Supplementary Materials:

Insight into Pt (111) surface predicts the selective hydrogenation catalyst

Tianzuo Wang[1,2], Lun Pan[1,2,*], Xiangwen Zhang[1,2]and Ji-Jun Zou[1,2]

[1] Key Laboratory for Green Chemical Technology of the Ministry of Education, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China

[2] Collaborative Innovative Center of Chemical Science and Engineering (Tianjin), Tianjin 300072, China

* Corresponding author:

Tel and fax: 86-22-27892340

E-mail: panlun76@tju.edu.cn (L. Pan)

Table of contents

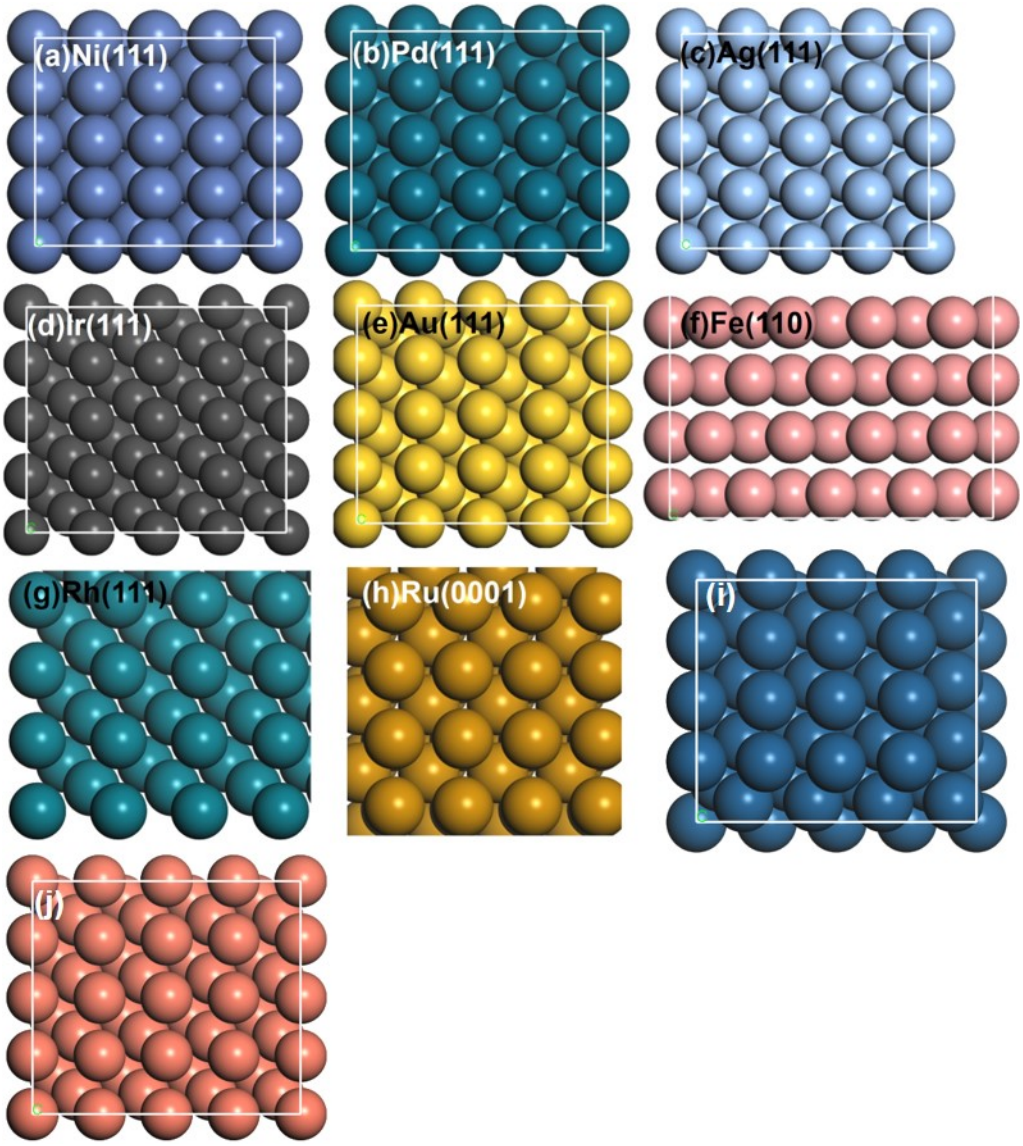

Fig. S1. Models of (a) Ni (111), (b) Pd (111), (c) Ag (111), (d) Ir (111), (e) Au (111), (f) Fe (110), (g) Rh (111), (h) Ru (0001), (i) Pt (111), (j) Cu (111) surfaces.

