Highly uniform Ni particles with phosphorus and adjacent defects catalyze 1,5-dinitronaphthalene hydrogenation with excellent catalytic performance

Wei Xiong[1,2], Susu Zhou[1], Zeyong Zhao[1], Fang Hao (✉)[1], Zhihui Cai[1], Pingle Liu (✉)[1], Hailiang Zhang[2], Hean Luo[1]

1 College of Chemical Engineering, National & Local United Engineering Research Centre for Chemical Process Simulation and Intensification, Xiangtan University, Xiangtan 411105, China

2 College of Chemistry, Xiangtan University, Xiangtan 411105, China

E-mails: haofang.happy@163.com (Hao F), liupingle@xtu.edu.cn (Liu P)

Electronic Supplementary Material

Table S1-S5, Figure S1-S8

Table S1 Textural properties of the different N,P-ACs supports

Sample	Specific surface area /(m^2 g^{-1})	Pore diameter /nm	Pore volume /(cm^3 g^{-1})
AC	1100.7	3.17	0.13
N,P-AC-800	1027.1	3.11	0.10
N,P-AC-900	1366.3	2.95	0.18

Table S2 Hydrogen chemisorption data of the different catalysts

Catalysts	H_2 uptake/Cumulative quantity /(μL·g^{-1})	Metallic surface areas / (m^2 g^{-1})	Dispersion /%
Ni/AC	97.67	0.34	0.20
Ni/N-P(IL)AC-800	132.88	0.47	0.28
Ni/N-P(IL)AC-900	157.09	0.55	0.33
Ni/N-AC-900	103.09	0.36	0.22
Ni/P-AC-900	133.63	0.47	0.29

The hydrogen chemisorption of N,P-ACs supported nickel catalysts was carried out to quantify the Hydrogen uptake and the metallic surface area. The results are shown in **Table S2**. Compared with undoped Ni/AC, Ni/N,P-AC-800 and Ni/N,P-AC-900 showed better hydrogen uptake, metal surface area and metal dispersion, of which Ni/N,P-AC-900 exhibits the maximum hydrogen uptake of 157.09 μL·g^{-1}, metallic surface area of 0.55m^2 g^{-1}, and metal dispersion of 0.33%.

Table S3 The comparison of the catalytic performance of the present work and the literatures

Entry	Samples	Reaction conditions	Substrate	Con./Sel. /%	Ref.
1	20Ni/CNTs-1	DMF, 393 K, 330 min 1 Mpa	1,5-dinitronaphthalene	100/70.59	[1]
2	10Ni/C	THF, 593K, 360 min 5.2 Mpa	1,5-dinitronaphthalene	96.6/2.4	[2]
3	10Ni-Zn/AC-350	DMF, 383K, 300 min 0.6 Mpa	1,5-dinitronaphthalene	100/95.63	[3]
4	20Ni/N-AC-900	DMF, 373 K, 300 min 0.6 Mpa	1,5-dinitronaphthalene	100/18.59	[4]
5	20Ni/N,P-AC-900	DMF, 373 K, 150 min 0.6 Mpa	1,5-dinitronaphthalene	100/94.79	This work

Table S4 The binding energies of Ni_n clusters (n=1-6)

Ni_n clusters mode	Total E /eV	E_{bind} (Ni_n) /eV
Ni	-41037.84809	/
2Ni	-82078.30853	1.306176000
3Ni	-123118.8481	1.767954569
4Ni	-164159.656	2.065901025
5Ni	-205200.5892	2.269747478
6Ni	-246242.1853	2.516130368

The results in **Table S4** indicate that the stability of the nickel atom clusters increase gradually with the increasing numbers of nickel atoms.

Table S5 The total energies of different modes of carbon supports

different support mode	Total E /eV
Original carbon support	-33163.68725
Graphite-N carbon	-33614.85347
Pyridine-N carbon	-32573.95175
Pyrrolic-N carbon	-32573.95259
Carbon with 12r-defect	-32119.61859
Carbon with 14r-defect	-31082.54807

