Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Contents

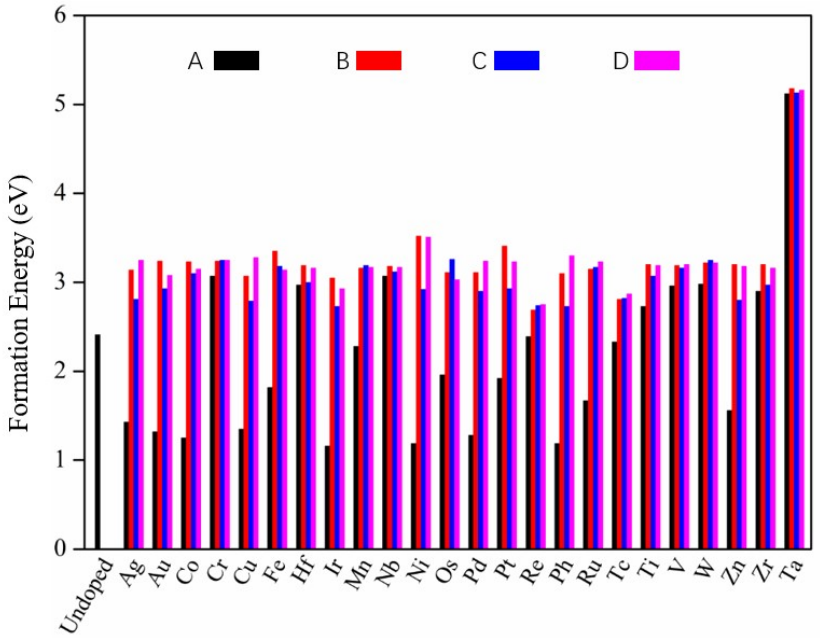


Fig. S1 Formation energies of S vacancy in TM-MoS_2. A, B, C and D represents the first nearest neighbor position (1NN), the second nearest neighbor position (2NN), the third nearest neighbor position (3NN) and the fourth nearest neighbor position (4NN) according to the distance between the dopants and S vacancy.

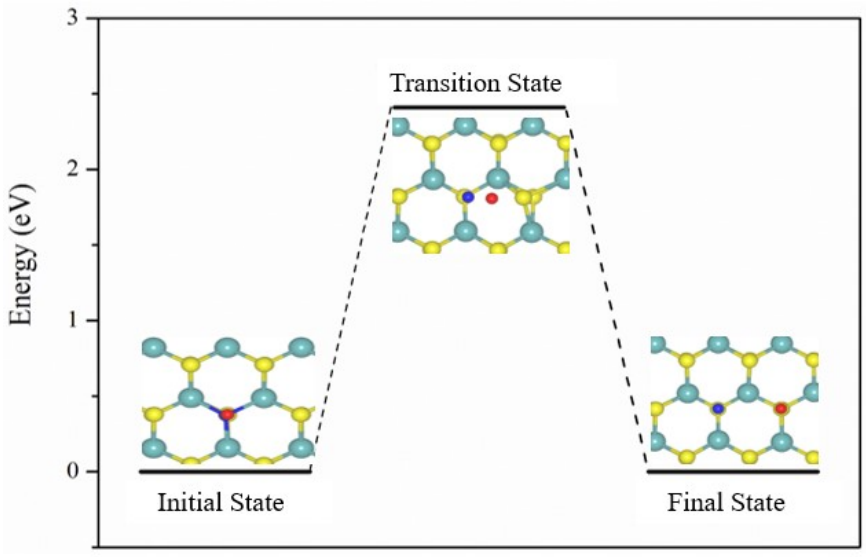
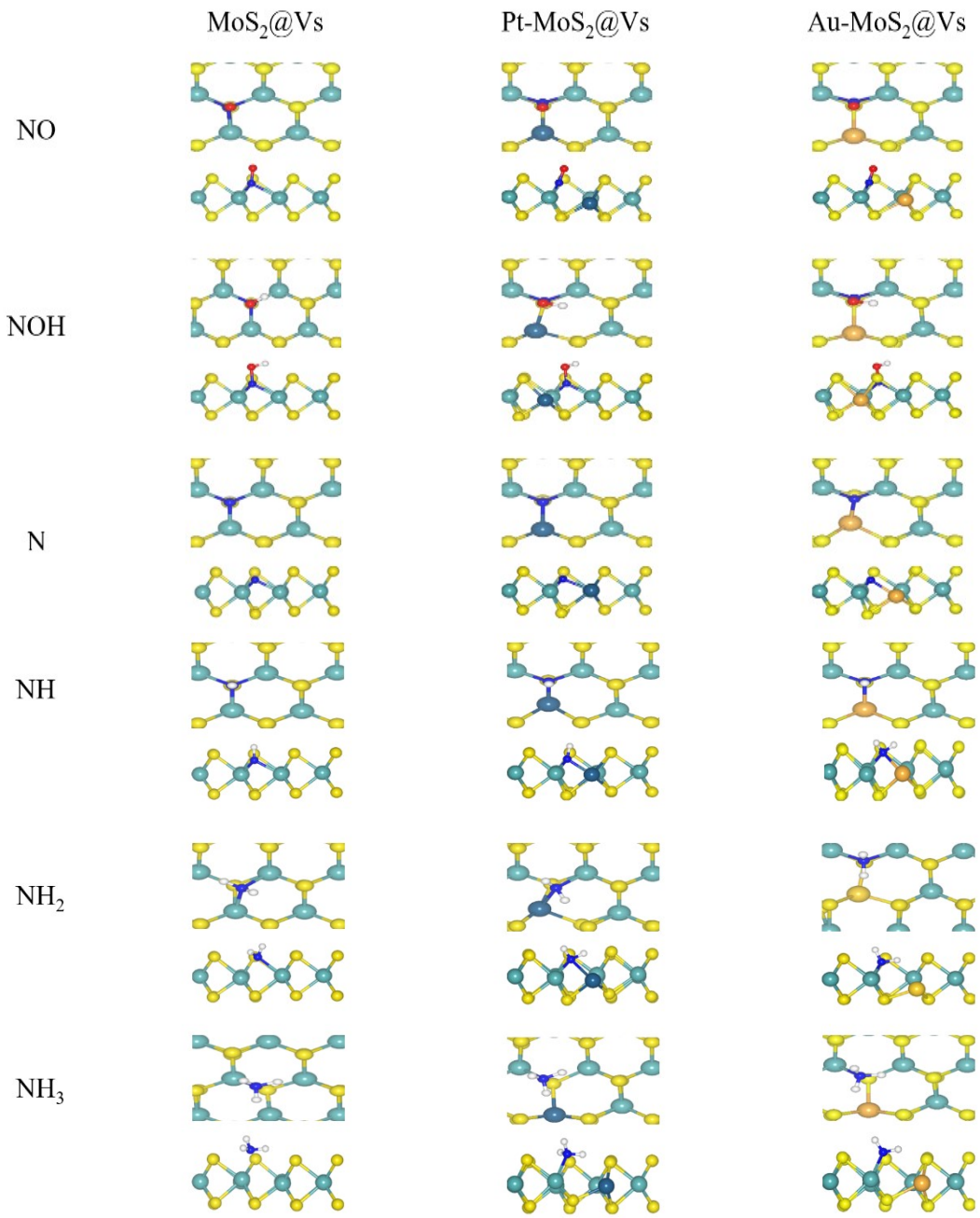