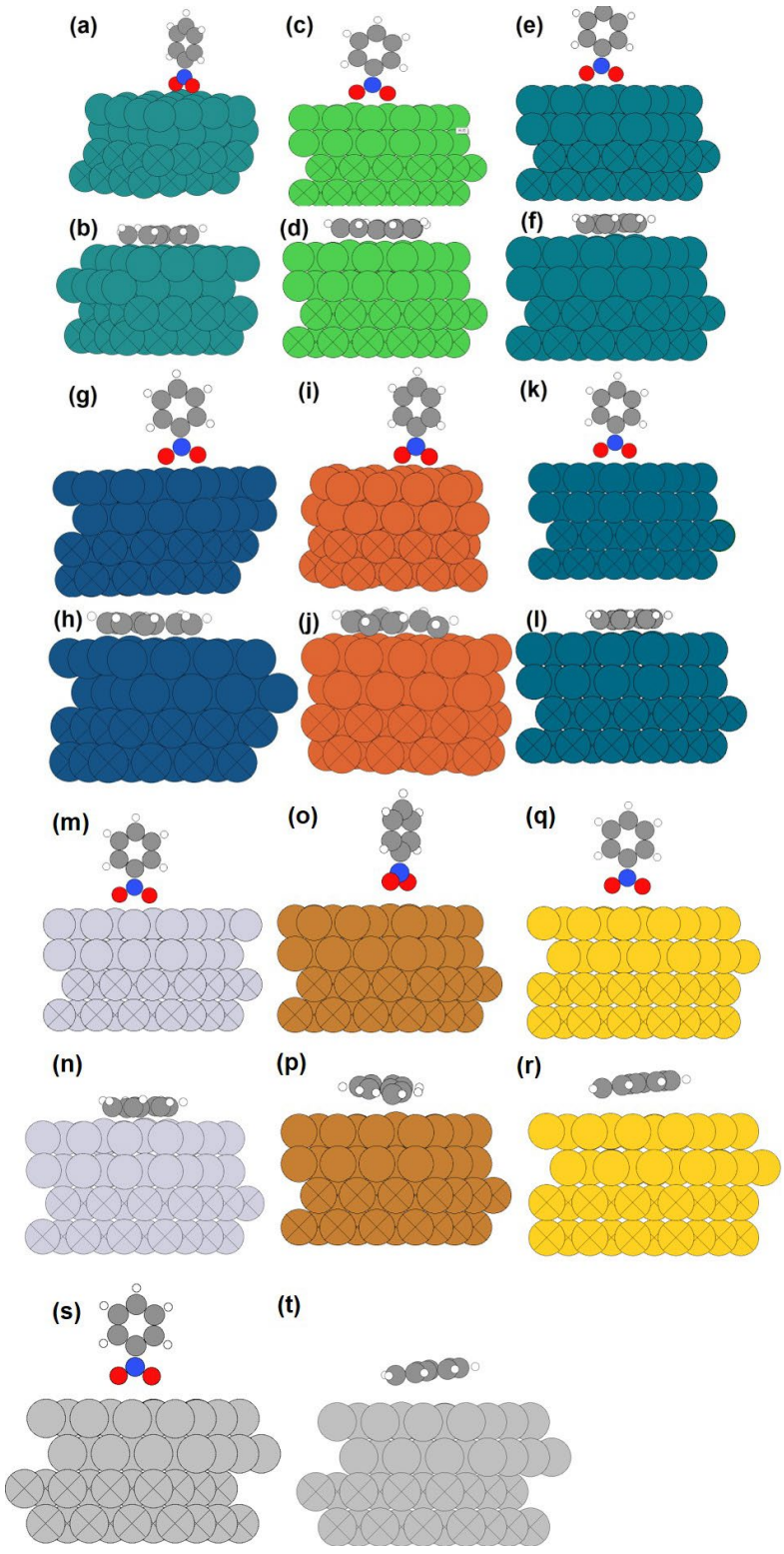

Fig. S2. Nitrobenzene and styrene are adsorbed stably on different metal surfaces. (a) $PhNO_2$/Ru, (b) PhC_2H_3/Ru, (c) $PhNO_2$/Ni, (d) PhC_2H_3/Ni, (e) $PhNO_2$/Rh, (f) PhC_2H_3/Rh, (g) $PhNO_2$/Pd, (h) PhC_2H_3/Pd, (i) $PhNO_2$/Fe, (j)

PhC_2H_3/Fe, (k) $PhNO_2$/Ir, (l) PhC_2H_3/Ir, (m) $PhNO_2$/Pt, (n) PhC_2H_3/Pt, (o) $PhNO_2$/Cu, (p) PhC_2H_3/Cu, (q) $PhNO_2$/Au, (r) PhC_2H_3/Au, (s) $PhNO_2$/Ag, (t) PhC_2H_3/Ag.

Table S1. Adsorption parameters of H and H_2 on Pt (111) and Cu (111).

Adsorption System	Bond Length(Å)	Adsorption Energy (eV)
$_2$-Pt-fcc	1.854	-1.0082
$_2$-Cu	3.788	-0.0044
-Pt-fcc	1.873	-0.5135
-Cu-fcc	1.740	-0.1726
-Pt-hcp	1.857	-0.4592
-Cu-hcp	1.738	-0.1702
-Pt-top	1.556	-0.4433

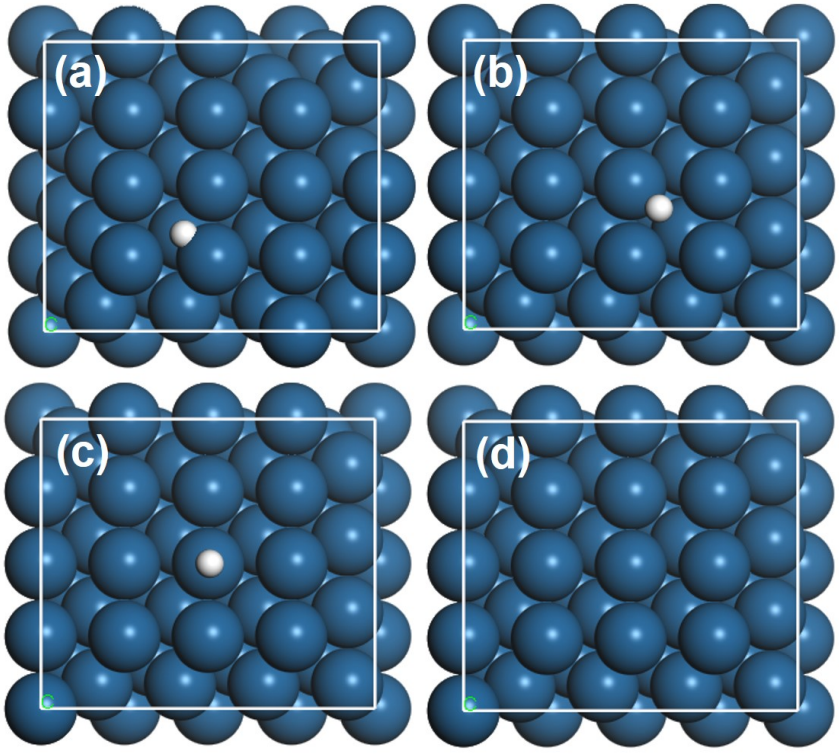

Fig. S3. The models of H atoms adsorbed on the top (a), hcp (b) and fcc (c) positions of Pt (111), and pure Pt (111) slab (d). The blue and white balls are Pt atoms and hydrogen atoms, respectively.