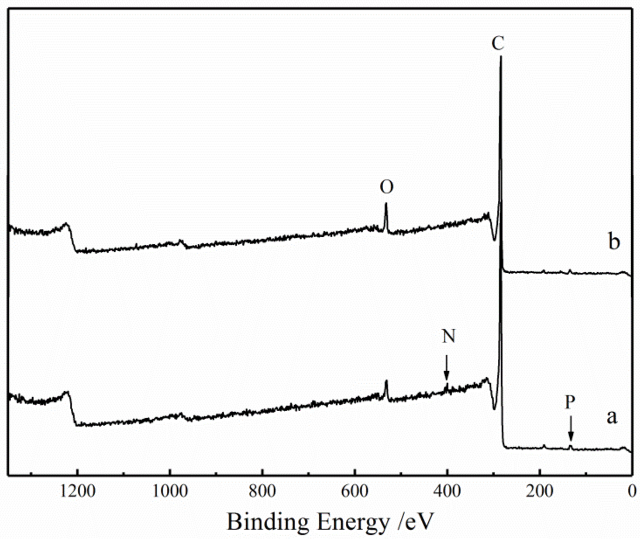


Figure S1 XPS survey spectra of the N,P-ACs-T: (a) N,P-AC-800, (b) N,P-AC-900

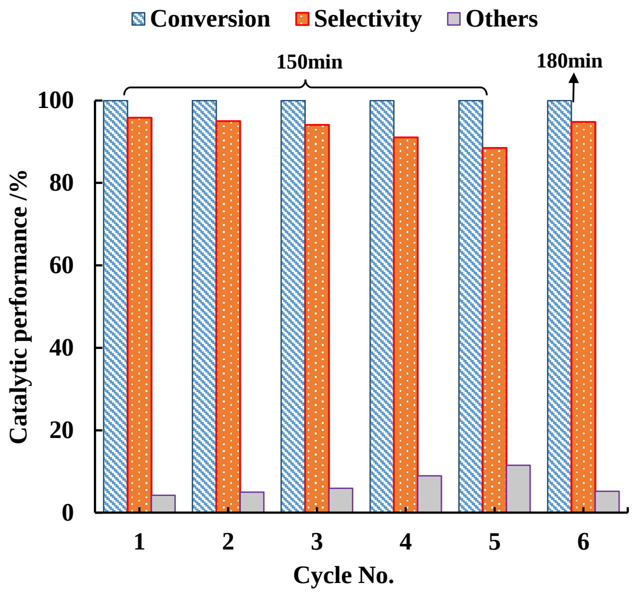


Figure S2 The recycle stability of Ni/N,P-AC-900

The recycle stability of the Ni/N,P-AC-900 has also been investigated and the results are shown in **Figure S2.** It can be seen that the catalytic performance could be stable in five cycles running, and the catalytic activity of the catalyst decreased gradually. The conversion and selectivity to the target product could be enhanced by prolonging the reaction time to 180 min.

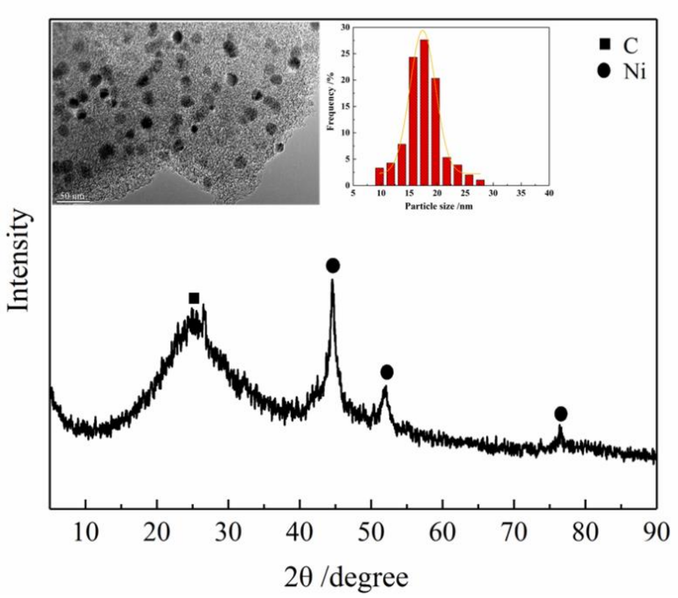


Figure S3 The XRD and TEM of Ni/N,P-AC-900 after recycle

The XRD and TEM of Ni/N,P-AC-900 after recycle were investigated and shown in **Figure S3**. It indicated that the crystallization of the nickel metal decreased and the particle size of nickel nanoparticle could be maintained around 18~20 nm after recycles for 6 times.

