Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Aerobic Oxidation of α-Pinene Catalyzed by Carbon Nanotubes

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Table S1 − Quantitative XPS analysis of the N-CNTs

Precursor (v% aniline)	atmosphere	N/(C+N) (%)	N_P (%)	N_{Pyr} (%)	N_Q (%)	N_{OX} (%)	N_{ads} (%)
0	Ar	0.00	0	0	0	0	0
10		0.31	28.7	17.1	33.9	6.1	14.3
50		0.63	35.2	5.4	37.9	13.5	7.9
100		2.21	29.8	2.4	53.1	10.8	3.8
0	NH_3	3.44	30.5	6.8	43.1	11.9	7.7
100		4.36	28.1	16.1	38.8	9.7	7.2

Table S2 − Effect of metal residuals on α-pinene oxidation catalyzed by NCNTs[a]

Catalyst	Metal species	Metal amount[b] (wt%)	X (%)	Selectivity[c] (%)			
							
NCNT-p[d]	Fe	0.263	53.2	35.9	12.6	18.1	17.8
NCNT-w[e]		0.015	54.5	37.9	14.2	17.6	15.4
FeOx/NCNT		3.284	52.4	39.8	11.9	18.4	18.1
FeNx/NCNT		3.682	53.9	37.1	16.6	18.1	14.8
NCNT-p[d]	Mo	0.089	53.2	35.9	12.6	18.1	17.8
NCNT-w[e]		0.013	54.5	37.9	14.2	17.6	15.4
MoOx/NCNT		2.65	50.8	35.6	13.3	16.9	19.4
MoNx/NCNT		1.83	52.9	38.1	17.8	17.1	15.5

[a] Reaction Conditions: 80 ºC, 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] Measured by ICP-AES. [c] Selectivity of major products. The by-products include pinocarveol, pinenol, myrtenal and others. [d] As-prepared NCNTs. [e] HCl-washed NCNTs.

Table S3 − Effect of nitrogen content of NCNTs on the aerobic oxidation of α-pinene[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] (%)			
								
0%AN+Ar	27.0	28.0	29.5	1.10	33.2	7.9	8.3	36.4
10%AN+Ar	48.5	29.2	36.9	0.76	32.0	9.2	11.4	35.9
50%AN+Ar	71.2	31.5	56.1	0.79	29.8	9.2	11.4	35.0
100%AN+Ar	49.3	34.2	57.7	1.17	35.6	9.0	11.5	30.3
0%AN+NH_3	129.3	52.7	217.9	1.68	35.7	12.8	14.9	22.7
100%AN+NH_3	155.1	54.5	272.4	1.76	37.8	14.2	17.5	15.3

[a] Reaction Conditions: 80 ºC, 1.5 MPa O_2, 10 mL α-pinene, 20 mL CH_3CN, 2 mL o-DCB, 70 mg catalyst, 4 h. [b] The volume fraction of aniline in precursor + reaction atmosphere. [c] α-Pinene conversion. [d] Initial reaction rate of α-pinene consumption normalized by catalyst mass. [e] Initial reaction rate of α-pinene consumption normalized by catalyst surface. [f] Selectivity of major products. The by-products include pinocarveol, pinenol, myrtenal and others.

Table S4 − 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]

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	383[d]	127.8	0.87	0.30	0.18	0.12	24.6	33.8	7.9	6.1	37.9
8	383[d]	149.4	1.16	0.59	1.13	0.97	6.6	26.2	12.5	5.4	35.4
8	1173	−	0.92	n.d.	n.d.	n.d.	13.5	32.2	9.1	9.1	31.6

[a] Conditions: 80 ºC, 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, 140 ºC. [c] In Ar gas for 4 h. [d] Vacuum drying at 333 K overnight. [e] Not detected.