Fig. S2 Minimum energy path (MEP) of NO dissociation on the $MoS_2@V_S$ monolayers.


MoS2@Vs
Pt-MoS2@Vs
Au-MoS2@Vs
NO
NOH
N
NH
NH2
NH3

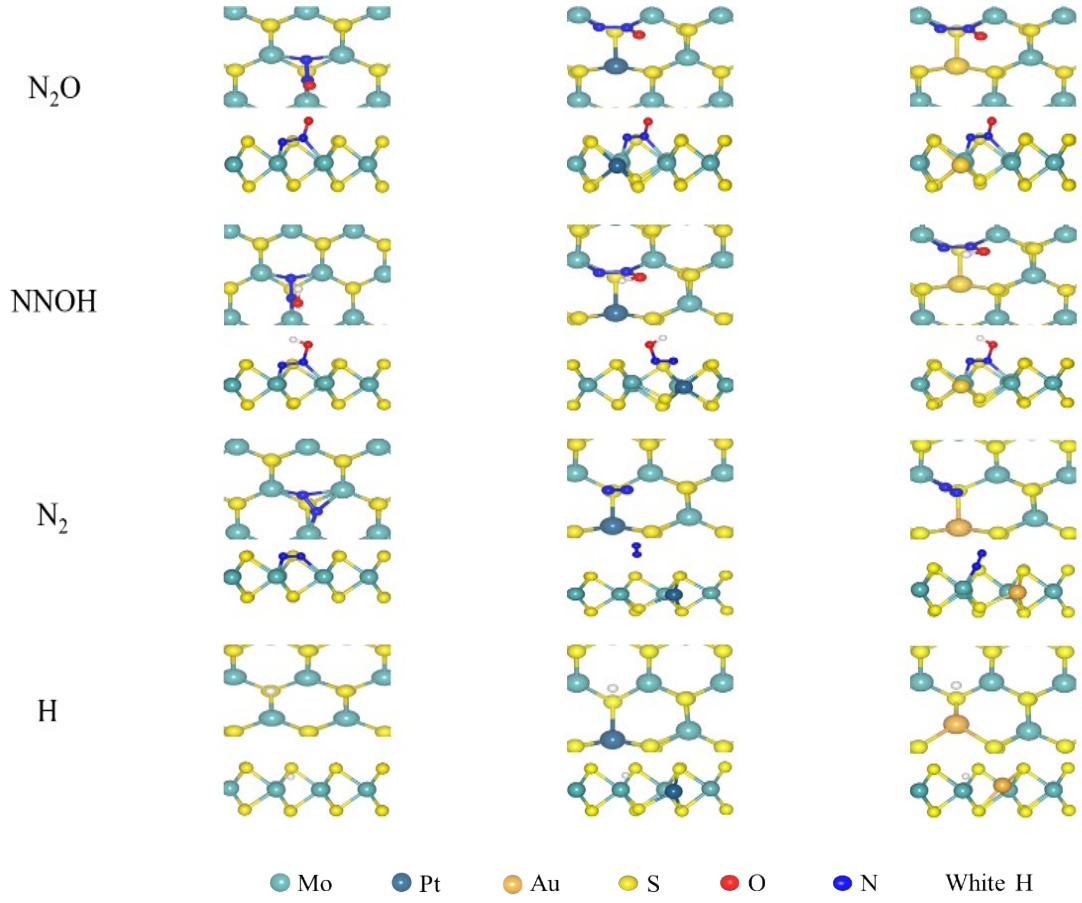


Fig. S3 Optimized structures of various species adsorbed on $MoS_2@V_S$, Pt-$MoS_2@$ V_S and Au-$MoS_2@$ V_S.

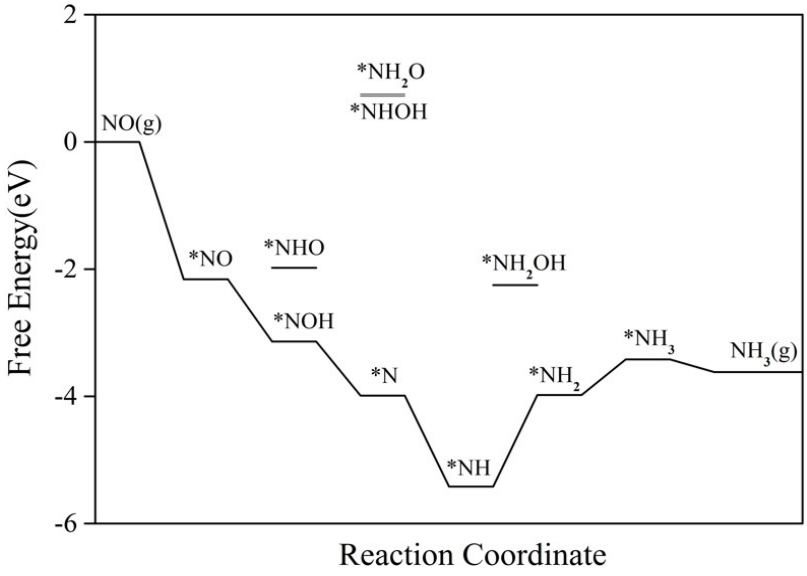


