SUPPORTING INFORMATION

Nitrogen Doped Carbon Nanotubes Functionalized by Transition Metal Atoms: A Density-Functional Study

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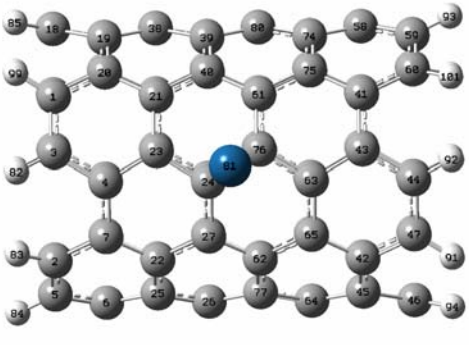
SI 1. NBO analysis for Pt/(5,5) CNT and Pt/(10,0) CNT

For deep insight into the interaction between Pt and CNTs, NBO analysis was performed for Pt/(5,5) CNT and Pt/(10,0) CNT. The results show that the adsorption of Pt on CNTs is promoted by the interaction between the *d* orbital of Pt and the π orbital of CNTs.

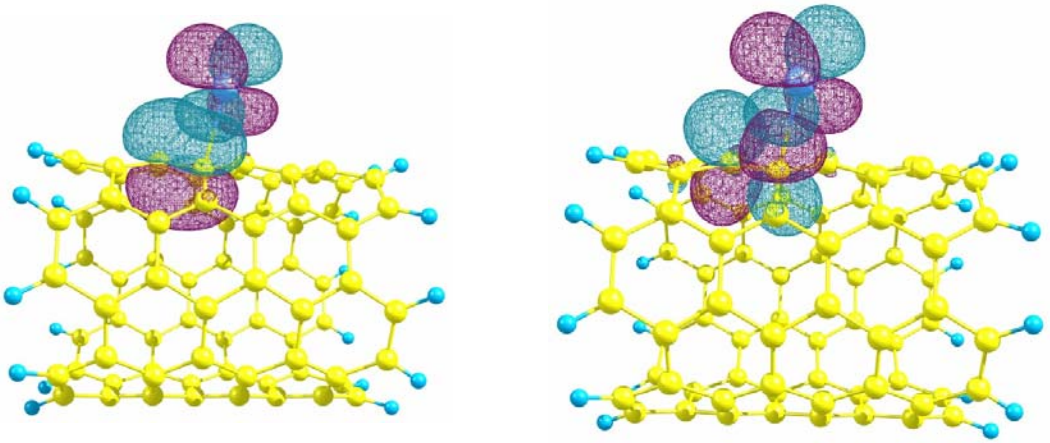
Table S1 Partial calculation results about the Pt/(5,5) CNT by NBO analysis

Donor (i)	Acceptor (j)	E(kcal/mol)	Donor (i)	Acceptor (j)	E(kcal/mol)
LP(5)Pt81	BD*(2)C23-C24	10.94	BD*(2)C61-C75	BD*(2)C39-C40	364.97
LP(4)Pt81	BD*(2)C23-C24	7.74	BD(2)C23-C24	BD*(2)C20-C21	31.08
BD(2)C23-C24	LP*(6)Pt81	14.02	BD*(2)C23-C24	BD*(2)C4-C7	139.26
BD*(2)C23-C24	LP*(6)Pt81	51.52	BD*(2)C23-C24	BD*(2)C20-C21	166.36
BD(2)C4-C7	BD*(2)C23-C24	41.77	BD(2)C23-C24	LP (1) C76	107.67
BD(2)C23-C24	BD*(2)C22-C27	33.10			

E denotes the stabilization energy; BD denotes bonding orbital; BD* denotes antibonding orbital; LP denotes lone-pair. For BD and BD*: (1) and (2) denote σ orbital and π orbital, respectively.