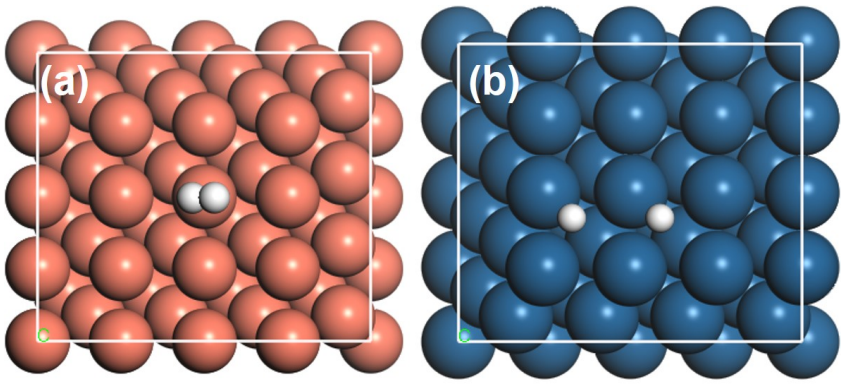

Fig. S4. The models of H_2 molecules adsorbed on Cu (111) (a) and Pt (111) (b) surface. The dark yellow, white, and blue balls are Cu atoms, hydrogen atoms, and Pt atoms, respectively.

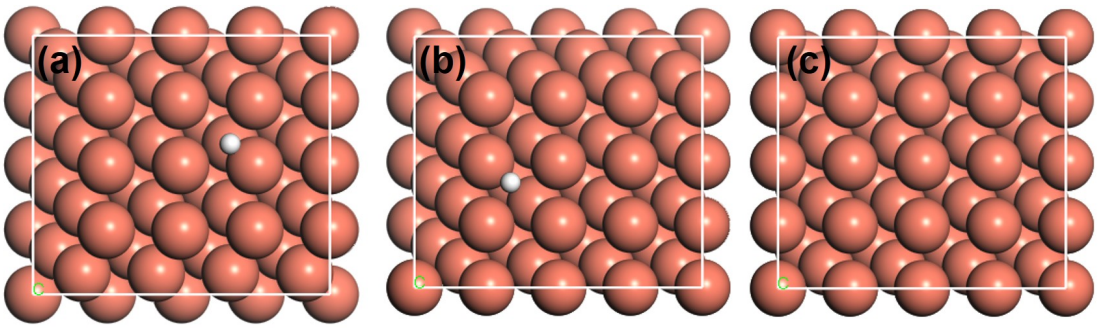

Fig. S5. The models of H atoms adsorbed on the hcp (a) and fcc (b) positions of Cu (111), and pure Cu (111) slab (c). The dark yellow and white balls are Cu and hydrogen atoms, respectively.

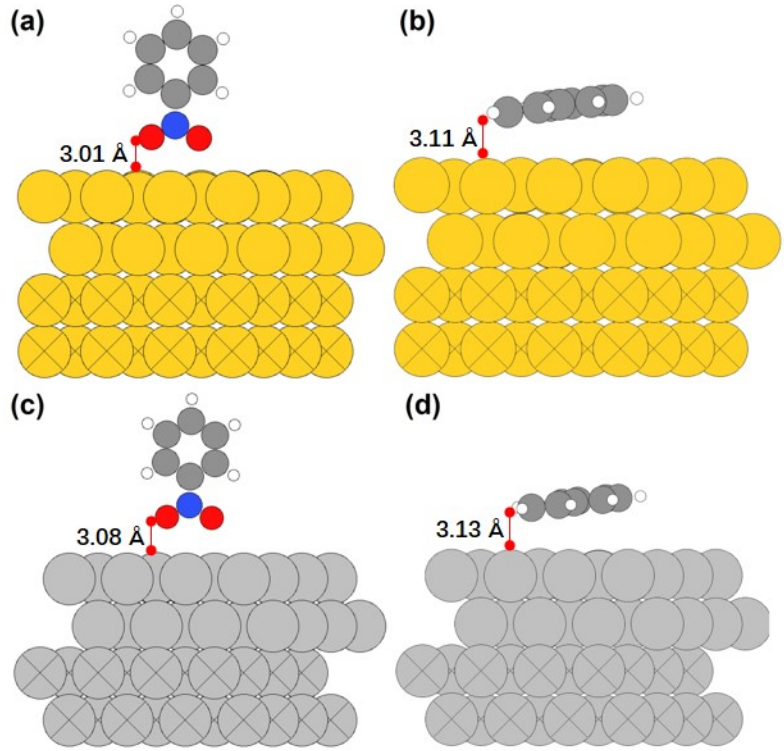

Fig. S6. Schematic diagram of nitrobenzene and styrene adsorbed on Au and Ag. $PhNO_2$/Au (a), PhC_2H_3/Au (b), $PhNO_2$/Ag (c), PhC_2H_3 (d).