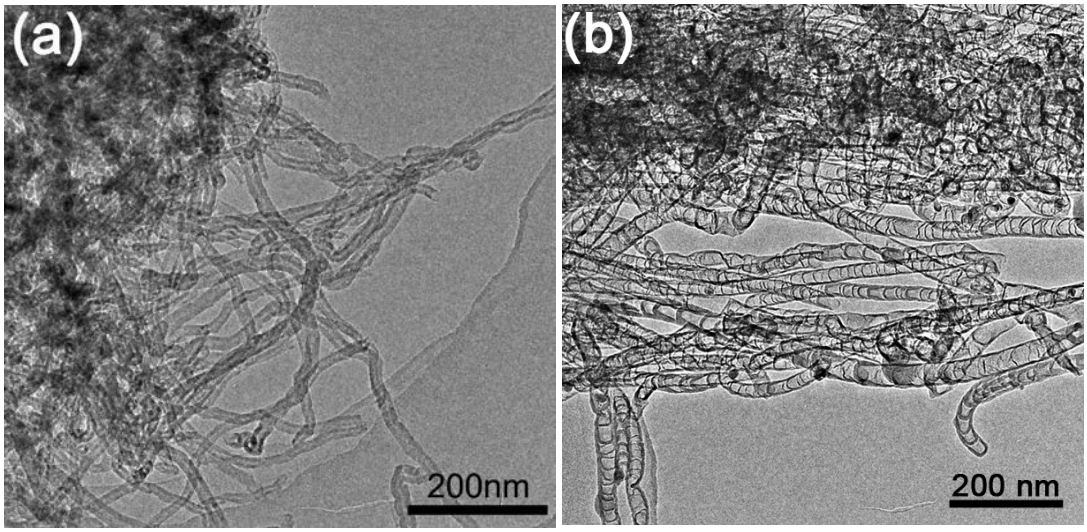

Fig.S1 − TEM images of (a) CNTs and (b) NCNTs

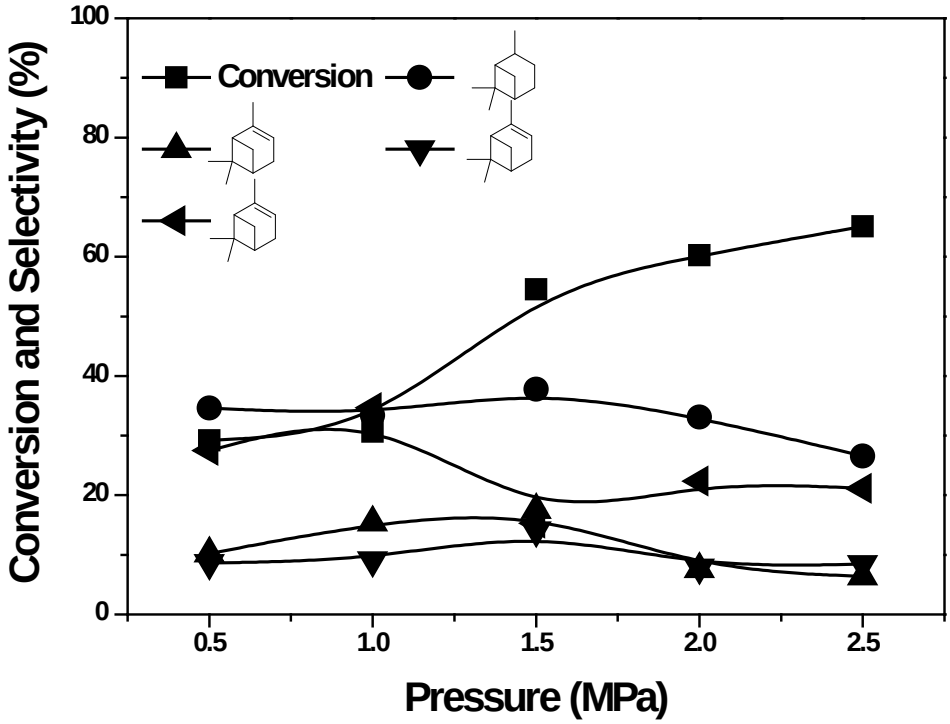

Fig. S2 – The effect of oxygen pressure on the α-pinene oxidation catalyzed by NCNTs.