Pt/(5,5) CNT



π (C-C) → d (Pt)
E=14.02 kcal/mol

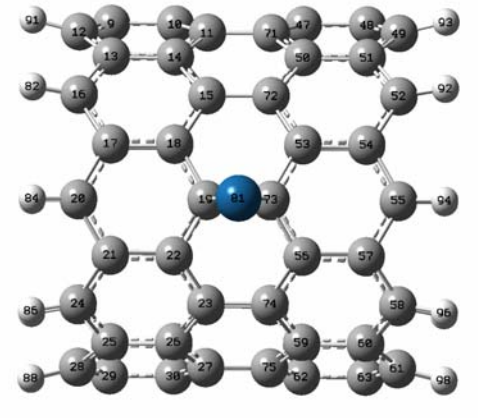
d (Pt) → π*(C-C)
E=10.94 kcal/mol

Fig S1. The natural bond orbital (NBO) graphs of the Pt/(5,5)CNT

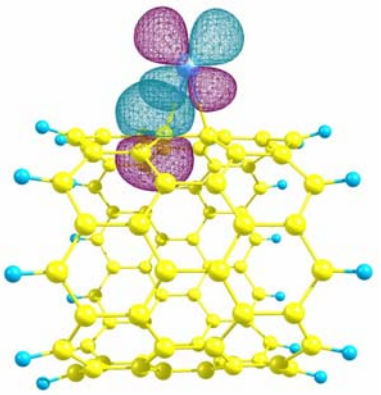
Table S2 Partial calculation results about the Pt/(10,0) CNT by NBO analysis

Donor (i)	Acceptor (j)	E(kcal/mol)	Donor (i)	Acceptor (j)	E(kcal/mol)
BD(2)C18-C19	LP*(6)Pt81	10.93	LP(4)Pt81	BD*(2)C53-C73	6.72
BD(2)C53-C73	LP*(6)Pt81	10.85	LP(4)Pt81	BD*(2)C18-C19	6.68
BD*(2)C18-C19	LP*(6)Pt81	91.71	BD(2)C18-C19	BD*(2)C53-C73	39.08
BD*(2)C53-C73	LP*(6)Pt81	92.61	BD(2)C18-C19	BD*(2)C14-C15	38.02
LP(5)Pt81	BD*(2)C18-C19	13.39	BD(2)C53-C73	BD*(2)C18-C19	39.04
LP(5)Pt81	BD*(2)C53-C73	13.30	BD(2)C53-C73	BD*(2)C56-C74	30.25

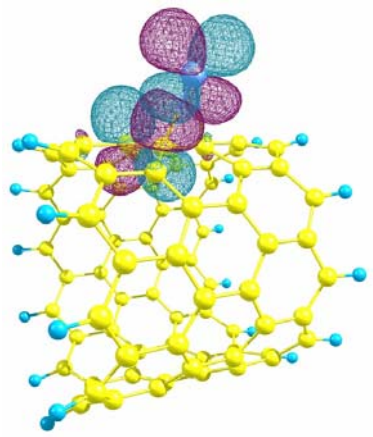
E denotes the stabilization energy; BD denotes bonding orbital; BD* denotes antibonding orbital; LP denotes lone-pair. For BD and BD*: (1) and (2) denote σ orbital and π orbital, respectively.



Pt/(10,0) CNT



π (C-C) → d (Pt)
E= 10.93Kcal/mol



d (Pt) → π*(C-C)
E= 13.39 Kcal/mol

Fig S2. The natural bond orbital (NBO) graphs of the Pt/(10,0)CNT

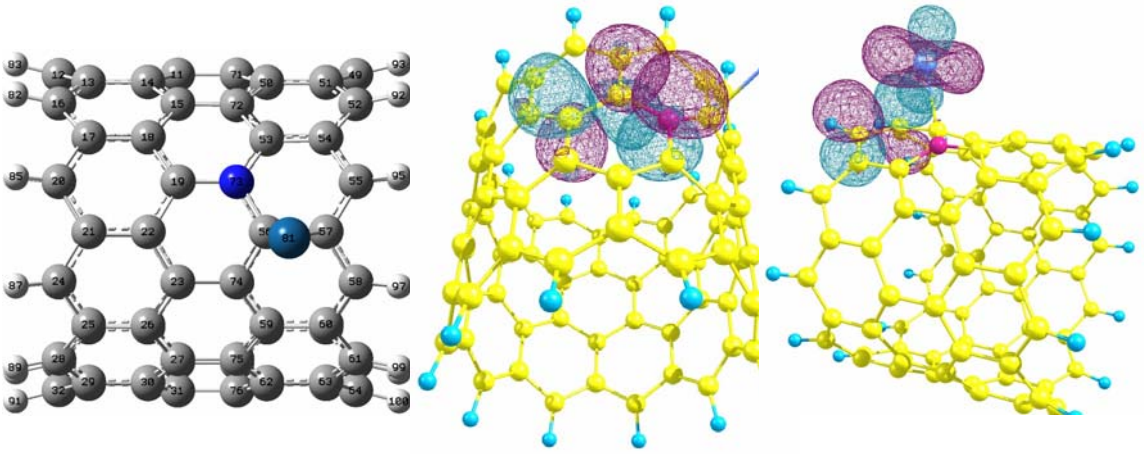
SI 2. NBO analysis for Pt/CN_xNT

For deep insight into the interaction between Pt and CN_xNT, the orbital analysis was performed for Pt/CN_xNT. For GN-CN_xNT, the GN uses three valence electrons for σ bonding with C, one for π bond, and the remaining one to generate the π* state which activates the neighboring C atoms. Hence, in comparison with the Pt on CNTs, the Pt on GN of CN_xNT bears the slightly (<0.1 eV) increased corresponding binding energy by the activated neighboring C atoms via the π*.