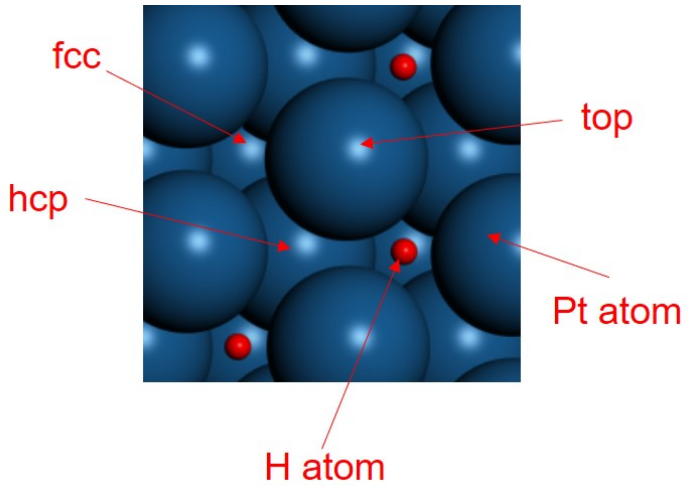

Fig. S7. Schematic diagram of the coverage of fcc-H atoms. The blue and red balls are Pt and hydrogen atoms, respectively.

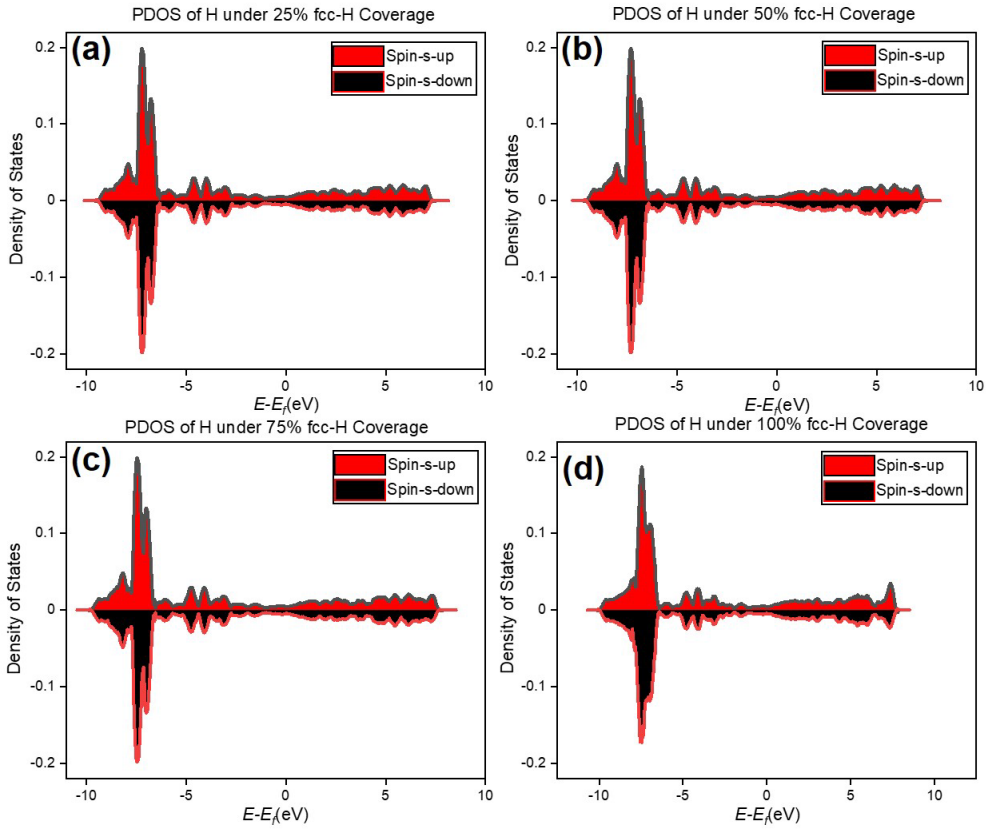

Fig. S8. Density of states of Pt (111) surface with 0% (a), 25% (b), 50% (c), 75% (d) and 100% (e) fcc-H coverage.

Table S2. The d-band center of Pt atoms covered by fcc-H in the surface layer of 25% (a), 50% (b), 75% (c), and 100% (d), respectively.

(a)	d band center (eV)			
Position coordinates (X, Y)	Y=1	Y=2	Y=3	Y=4
X=1	-1.951	-1.951	-1.952	-1.951
X=2	-1.951	-2.003	-1.951	-2.002
X=3	-1.951	-1.951	-1.952	-1.951
X=4	-1.951	-2.003	-1.951	-2.002

(b)	d band center (eV)			
Position coordinates (X, Y)	Y=1	Y=2	Y=3	Y=4
X=1	-2.140	-2.163	-2.140	-2.163
X=2	-2.163	-2.141	-2.163	-2.141
X=3	-2.140	-2.163	-2.140	-2.163
X=4	-2.163	-2.141	-2.163	-2.141

(c)	d band center (eV)			
Position coordinates (X, Y)	Y=1	Y=2	Y=3	Y=4
X=1	-2.184	-2.184	-2.184	-2.184
X=2	-2.23	-2.184	-2.23	-2.184
X=3	-2.184	-2.184	-2.184	-2.184
X=4	-2.23	-2.184	-2.23	-2.184

(d)	d band center (eV)			
Position coordinates (X, Y)	Y=1	Y=2	Y=3	Y=4
X=1	-2.248	-2.247	-2.248	-2.247
X=2	-2.247	-2.248	-2.247	-2.248
X=3	-2.248	-2.247	-2.248	-2.247
X=4	-2.247	-2.248	-2.247	-2.248

Table S3. The d-band center of Pt atoms covered by fcc-H in the second layer of 25% (a), 50% (b), 75% (c), and 100% (d), respectively.