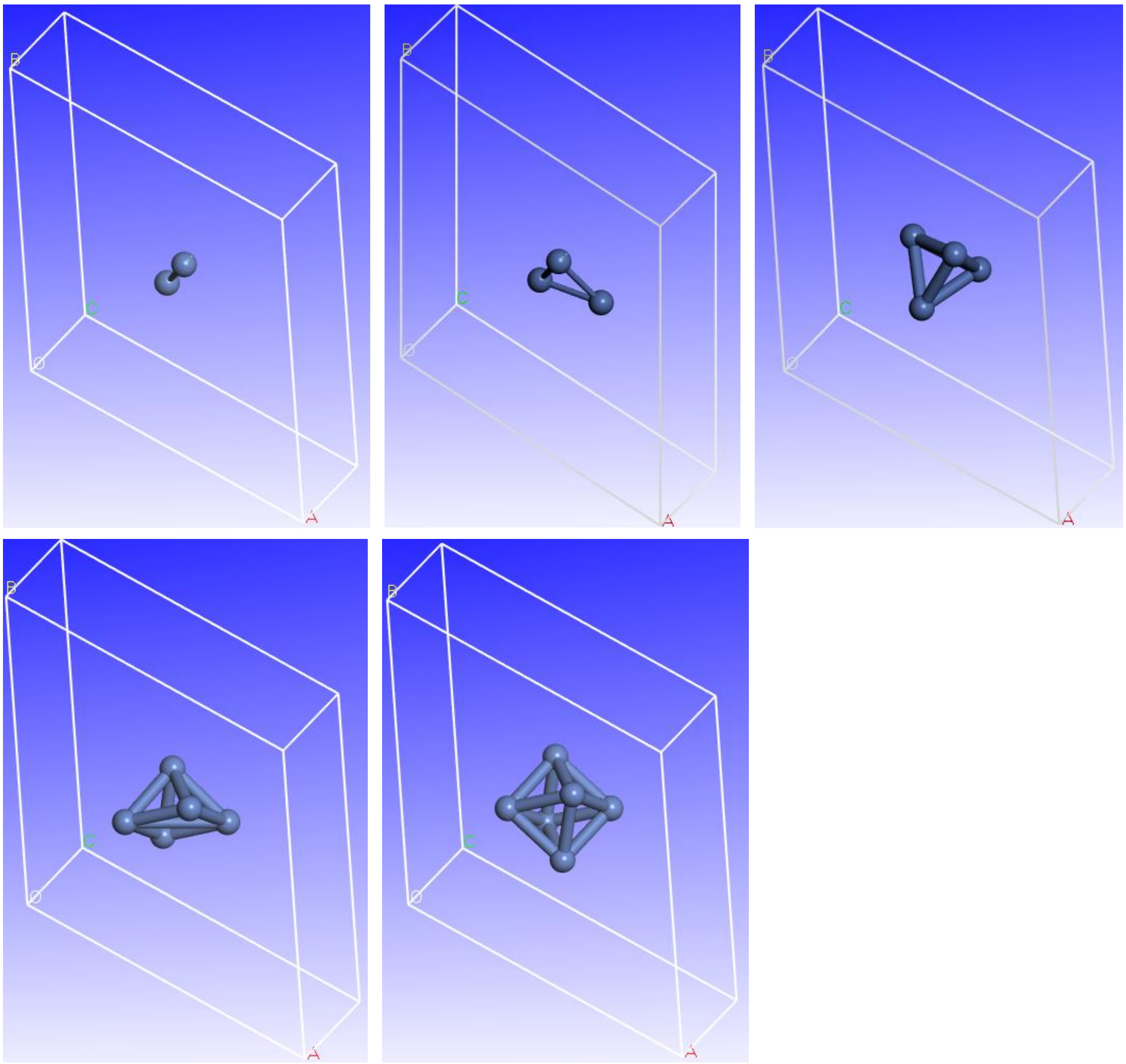
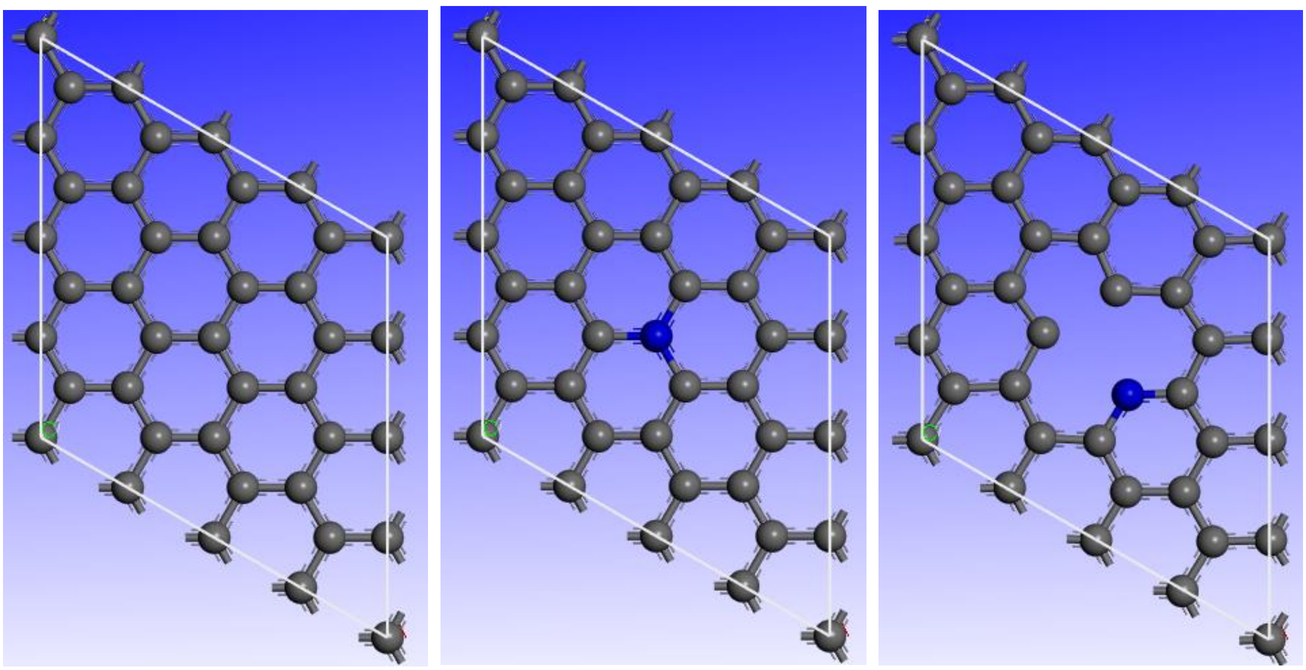


