably caused by the polar solvent facilitates the desorption of polar oxide products, therefore speeds up surface renewal of catalyst. For example, because acetonitrile is immiscible with α-pinene, the formed intermediate products on catalyst surfaces are rapidly transferred to solvent instead of contacting and reacting with neighboring α-pinene molecules, avoiding the over-oxidation.[33] It was noticed that, although the polarity of toluene is higher than n-hexane, the lower conversion of α-pinene was observed in toluene. It may be attributed to the competitive adsorption between substrate and toluene upon active sites of NCNTs, since toluene can strongly interact with and block active sites, as observed in the metal-free catalysis system with toluene involved.[62]

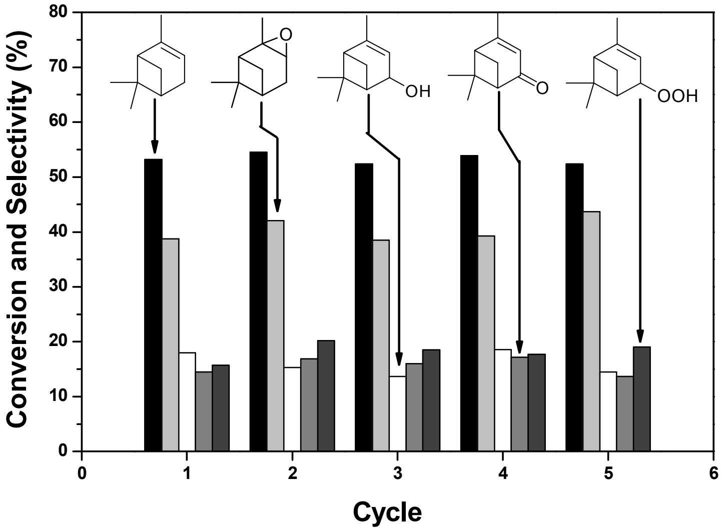

Fig. 6 The recyclability of NCNTs (100%AN+NH_3) in the oxidation of α-pinene in the liquid-phase.

Reaction conditions: 80 °C, 1.5 MPa O_2, 10 mL α-pinene, 20 mL CH_3CN, 2 mL o-DCB, 70 mg

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catalyst, 4 h.

The recyclability of catalyst is very important for practical applications. Here, we selected NCNTs (100%AN+NH_3) to evaluate the stability for 5 runs. After each run, the recycled catalyst was repeatedly washed by deionized water and acetone, and then dried at 110 ^{o}C overnight. The catalytic results are shown in Fig. 6. NCNTs showed outstanding recyclability. After five recycles, there were no noticeable changes in both the conversion of α-pinene and product distributions, demonstrating the structural stability of NCNTs under the reaction conditions (Fig.S5).

3.2 Reaction mechanism

It is widely accepted that the aerobic oxidation of α-pinene is a radical chain reaction. The addition of carbon catalysts can boost the overall reaction rate of the radical process, which has been proved in the cases of cyclohexane, cyclohexene, cumene and ethylbenzene.[6, 43, 46, 60] As shown in Table 4, when p-benzoquinone as a radical scavenger was added to the reaction, the conversion of α-pinene dramatically suppressed to 2.7%, even lower than that of blank experiment (Table 1). This result demonstrates that the oxidation of α-pinene catalyzed by carbons is a radical reaction as well. Furthermore, NCNTs cannot catalyze the conversion of verbenol, verbenone and α-pinene oxide, indicating that the radical reaction is initiated from reactive radicals derived from substrate α-pinene, e.g. alkyl, alkyol and dialkyl peroxide radicals. Thus, the carbon-radical interaction should be the essential for the process.[6, 41-45]

Table 4 Catalytic activities of oxidations of various substrates catalyzed by NCNTs