(a)	d band center (eV)			
Position coordinates (X, Y)	Y=1	Y=2	Y=3	Y=4
X=1	-2.185	-2.185	-2.185	-2.185
X=2	-2.185	-2.215	-2.185	-2.215
X=3	-2.185	-2.185	-2.185	-2.185
X=4	-2.185	-2.215	-2.185	-2.215

(b)	d band center (eV)			
Position coordinates (X, Y)	Y=1	Y=2	Y=3	Y=4
X=1	-2.356	-2.386	-2.356	-2.386
X=2	-2.386	-2.356	-2.386	--2.356
X=3	-2.356	-2.386	-2.356	-2.386
X=4	-2.386	-2.356	-2.386	-2.356

(c)	d band center (eV)			
Position coordinates (X, Y)	Y=1	Y=2	Y=3	Y=4
X=1	-2.427	-2.427	-2.427	-2.427
X=2	-2.435	-2.427	-2.435	-2.427
X=3	-2.427	-2.427	-2.427	-2.427
X=4	-2.435	-2.427	-2.435	-2.427

(d)	d band center (eV)			
Position coordinates (X, Y)	Y=1	Y=2	Y=3	Y=4
X=1	-2.462	-2.461	-2.462	-2.461
X=2	-2.461	-2.462	-2.461	-2.462
X=3	-2.462	-2.461	-2.462	-2.461
X=4	-2.461	-2.462	-2.461	-2.462

Table S4. The d-band center of Pt atoms covered by fcc-H in the third layer of 25% (a), 50% (b), 75% (c), and 100% (d), respectively.

(a)	d band center (eV)			
Position coordinates (X, Y)	Y=1	Y=2	Y=3	Y=4
X=1	-2.288	-2.288	-2.288	-2.288
X=2	-2.288	-2.308	-2.288	-2.308
X=3	-2.288	-2.288	-2.288	-2.288
X=4	-2.288	-2.308	-2.288	-2.308

(b)	d band center (eV)			
Position coordinates (X, Y)	Y=1	Y=2	Y=3	Y=4
X=1	-2.399	-2.405	-2.399	-2.405
X=2	-2.405	-2.399	-2.405	-2.399
X=3	-2.399	-2.405	-2.399	-2.405
X=4	-2.405	-2.399	-2.405	-2.399

(c)	d band center (eV)			
Position coordinates (X, Y)	Y=1	Y=2	Y=3	Y=4
X=1	-2.448	-2.448	-2.448	-2.448
X=2	-2.461	-2.448	-2.461	-2.448
X=3	-2.448	-2.448	-2.448	-2.448
X=4	-2.461	-2.448	-2.461	-2.448

(d)	d band center (eV)			
Position coordinates (X, Y)	Y=1	Y=2	Y=3	Y=4
X=1	-2.472	-2.472	-2.472	-2.472
X=2	-2.472	-2.472	-2.472	-2.472
X=3	-2.472	-2.472	-2.472	-2.472
X=4	-2.472	-2.472	-2.472	-2.472

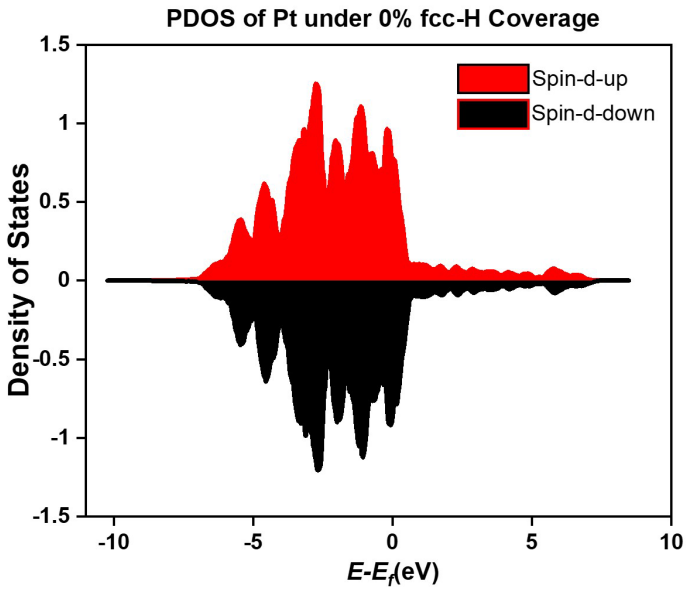

Fig. S9. The density of states of Pt (111) without fcc- coverage .

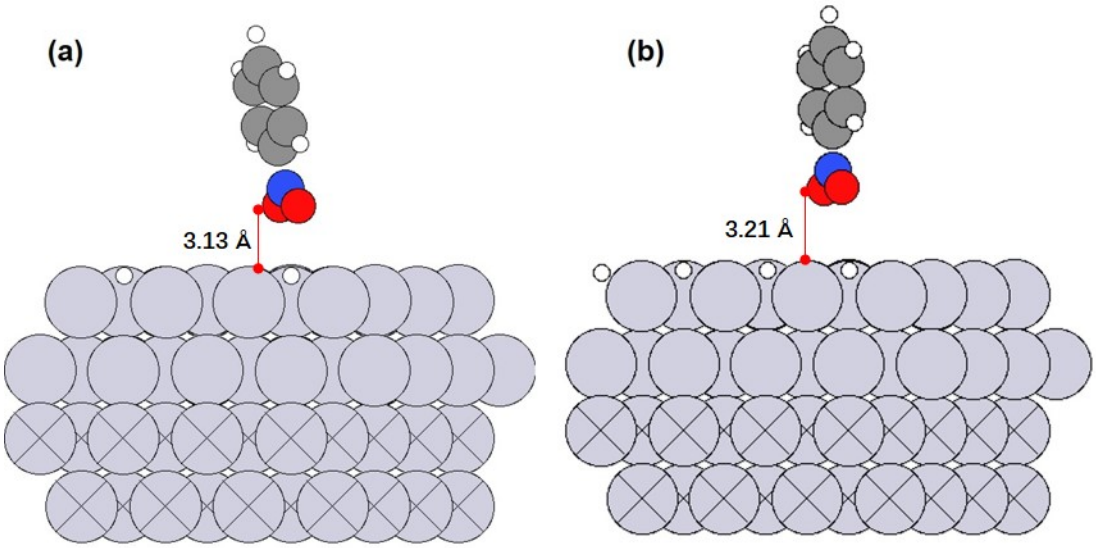

Fig. S10. Schematic diagram of nitrobenzene adsorbed on Pt (111) with 75% (a) and 100% (b) fcc-H coverage.