Table S3 Partial calculation results about the Pt/(10,0) GN-CN_xNT by NBO analysis

Donor (i)	Acceptor (j)	E(kcal/mol)	Donor (i)	Acceptor (j)	E(kcal/mol)
LP(3)Pt81	BD*(1)C56-N73	1.09	BD(1)C18-C19	BD*(1)C56-N73	1.52
LP(5)Pt81	BD*(2)C55-C57	9.72	BD(1)C19-N73	BD*(1)C53-N73	1.75
LP(4)Pt81	BD*(2)C55-C57	3.33	BD(1)C52-C54	BD*(1)C53-N73	2.43
LP(5)Pt81	BD*(1)C56-Pt81	5.89	BD(1)C53-C54	BD*(1)C19-N73	1.15
LP(1)N73	BD*(2)C53-C72	26.62	BD(1)C19-N73	BD*(1)C56-N73	1.58
LP(1)N73	BD*(2)C19-C22	36.69	BD*(1)C56-Pt81	BD*(2)C23-C74	25.83
LP(1)N73	BD*(1)C56-Pt81	4.05	BD*(2)C23-C74	BD*(1)C56-N73	1.15
BD(1)C53-N73	BD*(1)C19-N73	1.81	BD(1)C57-C58	BD*(1)C56-N73	2.18
BD(1)C56-N73	BD*(1)C18-C19	1.14			

E denotes the stabilization energy; BD denotes bonding orbital; BD* denotes antibonding orbital; LP denotes lone-pair. For BD and BD*: (1) and (2) denote σ orbital and π orbital, respectively.



Pt/(10,0) GN-CN_xNT

P (N) → π* (C-C)
E= 26.62Kcal/mol

d (Pt) → π*(C-C)
E= 9.72Kcal/mol

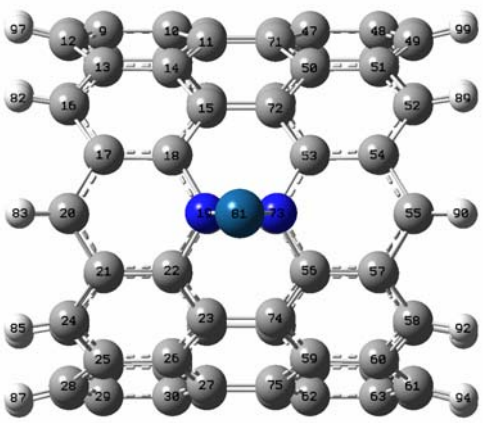
Fig S3. The natural bond orbital (NBO) graphs of the Pt/GN-CN_xNT

For PN-CN_xNT, the PN uses two valence electrons for σ bonds, one for π bond, and the remaining two to form a filled *p*-like nonbonding state. This *p*-like nonbonding of the PN results in the strong hybridization with the *d* orbital of the Pt atom. For the Pt on PN, the corresponding binding energy (bridge site) is further obviously (0.12~0.19eV) enhanced by the stronger hybridization of the *p*-like nonbonding with the *d* orbital of the Pt atom.

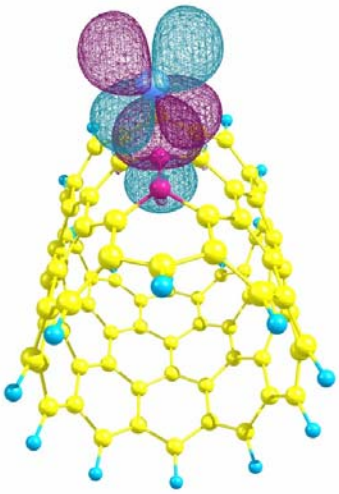
Table S4 Partial calculation results about the Pt/(10.0) PN-CN_xNT by NBO analysis