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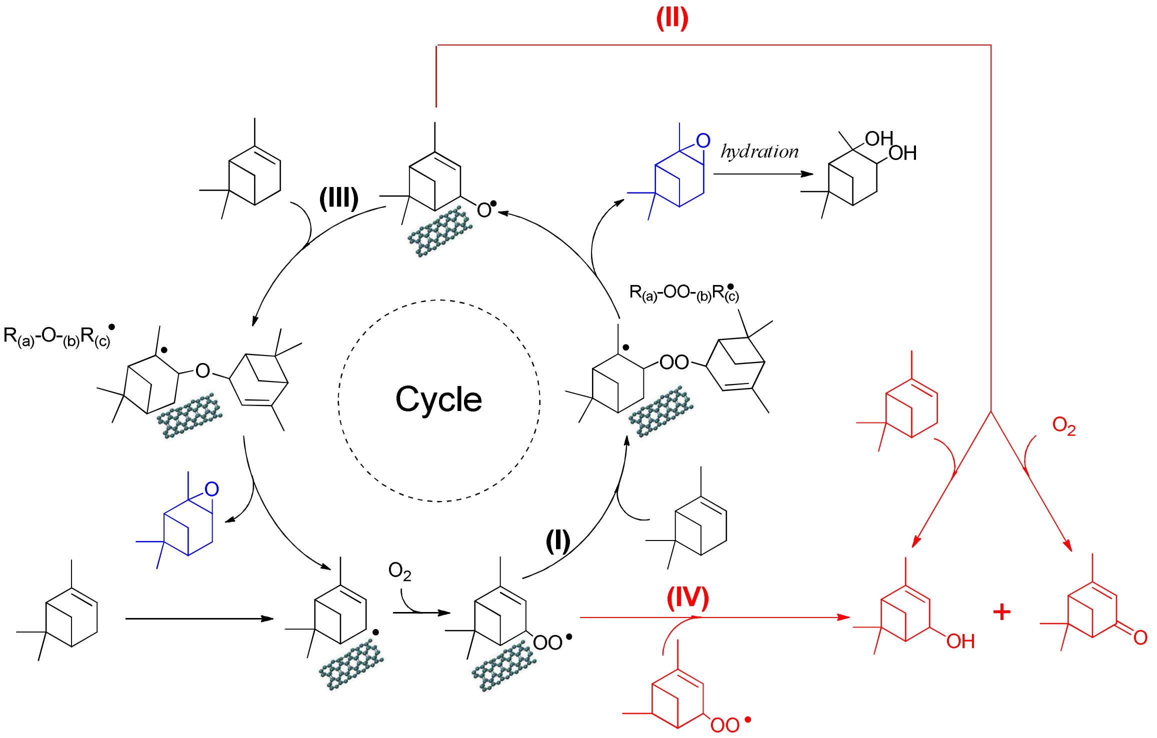
(100%AN+NH_3).[a]

Substrate	Additive	X (%)
α-Pinene [b]	p-benzoquinone	2.7
α-Pinene oxide	—	<1
Verbenol	—	<1
Verbenone	—	<1

[a] Conditions: 353 K, 1.5 MPa O_2, 10 mmol substrates, 20 mL CH_3CN, 2 mL o-DCB, 70 mg catalyst.

[b] 10 mL α-pinene.



Scheme 3. Proposed reaction pathways of the NCNT-catalyzed oxidation of α-pinene.

Compared with the cyclohexene oxidation in the liquid phase,[6] allylic regioisomers of α-pinene lead to the formation of the more complex radical intermediates, depending on the sites “b”, “c” and “d” involved (Scheme 1). A plausible mechanism of the aerobic α-pinene oxidation was proposed to elucidate the observed catalytic behaviors of CNTs and NCNTs. As shown in Scheme 3, α-pinene is oxidized by molecular oxygen via allylic oxidation and epoxidation routes. Alkyl radicals are formed through pyrolysis of α-pinene, and then peroxyl radicals are formed by the insertion of oxygen, through which the chain reaction propagates. Similar actions were also observed in the Baeyer−Villiger oxidation catalyzed by carbons.[39] In the case of α-pinene oxidation, peroxyl radicals are preferably added to the unsubstituted C-atom, i.e. the b-site, forming an epoxide and alcoxyl radical (**Pathway I**), resulting in the selective production of epoxide.[3] The stabilization effect of CNTs or NCNTs on radicals can improve the lifetime of $R_{(a)}$-OO-$_{(b)}R_{(c)}^{\bullet}$ radicals, which are supported by the theoretical calculations as detailed later, thereby NCNT can efficiently increase the overall conversion of substrate.[44] Alkoxyl radicals undergo further propagation by abstracting a hydrogen atom from the substrate (**pathway II**). Finally, the alkoxyl radical may be converted to ketone product through the abstraction of the weakly bonded αH atom by O_2.[3] Meanwhile, the termination of two peroxyl radicals on surfaces of CNTs also formed verbenol and verbenone (**pathway IV**).