Figure S4 The Ni_n clusters (n=2-6) mode after geometry optimization



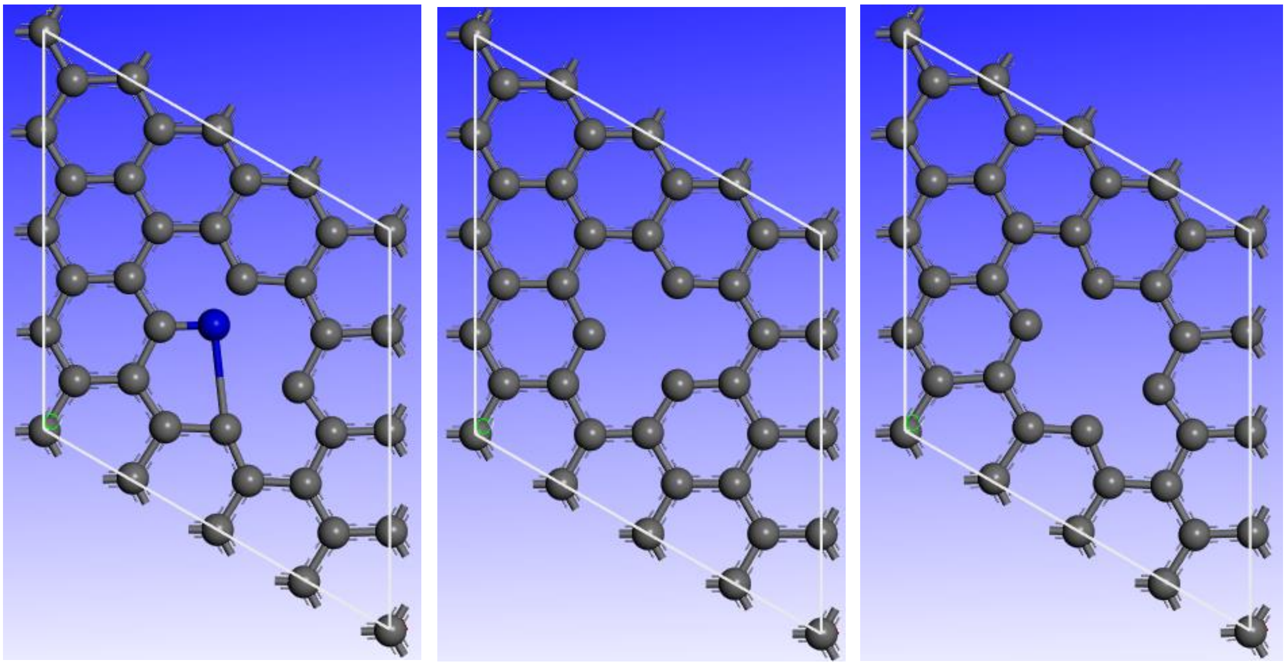
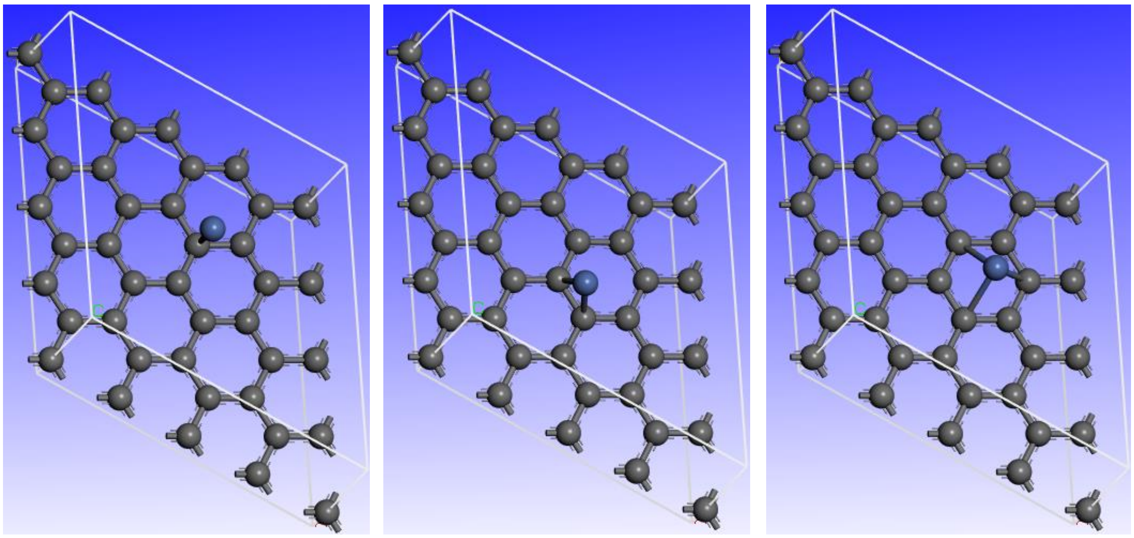
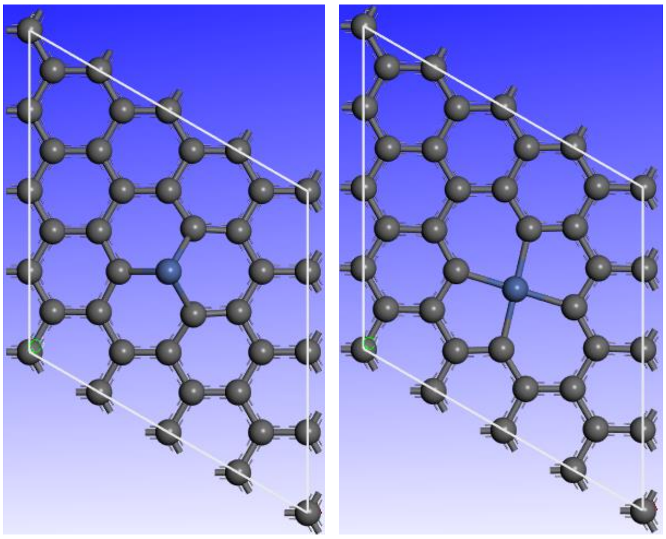