Donor (i)	Acceptor (j)	E(kcal/mol)	Donor (i)	Acceptor (j)	E(kcal/mol)
LP(1)N19	LP*(6)Pt81	9.63	LP(1)N73	BD*(2)C56-C74	24.45
LP(1)N73	LP*(6)Pt81	6.02	LP(1)N73	BD*(2)C53-C72	24.04
BD(1)N19-N73	LP*(6)Pt81	1.21	BD(1)C17-C18	BD*(1)N19-N73	2.73
LP(5)Pt81	BD*(1)N19-N73	0.47	BD(1)C15-C18	BD*(1)N19-C22	1.29
LP(3)Pt81	BD*(2)C15-C18	0.17	BD(1)C16-C17	BD*(1)C18-N19	4.71
LP(1)N19	BD*(2)C15-C18	19.96	BD(1)C14-C15	BD*(1)C18-N19	3.88
LP(1)N19	BD*(2)C22-C23	20.35			

E denotes the stabilization energy; BD denotes bonding orbital; BD* denotes antibonding orbital; LP denotes lone-pair. For BD and BD*: (1) and (2) denote σ orbital and π orbital, respectively.



Pt/(10,0) PN-CN_xNTs



p (N)→ d (Pt)
E = 9.63Kcal/mol

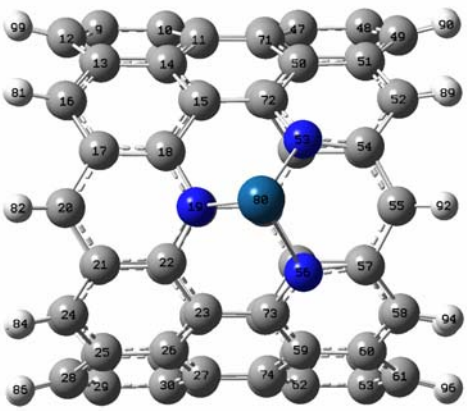
Fig S4. The natural bond orbital (NBO) graphs of the Pt/PN-CN_xNT

For the Pt on VN, the adsorption is further enhanced by the stronger hybridization of the *p*-like nonbonding with the *d* orbital of the Pt atom. The corresponding binding energy is the highest which shows strongest interaction between VN and Pt atom.

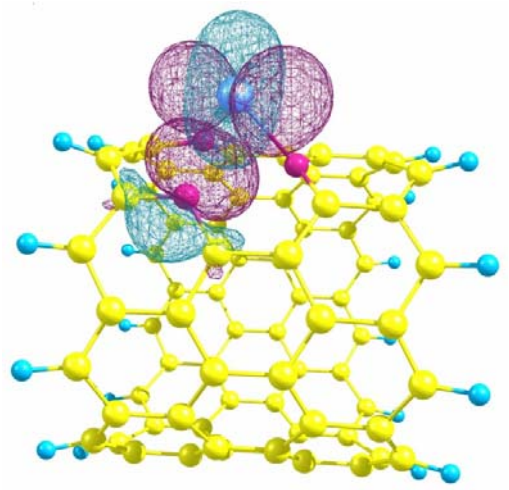
Table S5 Partial calculation results about the Pt/(10,0) VN-CN_xNT by NBO analysis

Donor (i)	Acceptor (j)	E(kcal/ mol)	Donor (i)	Acceptor (j)	E(kcal/ mol)
LP(1)N19	LP*(6)Pt80	8.06	BD(2)C55-C57	BD*(2)N53-C54	29.24
LP(1)N53	LP*(6)Pt80	10.12	BD(2)N56-C73	BD*(2)C55-C57	26.18
LP(1)N53	LP*(6)Pt80	4.72	BD(2)C59-C74	BD*(2)N56-C73	30.17
LP(5)Pt80	BD*(2)N19-C22	16.84	BD(2)N19-C22	BD*(2)C15-C18	27.39
BD(1)C18-N19	LP*(6)Pt80	1.27	BD(2)N19-C22	BD*(2)C20-C21	10.76
BD(1)N19-C22	LP*(6)Pt80	1.14	BD(2)N19-C22	BD*(2)C23-C26	11.82
BD(2)N19-C22	LP*(6)Pt80	2.49	BD(2)C20-C21	BD*(2)N19-C22	23.66
LP(1)N56	BD*(1)C59-C73	5.25	BD(2)C23-C26	BD*(2)N19-C22	23.02
LP(1)N53	BD*(1)C50-C72	5.11	BD(2)C23-C26	BD*(2)N56-C73	16.14
LP(1)N19	BD*(1)C17-C18	5.13	BD(2)C15-C18	BD*(2)N19-C22	12.80
BD*(2)N19-C22	LP*(6)Pt80	5.35	BD(2)C15-C18	BD*(2)N19-C22	12.80

E denotes the stabilization energy; BD denotes bonding orbital; BD* denotes antibonding orbital; LP denotes lone-pair. For BD and BD*: (1) and (2) denote σ orbital and π orbital, respectively.