Fig. S11. Schematic diagram of the reaction path of ethylene on Pt (111) under different fcc-H coverage. The blue, white and gray balls are Pt, H and C atoms, while the red one is the H atom to be added.

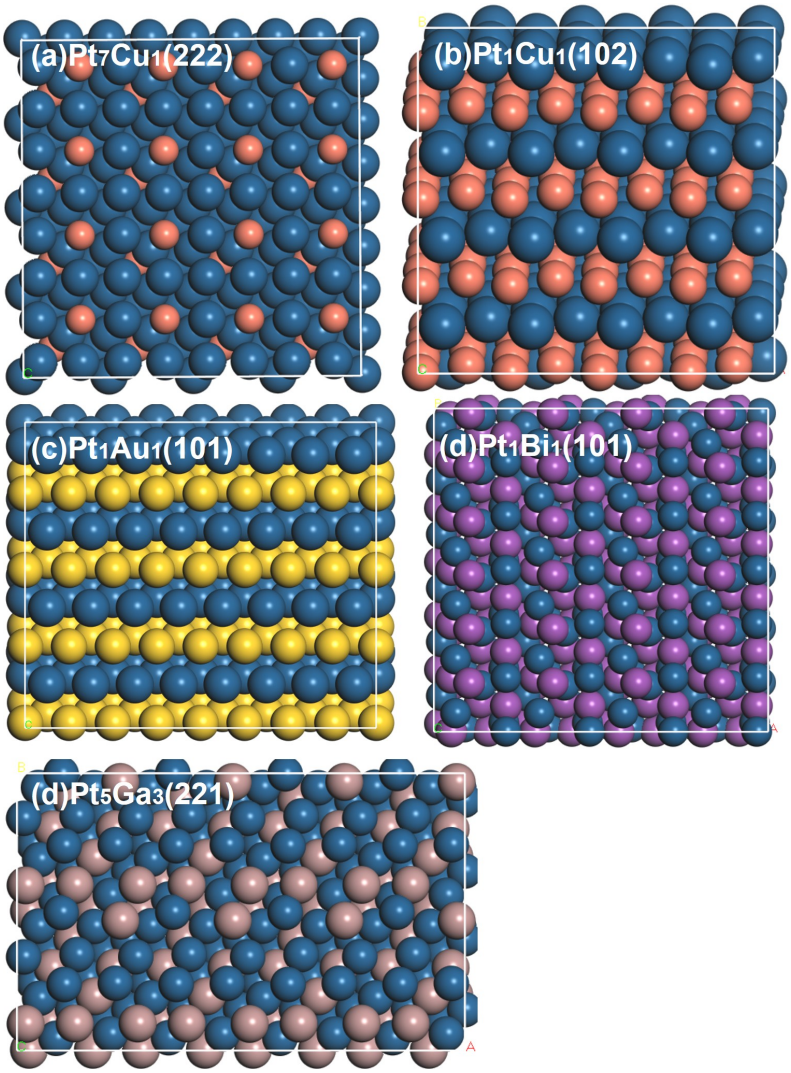

Fig. S12. Pt-based alloys: (a)Pt_7Cu_1; (b) Pt_1Cu_1; (c) Pt_1Au_1; (d) Pt_1Bi_1; (e)Pt_5Ga_3. The blue balls are Pt atoms, the dark yellow balls are Cu atoms, the light-yellow balls are Au atoms, the purple balls are Bi atoms, and the brown balls are Ga atoms.

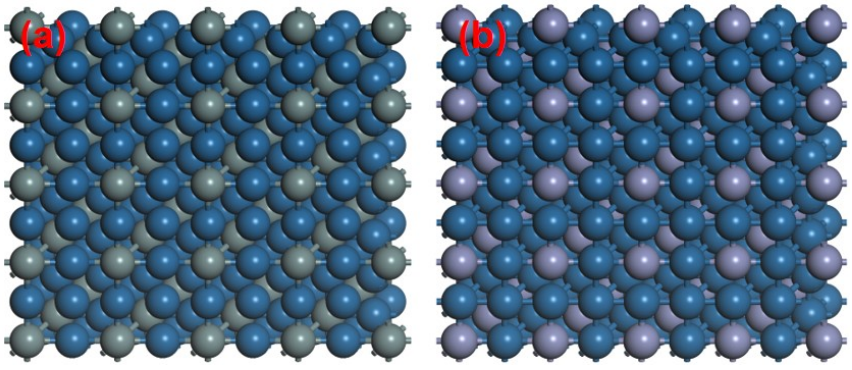

Fig. S13. (a) $Pt_3Sn_1(111)$; (b) $Pt_3Zn_1(111)$. The blue, gray and dark pink balls are Pt, Sn and Zn atoms.