Pathways II and **IV** are similar to the autoxidation process. However, the autoxidation cannot afford the selective formation of α-pinene oxide, because **pathway II** produces equimolar amounts of epoxidation and allylic oxidation products. Hence, the more allylic oxides are usually obtained through autoxidation (Table 1), taking into consideration the contribution of **pathway IV**.[8]

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In the cases of carbon catalyzed oxidation, the higher epoxide selectivity was reached, indicated by the E/A ratio more than unity (Table 1 and Fig. 3). This result suggests the unique catalytic role of carbons. Being similar to peroxyl radicals, alkoxy radicals might interact with substrate to form $R_{(a)}$-O-$_{(b)}R_{(c)}^{\bullet}$ (**Pathway III**). Its propagation may be different from the autoxidation in the presence of carbon materials.[8] In the autoxidation, $R_{(a)}$-O-$_{(b)}R_{(c)}^{\bullet}$ is very vulnerable and disintegrated quickly, releasing an epoxide and an alkyl radical. The alkyl radical may propagate the chain reaction. In the presence of CNTs or NCNTs, the stability of $R_{(a)}$-O-$_{(b)}R_{(c)}^{\bullet}$ might be improved, thus additional α-pinene oxide can be obtained, resulting in the higher selectivity of epoxide.

The role of NCNTs in the reaction is dualfunctional. In addition to stabilize radicals as discussed above, NCNTs have a strong ability to decompose peroxides, which has been demonstrated in our previous works.[6, 43, 46, 60] Hence, the **pathway II or IV** may be enhanced as the same time, resulting in the enhanced selectivity of allylic oxides, verbenol and verbenone (Fig. 4). As a result, the formations of epoxide and allylic oxides were both improved over NCNTs. It explains the highly efficient conversion of α-pinene and the low selectivity of verbenyl-hydroperoxide over NCNTs.

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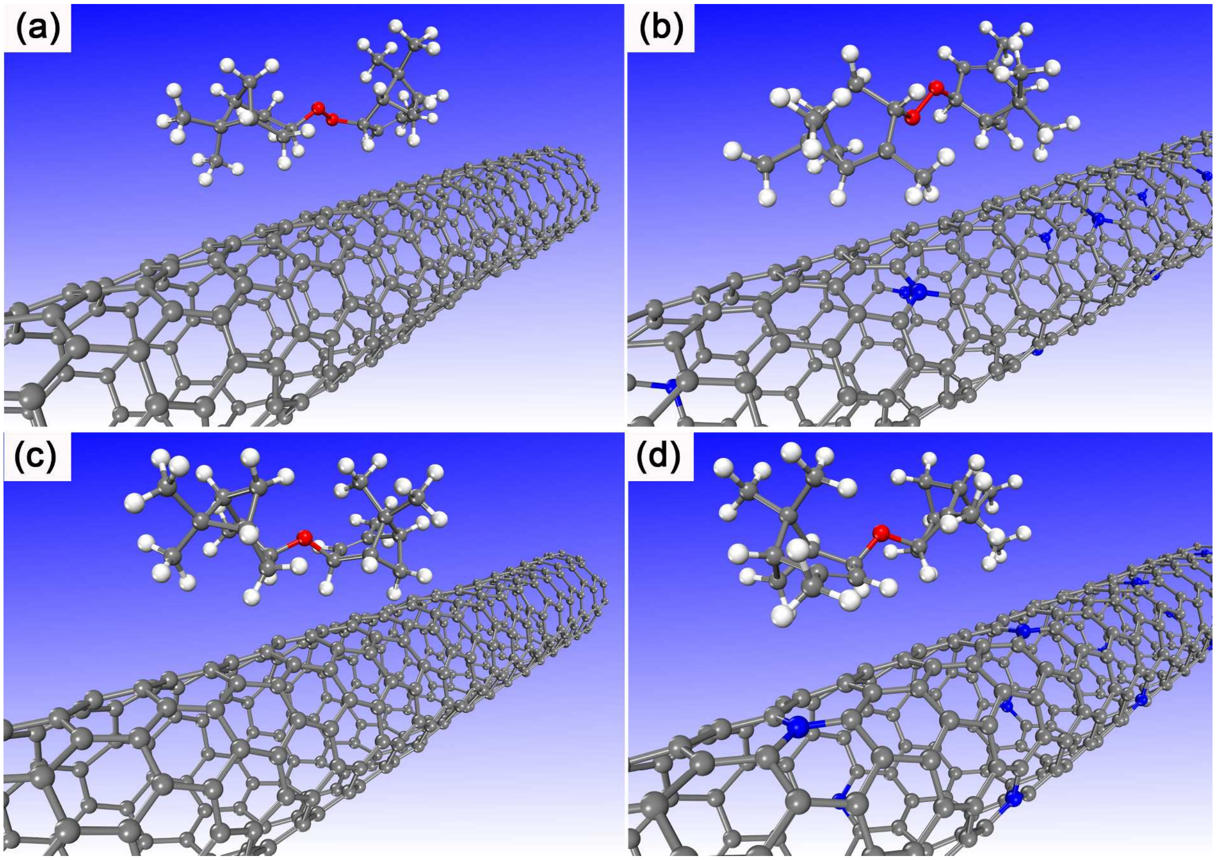