Pt/(10,0) VN-CN_xNTs



p (N) → d (Pt)
E= 10.12 Kcal/mol

Fig S5. The natural bond orbital (NBO) graphs of the Pt/VN-CN_xNT

SI 3. NBO analysis for CH_3OH-Pt/CN_xNT

For deep insight into the interaction between methanol and Pt/CN_xNT catalyst, the orbital analysis was performed for CH_3OH-Pt/CN_xNTs. It is seen that the *p* orbtial of the O in methanol forms strong hybridization with the *d* orbital of the Pt for Pt/PN-CN_xNT and Pt/VN-CN_xNT, while the interaction is promoted via *p* orbtial of the O in methanol interacting with σ* bond of C-Pt for Pt/GN-CN_xNT.

Table S6 Partial calculation results about the CH_3OH-Pt/GN-CN_xNT by NBO analysis

Donor (i)	Acceptor (j)	E(kcal/ mol)	Donor (i)	Acceptor (j)	E(kcal/ mol)
BD(1)C56-Pt81	BD*(2)C55-C57	43.78	LP(2)O83	BD*(1)C56-Pt81	20.95
BD(1)C56-Pt81	BD*(2)C59-C74	15.99	LP(1)O83	BD*(1)C82-H84	3.28
LP(5)Pt81	BD*(2)C55-C57	15.78	LP(1)O83	BD*(1)C56-Pt 81	1.18
BD*(2)C59-C74	BD*(1)C56-Pt81	16.99	LP(5)Pt81	BD*(1)C82-H86	0.20
BD*(1)C56-Pt81	BD*(1)C82-O83	0.34			

E denotes the stabilization energy; BD denotes bonding orbital; BD* denotes antibonding orbital; LP denotes lone-pair. For BD and BD*: (1) and (2) denote σ orbital and π orbital, respectively.