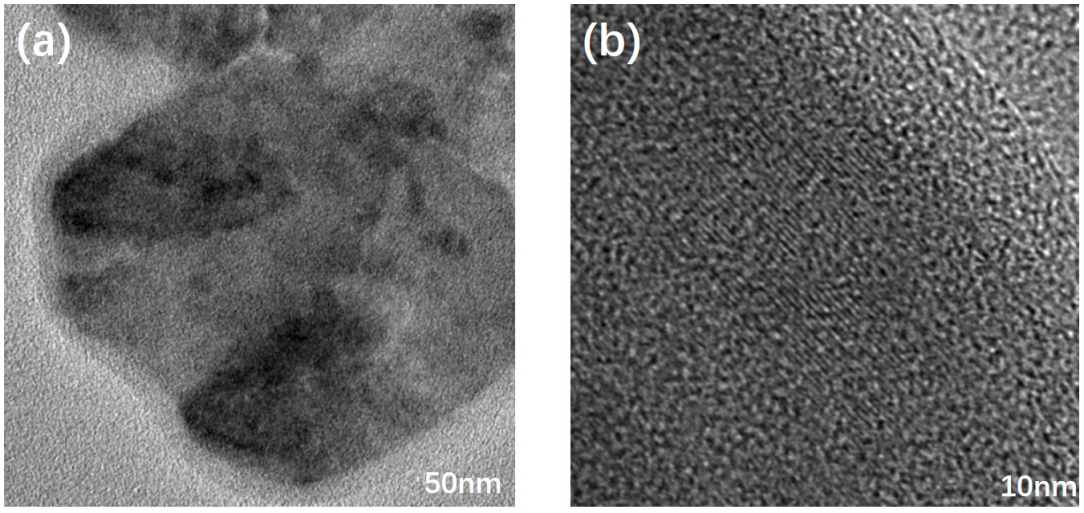

Fig. S14.Transmission electron microscope (TEM) images of Pt/CN in different scales (a)50nm, (b)10nm.

General computational details

All calculations were performed using spin-polarization density functional theory (DFT) by using Vienna ab initio simulation package (VASP). [1] The generalized gradient approximation (GGA) and Perdew-Burke-Emzerhof (PBE) functionals were used to describe the exchange correlation energy. [2-3] The projector augmented wave (PAW) method was used to simulate the potential characteristics and the van der Waals interaction was described in terms of empirical correction (D3).[4] In all calculations, the plane wave cutoff energy was set at 400 eV, and the atoms relaxed completely until the residual force was less than 0.02 eV $Å^{-1}$. Different metals have different K points. The adsorption energy was calculated using fcc (111) and hcp (0001) surfaces 4×4×1 Monkhorst-

Pack mesh, bcc (110) surfaces 4×6×1 Monkhorst-Pack mesh, and the electronic structure was calculated using 9×9×1 k point grid.

We used (0001) surfaces for hcp metals (Ru), (111) surfaces for fcc metals (Ni, Cu, Rh, Pd, Ag, Ir, Pt, Au) and (110) surfaces for bcc metals (Fe). All slab surfaces were modeled with four layers of atoms (4×4×4). For the construction of Pt-based alloys, Pt_7Cu_1 (222), Pt_1Au_1 (101), Pt_1Cu_1 (102), Pt_3Sn_1 (111), Pt_3Zn_1 (111), Pt_1Bi_1 (101), Pt_5Ga_3 (221) were selected as the basis for crystal modeling (8×8×4), these crystal planes were the most stable crystal planes for these transition metal alloys. The atoms in the bottom two layers were anchored to their main positions, while the other atoms were relaxed. A sufficient vacuum layer (20 Å) was added to the *z*-axis to eliminate all hypothetical interactions between metal surfaces.

The adsorption energy (E_{ads}) is expressed as:

$$E_{ads} = E_{tatol} - (E_{adsorbate} + E_{surface}) \qquad \text{(eqn. 1)}$$

where E_{tatol} is the total energy of the adsorbed surface, $E_{adsorbate}$ is the energy of the adsorbed surface, and $E_{surface}$ is the energy of the pure surface. By empirical definition, the negative value of E_{ads} represents the energy released or relatively stable adsorption.

The adsorption free energy of * (G_*) on different surfaces are calculated as:

$$\Delta G_* = \Delta E_* + \Delta ZPE - T\Delta S \qquad \text{(eqn. 2)}$$

where ΔG_* is the free energy of the atom on the metal, and ΔE_*, ΔZPE,

T(328.15K), and ΔS are the change value of the adsorption energy, zero point energy, temperature and entropy of the H atom, respectively. The zero point can also contain insignificant internal energy changes, which are uniformly corrected and processed by the ***vaspkit*** script. [5]

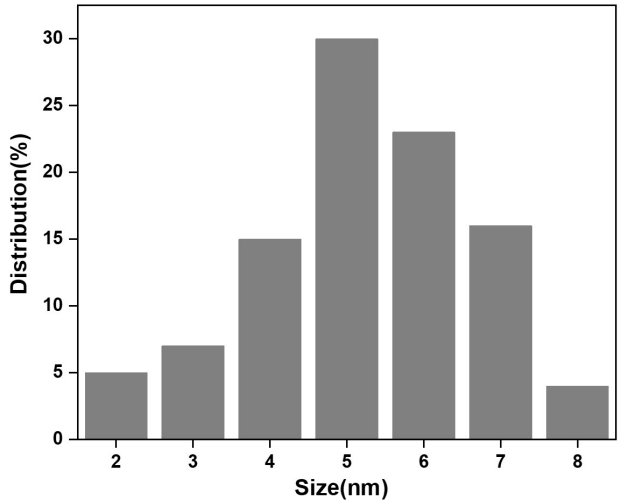

Fig. S15. PtSn catalyst particle size distribution diagram.

Table S5. The d-band center of Pt alloy at 0% and 100% fcc-H coverage.

Material system	d band center at 0% fcc-H coverage (eV)	d band center at 100% fcc-H coverage (eV)
Pt_7Cu_1	-2.041	-2.116
Pt_1Au_1	-1.804	-2.113
Pt_1Cu_1	-2.055	-2.118
Pt_3Sn_1	-2.123	-2.127
Pt_3Zn_3	-2.151	-2.161
Pt_1Bi_1	-2.098	-2.211
Pt_5Ga_3	-2.216	-2.241

Table S6. Comparison of the activity and selectivity with traditional research.