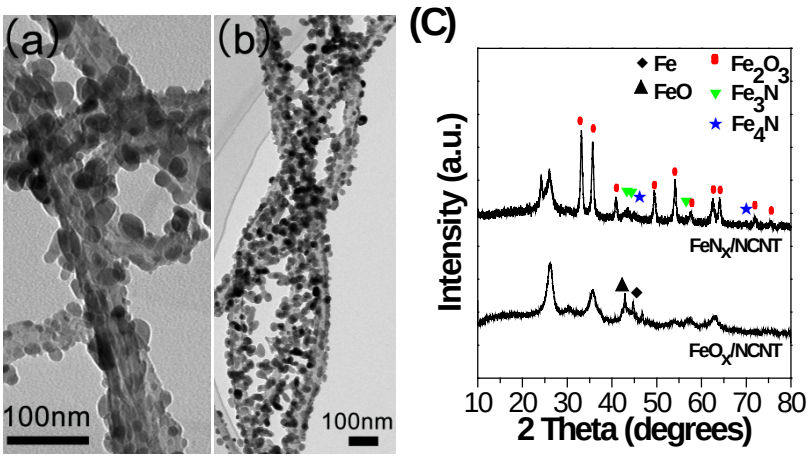

Fig. S3 − TEM images of (a) Fe_2O_3 loaded N-CNTs, (b) iron nitrides loaded N-CNTs and (c) XRD patterns of the catalysts.

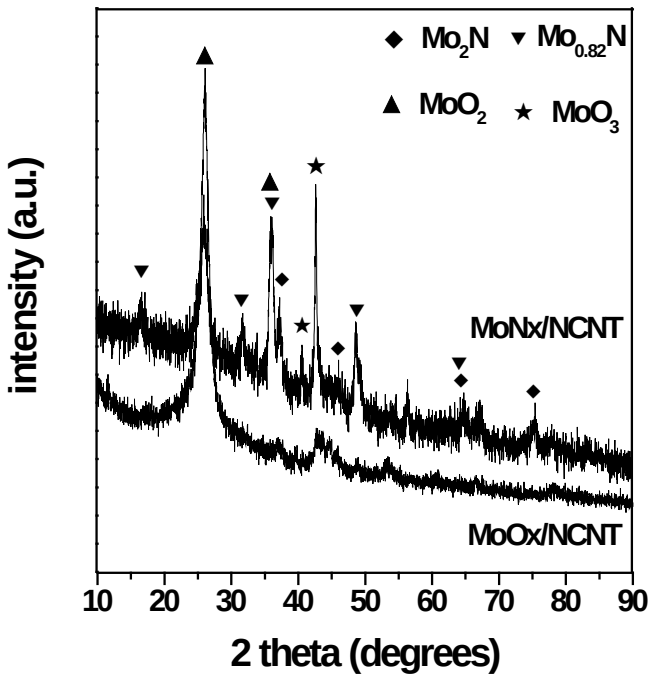

Fig. S4 − XRD patterns of the MoOx/NCNT and MoNx/NCNT.