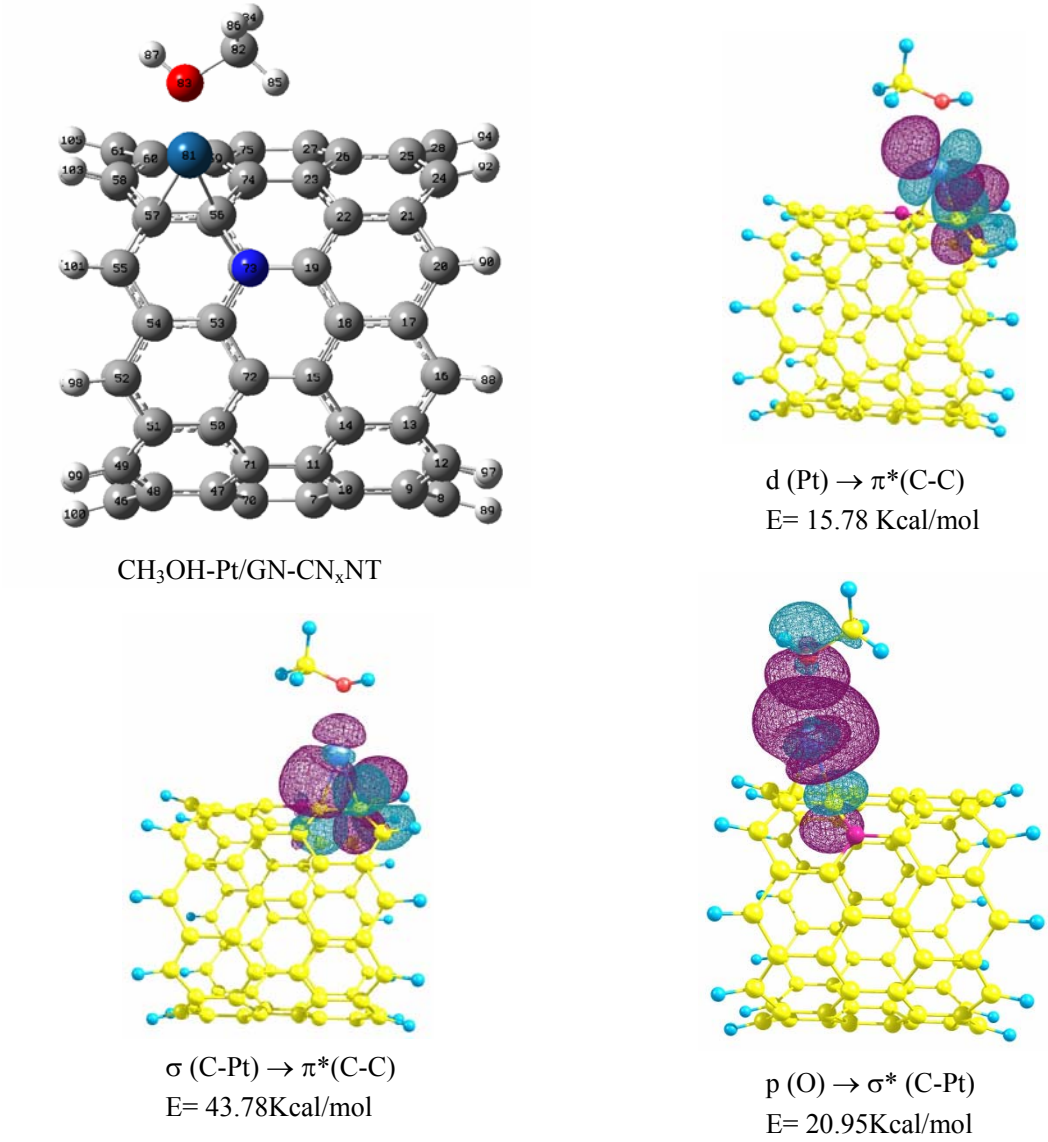
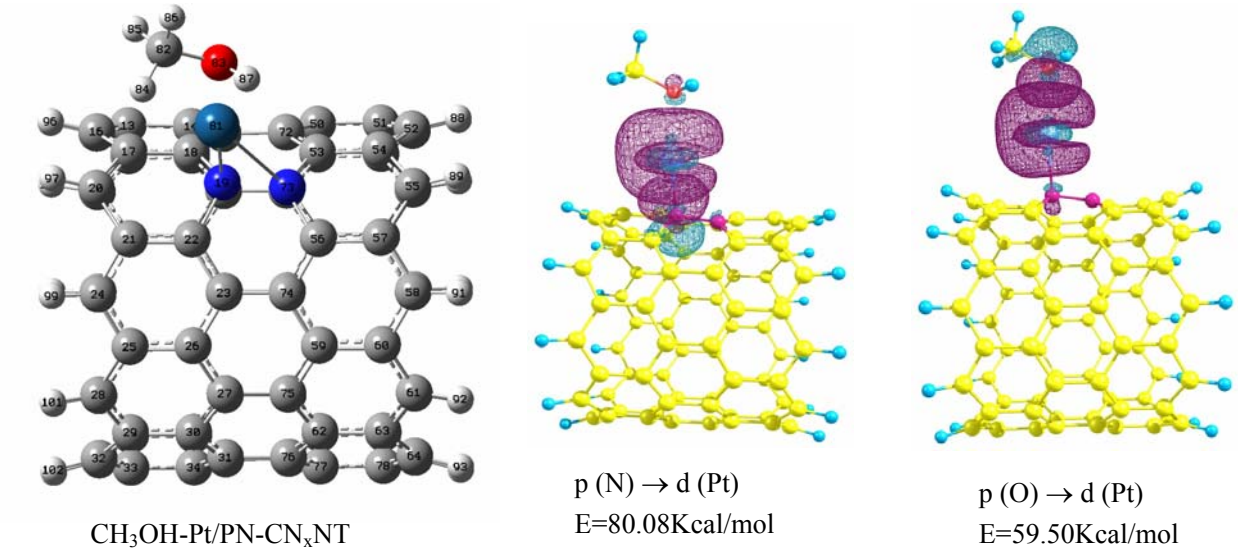


Fig S6. The natural bond orbital (NBO) graphs of the CH_3OH-Pt/GN-CN_xNT

Table S7 Partial calculation results about the CH_3OH-Pt/PN-CN_xNT by NBO analysis

Donor (i)	Acceptor (j)	E(kcal/ mol)	Donor (i)	Acceptor (j)	E(kcal/ mol)
BD(1)C18-N19	LP*(6)Pt81	6.37	LP(4)Pt81	BD*(1)N19-N73	1.21
BD(1)N19-C22	LP*(6)Pt81	6.29	LP(5)Pt81	BD*(1)N19-N73	0.60
BD(1)N19-N73	LP*(6)Pt81	3.77	BD(1)C82-O83	LP*(6)Pt81	2.14
LP(1)N19	LP*(6)Pt81	80.08	BD(1)O83-H87	LP*(6)Pt81	3.26
LP(2)O83	BD*(1)C82-H86	4.73	LP(1)O83	LP*(6)Pt81	2.88
LP(1)O83	BD*(1)C82-H84	6.67	LP(2)O83	LP*(6)Pt81	59.50

E denotes the stabilization energy; BD denotes bonding orbital; BD* denotes antibonding orbital; LP denotes lone-pair. For BD and BD*: (1) and (2) denote σ orbital and π orbital, respectively.