Catalysis	Treatment	Sel(%)	TOF(h^{-1})	Reference
PtSn/CN	40° C	>99	1034	This work
Pt/SiO2	40° C	70	60	[6]
Co−N−C	80° C	>99	35.9	[7]
Co@C	120° C	93	8.2	[8]
Pt/ZnO	75° C	97	744	[9]

AuSn-TiO2	70° C	>99	319	[10]
Pt/ TiO2	40° C	91	5300	[11]

Table S7. Reaction data of other reactants.

Reactant	Treatment	Sel(%)	TOF (h^{-1})
2-nitrostyrene	40° C	>99	660
4-nitrostyrene	40° C	>99	443

Table S8. Support catalytic performance.

catalyst	selectivity	Conversion	TOF
carbon nanosheet	0	0	0

Experimental Section

Synthesis of Pt/CN, PtSn/CN

The preparation method of Pt/CN and PtSn/CN adopts steam dry dipping method. $SnCl_2$ (Shanghai Aladdin Bio-Chem Technology Co., LTD) and $_2PtCl_6{\cdot}6\ _20$ (Shanghai Aladdin Bio-Chem Technology Co., LTD)are configured into aqueous solutions containing 0.53 mg/ml (Sn) and 3.78 mg/ml (Pt), respectively (We named the front and the back A and B respectively).

0.8%wt Pt/CN preparation process: 2.117ml of A was slowly added to 30ml aqueous solution containing 1g nitrogen-doped carbon nanosheets (CN) (Nanjing XFNANO Materials Tech Co., Ltd) under electromagnetic stirring, and the temperature was raised to 80 degrees and evaporated to dryness. Take the remaining powder to the muffle furnace and evaporate it overnight for 12

hours, and reduce it at 350 degrees for 2 hours in an Ar gas tube furnace containing 5% $_2$.

0.8%wt PtSn/CN preparation process: 1.76ml A and 2.57ml B were mixed thoroughly under ultrasound for 20min, and then added dropwise to 30ml CN aqueous solution. The subsequent steps are the same as the preparation of Pt/CN.

Catalytic ydrogenation

50mg of Pt/CN catalyst was put into 18ml methanol solution filled with 0.8ml 3-nitrostyrene (Shanghai Aladdin Bio-Chem Technology Co., LTD). After replacing the air in the hydrogenation kettle with N_2 for 3 times, react at 60°C for 40 minutes under 8 bar of pure $_2$ atmosphere. Then it was cooled down to room temperature for sampling and analysis. The catalytic reaction process of PtSn/CN is the same as that of Pt/CN, and the reaction conditions of 40, 50, and 70 degrees are also tested.

Characterization of Catalysts

Transmission electron microscopy (TEM) studies wereconducted on a JEOL JEM-2100F transmission electron microscope with an accelerating voltage of 200 kV.

References

[1] Kresse G, Hafner J. Ab Initio Molecular-Dynamics Simulation of the Liquid-Metal–Amorphous-Semiconductor Transition in Germanium. Phys Rev B, 1994, 20, 1425-14265

[2] Anisimov V I, Zaanen J, Andersen O K. Band Theory and Mott Insulators: Hubbard U Instead of Stoner I. Phys Rev B, 1991, 3, 943-947

[3] Kresse G, Furthmüller J. Efficiency of Ab-Initio Total Energy Calculations for Metals and Semiconductors Using a Plane-Wave Basis Set. Comp Mater Sci, 1996, 1, 15-50

[4] Grimme S. Semiempirical GGA-type Density Functional Constructed with a Long-Range Dispersion Correction. J Comput Chem, 2006, 15, 1787-1799

[5] Yan H, Xie Y, Jiao Y et al. Holey Reduced Graphene Oxide Coupled with an Mo_2N-Mo_2C Heterojunction for Efficient Hydrogen Evolution. Adv Mater, 2018, 2, 1704156-1704163

[6] Dhiman, M.; Polshettiwar, V. Ultrasmall nanoparticles and pseudo-single atoms of platinum supported on fibrous nano silica (KCC-1/Pt): engineering selectivity of hydrogenation reactions. J. Mater. Chem. A 2016, 4, 12416−12424.

[7] Liu, W.; Zhang, L.; Yan, W.; Liu, X.; Yang, X.; Miao, S.; Wang, W.; Wang, A.; Zhang, T. Single-atom dispersed Co-N-C catalyst: structure identification and performance for hydrogenative coupling of nitroarenes. Chem. Sci. 2016, 7, 5758−5764.

[8] Liu, L.; Concepción, P.; Corma, A. Non-noble metal catalystsfor hydrogenation: A facile method for preparing Co nanoparticles covered with thin layered carbon. J. Catal. 2016, 340, 1−9.

[9] Berguerand, C.; Yarulin, A.; Cárdenas-Lizana, F.; Wa¨rnå, J.; Sulman, E.; Murzin, D. Y.; Kiwi-Minsker, L. Chemoselective Liquid Phase Hydrogenation of 3-Nitrostyrene over Pt Nanoparticles: Synergy with ZnO Support. Ind. Eng. Chem. Res. 2015, 54, 8659−8669.

[10] Wang, L.; Guan, E.; Zhang, J.; Yang, J.; Zhu, Y.; Han, Y.; Yang, M.; Cen, C.; Fu, G.; Gates, B. C.; Xiao, F.-S. Single-site catalyst promoters accelerate metal-catalyzed nitroarene hydrogenation. Nat. Commun. 2018, 9, 1362-1369.

[11] Macino, M.; Barnes, A. J.; Althahban, S. M.; Qu, R.; Gibson, E. K.; Morgan, D. J.; Freakley, S. J.; Dimitratos, N.; Kiely, C. J.; Gao, X.et al. Tuning of catalytic sites in Pt/TiO2 catalysts for the chemoselective hydrogenation of 3-nitrostyrene. Nat Catal 2019, 2, 873-881.