Figure S5 The modes of the original carbon support (without heteroatoms doping and defect), Doped carbon support with nitrogen species (graphite N, pyridine N and pyrrolic N, respectively), and carbon support with defect but without nitrogen species after geometry optimization.

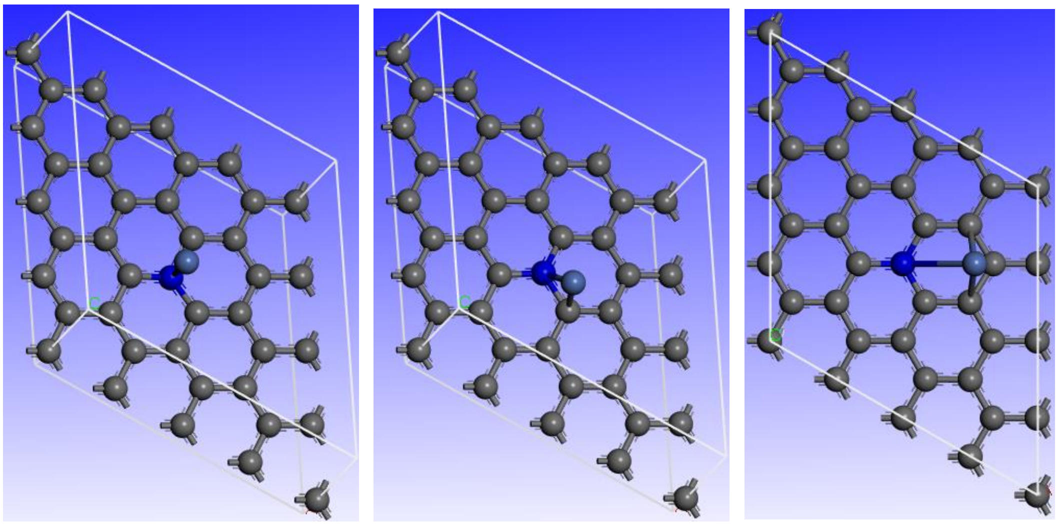
Figure S6 (1) Ni on carbon without defects and nitrogen species after geometry optimization (Top, Bridge and Hollow sites)



(2) Ni on carbon with two different kinds of defects after geometry optimization (12 ring defect and 14 ring defect)