CH_3OH-Pt/PN-CN_xNT

p (N) → d (Pt)
E=80.08Kcal/mol

p (O) → d (Pt)
E=59.50Kcal/mol

Fig S7. The natural bond orbital (NBO) graphs of the CH_3OH-Pt/PN-CN_xNT

Table S8 Partial calculation results about the CH_3OH-Pt/VN-CN_xNT by NBO analysis

Donor (i)	Acceptor (j)	E(kcal/ mol)	Donor (i)	Acceptor (j)	E(kcal/ mol)
LP(1)N53	LP*(6)Pt80	37.08	LP(2)Pt80	BD*(2)N19-C22	0.21
LP(1) N56	LP*(6)Pt80	4.04	LP(2)Pt80	BD*(1)N53-C54	0.19
LP(2)N53	LP*(6)Pt80	1.44	LP (2)Pt80	BD*(1)C81-O82	0.18
LP(1)N19	LP*(6)Pt80	4.80	LP*(6)Pt80	BD*(1)C81-O82	0.54
BD(1)N53-C72	LP*(6)Pt80	2.47	LP (5)Pt80	RY*(1) O82	0.14
BD(1)N53-C54	LP*(6)Pt80	2.61	BD(1)C81-O82	LP*(6)Pt80	0.68
BD(2)N19-C22	LP*(6)Pt80	1.02	LP(1)O82	LP*(6)Pt80	1.24
BD(1)C18-N19	LP*(6)Pt80	1.09	LP(2)O82	LP*(6)Pt80	26.42
LP(1)N53	BD*(1)C81-O82	0.05	LP(1)O82	BD*(1)C81-H83	3.17
LP(5)Pt80	BD*(2)N19-C22	10.56	LP (2)Pt80	BD*(1)N53-C72	0.29
LP*(6)Pt80	BD*(2)C52-C54	1.12			

E denotes the stabilization energy; BD denotes bonding orbital; BD* denotes antibonding orbital; LP denotes lone-pair. For BD and BD*: (1) and (2) denote σ orbital and π orbital, respectively.

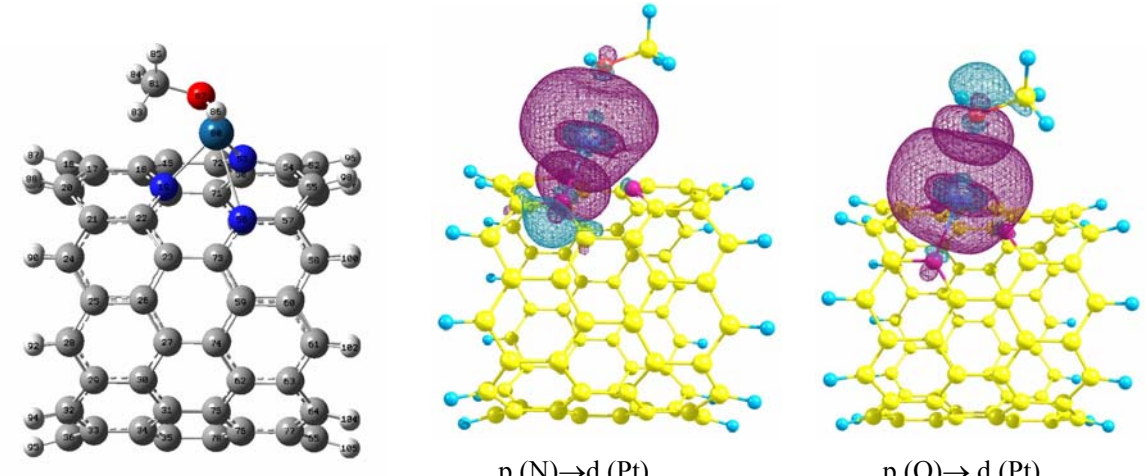


Fig S8. The natural bond orbital (NBO) graphs of the CH_3OH-Pt/VN-CN_xNT

SI 4. The adsorption configuration of TM on (10,0) VN-CN_xNT

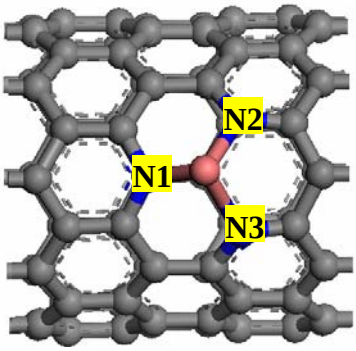


Fig S9. The adsorption configuration of TM on (10,0) VN-CN_xNT. The blue and orange dots denote the N and TM atoms, respectively