Fig.7 − Optimized structures of (a, b) $R_{(a)}$-OO-$_{(b)}R_{(c)}^{\bullet}$ and (c, d) $R_{(a)}$-O-$_{(b)}R_{(c)}^{\bullet}$ on the surface of (a, c) CNT and (b, d) NCNT.

Table 5 The adsorption energies (ΔE_a) of free-radicals on the CNTs and NCNTs from theoretical calculations.

Catalyst	ΔE_a (kJ/mol)	
	$R_{(a)}$-OO-$_{(b)}R_{(c)}^{\bullet}$	$R_{(a)}$-O-$_{(b)}R_{(c)}^{\bullet}$
CNT	-43.09	-68.52
NCNT	-60.56	-30.16

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The aforementioned discussion indicates that the stabilization of radicals, i,e, $R_{(a)}$-OO-$_{(b)}R_{(c)}^{\bullet}$ and $R_{(a)}$-O-$_{(b)}R_{(c)}^{\bullet}$, plays important roles in the α-pinene oxidation upon CNTs and NCNTs. Molecular dynamics simulations were carried out to further understand the interaction between the radicals and the pristine CNTs and NCNTs (represented by a nitrogen atom embedded in a graphene sheet). Fig. 7 shows the calculated configurations of radical-nanotube complexes. The relative position between radicals and nanotube demonstrated that an adsorption occurred (Fig. S6), supporting the scenario that CNTs and NCNTs stabilize the radicals. The adsorption energies between the radicals and CNT or NCNT displayed significant difference. As shown in Table 5, the adsorption energy of $R_{(a)}$-OO-$_{(b)}R_{(c)}^{\bullet}$ radicals on the NCNT is more negative than CNT, suggesting a stronger interaction between the radical and NCNT. However, for the $R_{(a)}$-O-$_{(b)}R_{(c)}^{\bullet}$, CNT displays a much more negative adsorption energy than NCNT. These results offered an excellent explanation that the E/A ratios of α-pinene oxidation were efficiently modulated upon CNTs and NCNTs (Table 1). On CNTs, although the relatively weak adsorption of $R_{(a)}$-OO-$_{(b)}R_{(c)}^{\bullet}$ may lead to the lower overall production of α-pinene oxide, the higher adsorption energy of $R_{(a)}$-O-$_{(b)}R_{(c)}^{\bullet}$ may be favorable for the production of α-pinene oxide through **pathway III**, resulting the higher E/A ratio. On NCNTs, actually **pathway I** and **III** are enhanced for the production of α-pinene oxide, meanwhile, the relatively weak adsorption between $R_{(a)}$-O-$_{(b)}R_{(c)}^{\bullet}$ and NCNTs may be favorable for the sequential allylic oxide production through **pathway II** or **IV**.[43] Thus, NCNT improved not only the catalytic efficiency but also the selectivities of both the

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epoxide and allylic oxides.

4. Conclusions

In summary, we have demonstrated that excellent performances in the epoxidation of α-pinene can be achieved in the presence of CNTs and NCNTs as metal-free catalysts. Nitrogen dopant significantly enhances not only the mass specific activity in the oxidation of α-pinene, but also the selectivity of allylic oxidation products, featured by the considerably decreased E/A ratio. An improved selectivity of epoxide was obtained as NCNTs treated by the HNO_3 and thermal reduction. As revealed in the mechanism proposed, the interaction between radicals and carbon catalysts plays central role in this reaction. The radicals, i.e., the $R_{(a)}\text{-OO-}_{(b)}R_{(c)}^{\bullet}$ and $R_{(a)}\text{-O-}_{(b)}R_{(c)}^{\bullet}$, played important role in the radical propagation process for producing α-pinene oxide. The theoretical simulations displayed that the remarkable improvement of catalytic performance is caused by the strong interaction between CNTs/NCNTs with $R_{(a)}\text{-OO-}_{(b)}R_{(c)}^{\bullet}$ and alkoxy radicals. The results presented here demonstrate that NCNTs is a promising alternative catalyst for the selective production of epoxide products in the terpene oxidation by using molecular oxygen as ultimate oxidant.

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