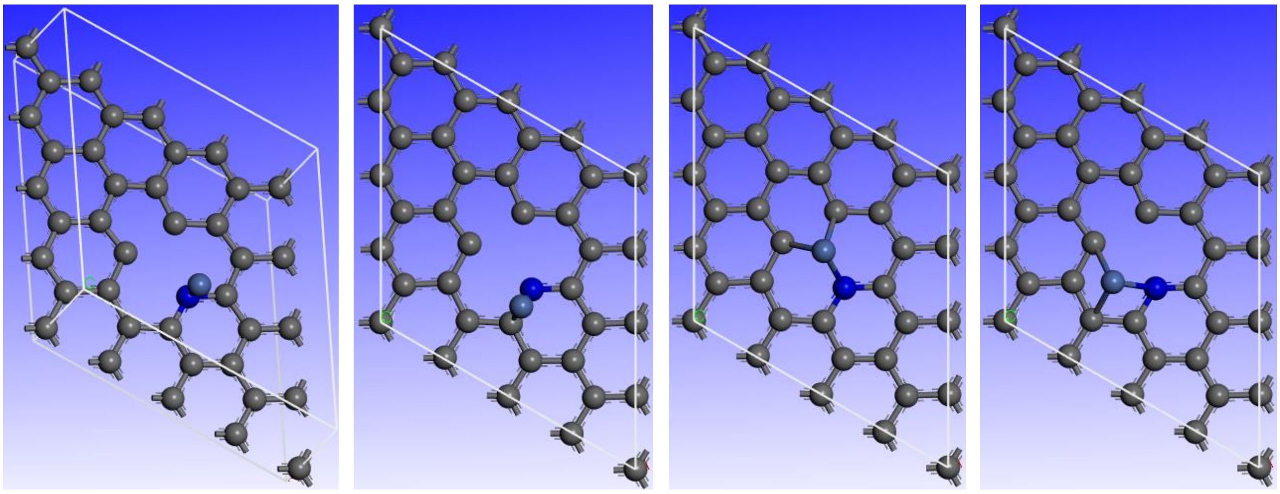


(3) Ni on graphite N doped carbon after geometry optimization (Top, Bridge and Hollow sites)

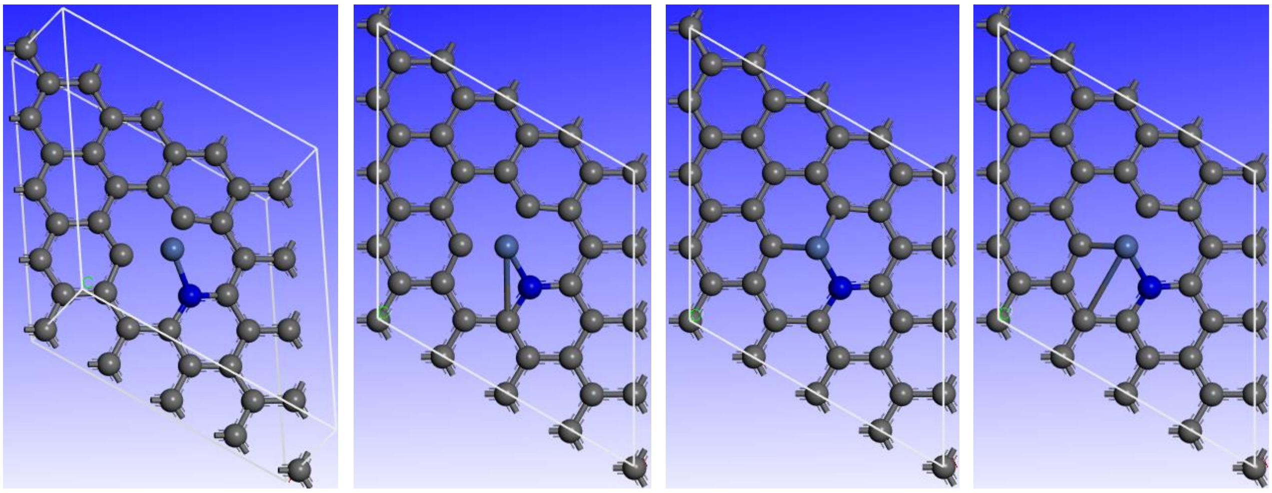


(4) Ni on pyridine N doped carbon before and after geometry optimization (Top, Bridge and two different Hollow sites)

Before:

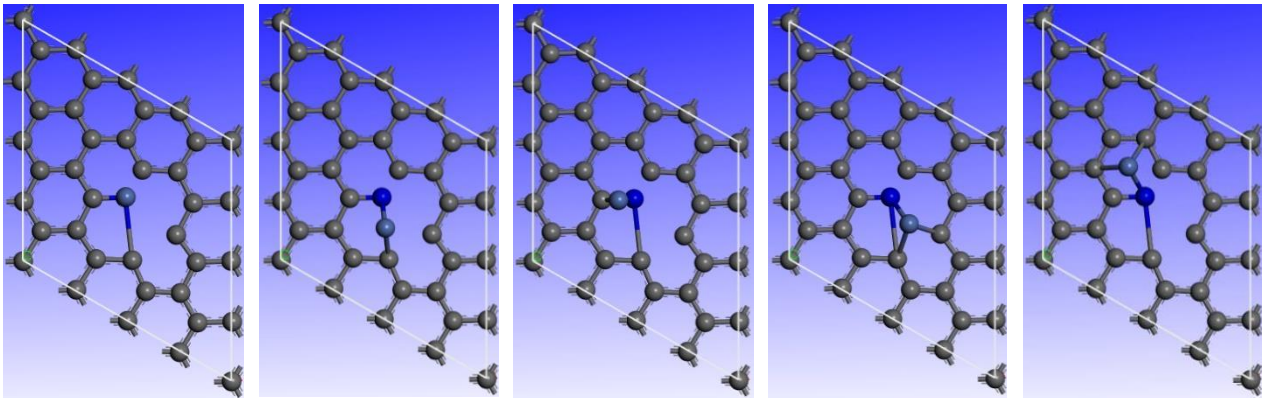


After:



(5) Ni on pyrrolic N doped carbon before and after geometry optimization (Top, two different Bridge and Hollow sites)

Before:



After:

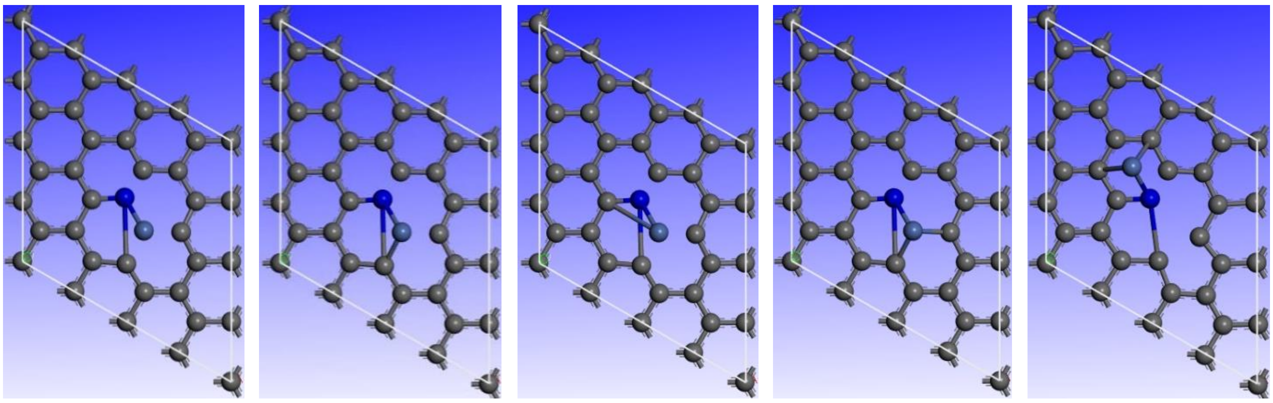


Figure S6 The nickel binding configurations of three different binding sites (top, bridge and hollow) on different support before and after geometry optimization.