The adsorption configuration of TM on (10,0) VN-CN_xNT is shown in Figure S9. N2 and N3 in VN-CN_xNT are two equivalent nitrogen atoms, and the distance between TM and N2 (d_{TM-N2}) is equal to that between TM and N3 (d_{TM-N3}). In the main text, the distances between TM and two nonequivalent nitrogen atoms (d_{TM-N1} and d_{TM-N2}) are listed.

SI 5. The adsorption of TMs on CN_xNT and the interaction of methanol with Pt/CN_xNT catalyst calculated using effective core potentials (ECPs)

The adsorptions of all the transition metals (TMs = Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Pd and Pt) on CN_xNT have been calculated by using effective core potentials (ECPs) to examine the influence of relative effect. The results are compared with those by using all-electron basis sets. It is found that the adsorption energies and bond lengths of all the TMs except for Pt are close to each other in the situations with and without ECPs, respectively (see Table S9 below and Table 4 in the text). Hence, the adsorptions of Pt on the bridge site (B1) of (10,0) CNT and three typical stable nitrogen configurations (GN, VN and PN) of (10,0) CN_xNT, as well as the interaction of methanol with Pt/CN_xNT catalyst were further calculated using ECPs (see Table S10 and Table S11 below). The results show that, after employing the ECPs, the binding energy is increased and the bond length is decreased in comparison with the corresponding ones (see Tables 1-3,5 in the text). Anyway, all the qualitative conclusions with or without the involvement of ECPs are not changed.

Table S9 The adsorptions of TMs on the VN configuration of (10,0) CN_xNT by using ECPs

TM	E_b(eV)[a]	d_{TM-N1} (Å)[b]	d_{TM-N2} (Å)[c]
Sc	7.88	1.95	2.05
Ti	8.41	1.87	1.98
V	6.70	1.86	1.96
Cr	4.89	1.81	1.90
Mn	4.82	1.79	1.87
Fe	8.24	1.78	1.85
Co	6.97	1.80	1.88
Ni	5.57	1.82	1.87
Cu	3.63	1.91	1.90
Zn	1.93	1.87	1.95
Pd	2.58	2.03	2.27
Pt	2.63	2.03	2.12

[a] E_b denotes the binding energy of TM on CN_xNT. [b]d_{TM-N1} and [c]d_{TM-N2} denote the distance between TM and two nonequivalent nitrogen atoms in CN_xNT.

Table S10 The adsorptions of a Pt atom on (10,0) CNT and (10,0) CN_xNT by using ECPs

	E_b(eV)[a]	d_{Pt-N}(Å)[c]
Pt/(10,0)CNT	1.77	2.07, 2.07
Pt/GN-(10,0)CN_xNT	1.98	2.22, 2.29
Pt/PN-(10,0)CN_xNT	2.24	1.95, 2.83
Pt/VN-(10,0)CN_xNT	2.63	2.03, 2.12, 2.12

[a] E_b denotes the binding energy of Pt atom on the nanotubes. [b]d_{Pt-N} denotes the Pt-N bond length.

Table S11 The interactions of methanol with Pt/CNT and Pt/CN_xNT catalysts by using ECPs

	E_b(eV)[a]	d_{Pt-O}(Å)[b]	d_{Pt-C}(Å)[c]
CH_3OH-Pt/(10,0)CNT	0.98	2.22	2.09, 2.08
CH_3OH-Pt/GN-(10,0)CN_xNT	1.09	2.19	2.05, 2.08
CH_3OH-Pt/PN-(10,0)CN_xNT	1.30	2.10	1.98, 2.82
CH_3OH-Pt/VN-(10,0)CN_xNT	1.23	2.16	2.03, 2.16, 2.73

[a] E_b denotes the binding energy of the interaction. [b] d_{Pt-O} denotes the distance between O atom of the adsorbed molecule and the Pt atom. [c] d_{Pt-C} denotes the distance between the Pt atom and the C atoms in CNT.