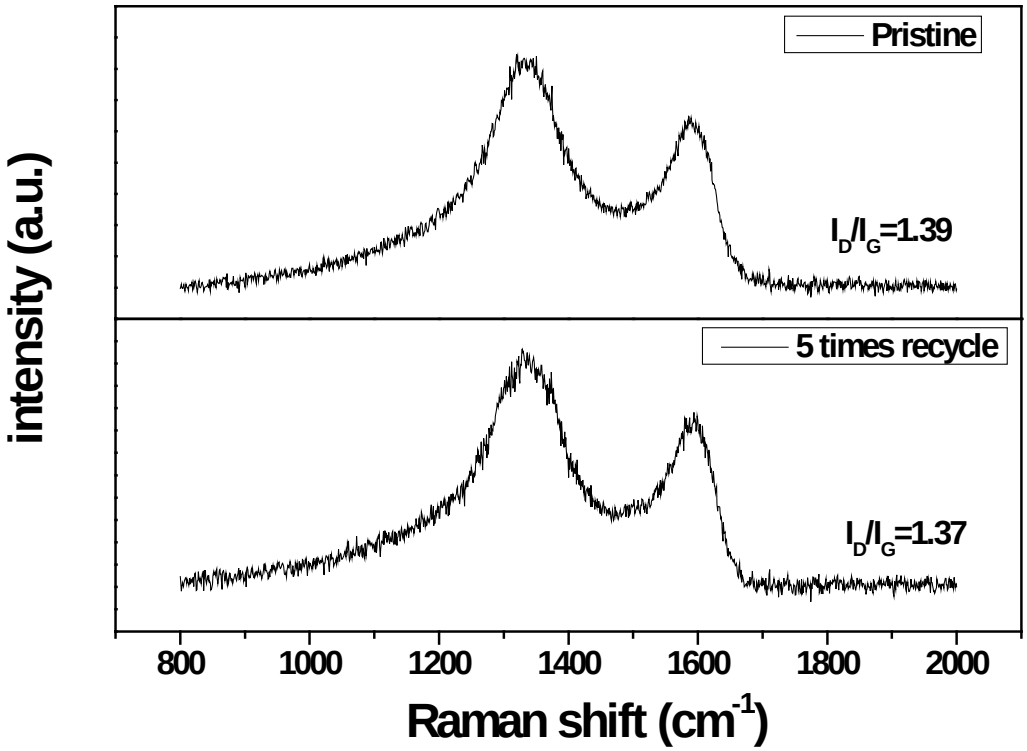

Fig. S5 − Raman spectra of the pristine NCNTs and used NCNT for 5 times.

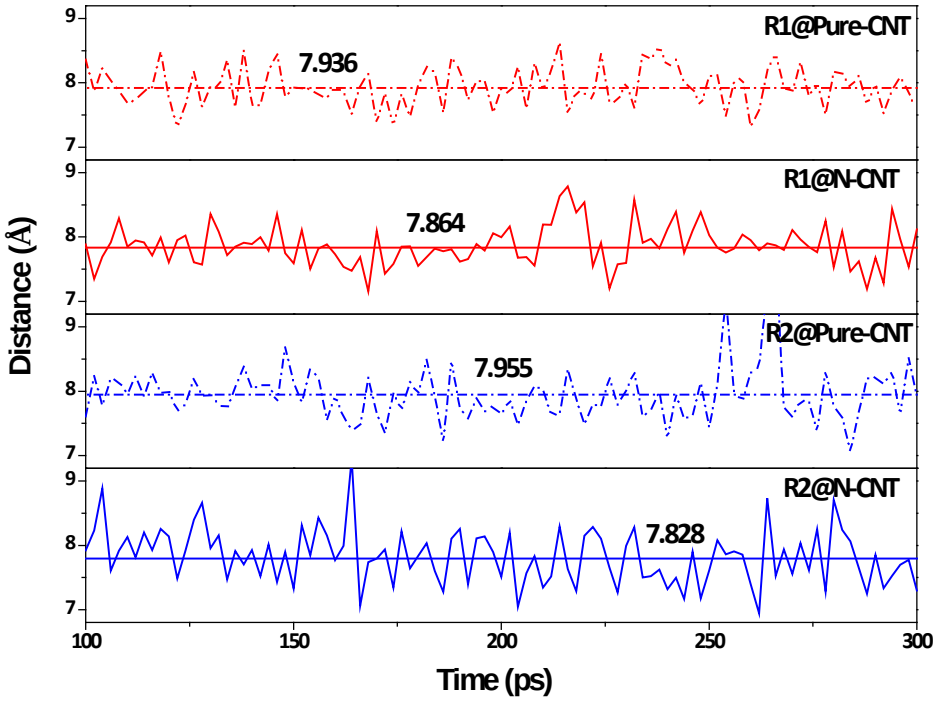

Fig. S6 − Evolution of distances between the centroid of radical and the CNT axis. Horizontal lines represent the averages. R1: $R_{(a)}$-O-$_{(b)}R_{(c)}^{\bullet}$, R2: $R_{(a)}$-OO-$_{(b)}R_{(c)}^{\bullet}$.