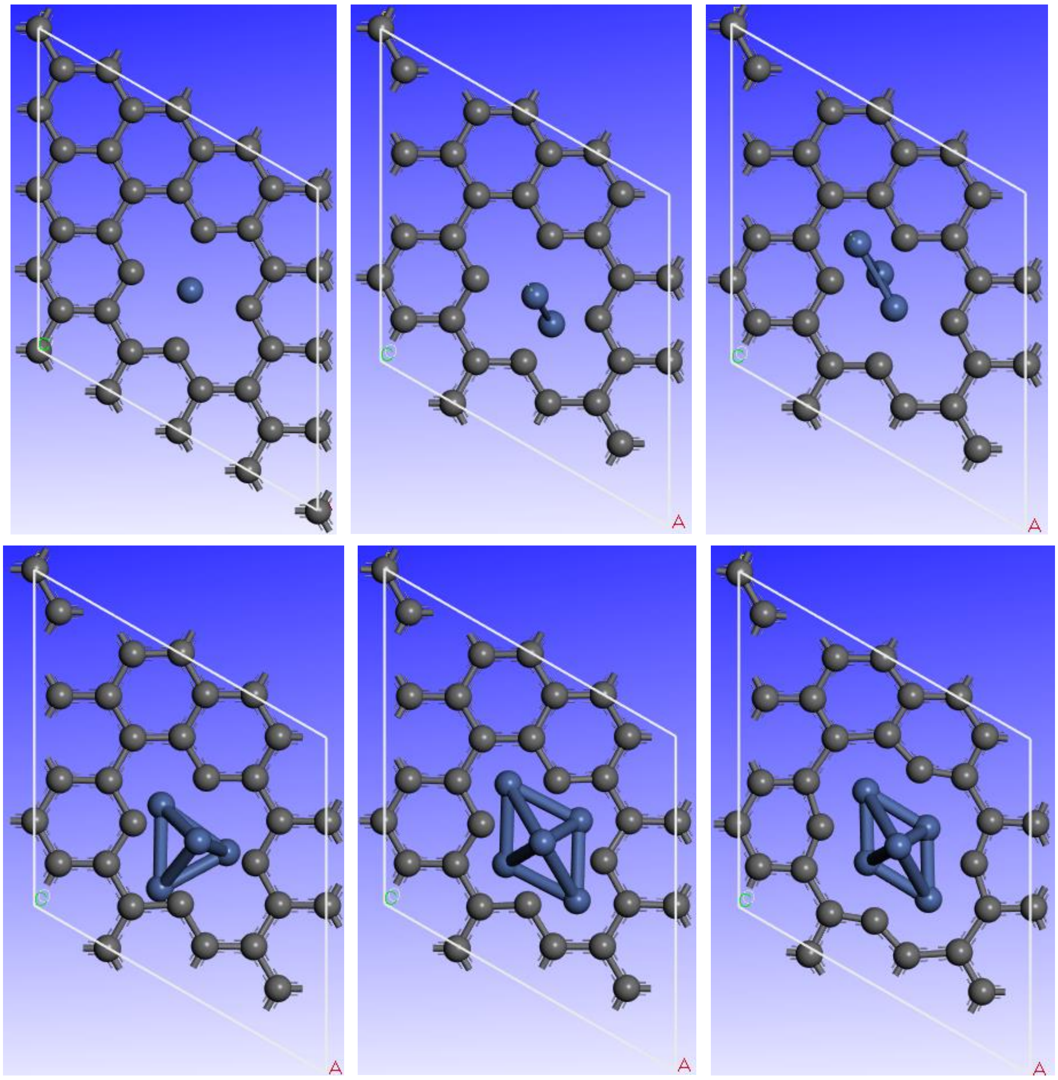


Figure S7 The Ni_n (n=1-6) clusters loaded on the mode of carbon support with 14-ring defect after geometry optimization.

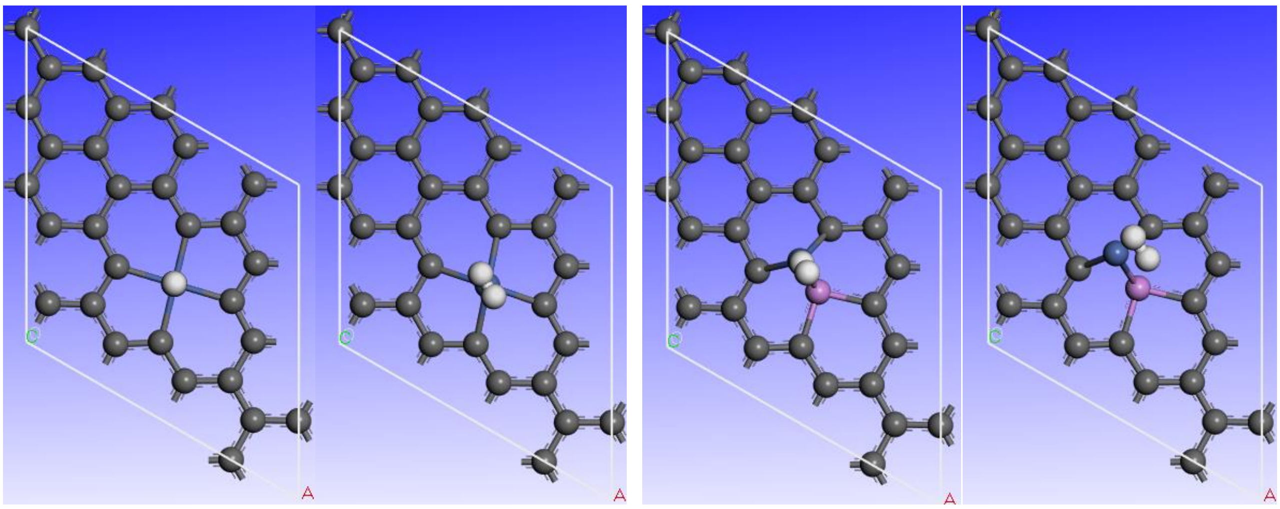


Figure S8 The optimized H_2 adsorption configurations on Ni loaded on different supports with or without phosphorus doping (Top and parallel sites)

References

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[3] Huang L, Lv Y, Wu S T, Liu P L, Xiong W, Hao F, Luo H A. Activated carbon supported bimetallic catalysts with combined catalytic effects for aromatic nitro compounds hydrogenation under mild condition. Applied Catalysis A: General, 2019, 577: 76-85

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