Fig. S4 Gibbs free adsorption energies of all species on the $MoS_2@V_S$ monolayers. The connected line is the most preferable pathway.

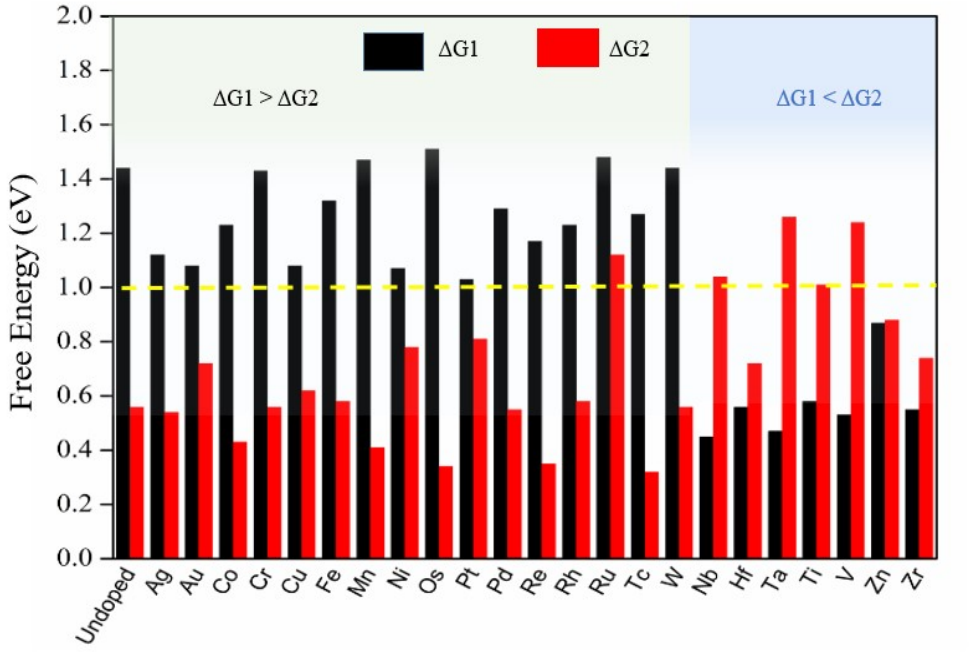


Fig. S5 Gibbs free adsorption energies changes of two *NH hydrogenation steps over second nearest neighbor (2NN) positions of 24 TM-MoS_2@V_S catalysts. *NH → *NH_2 (ΔG1); *NH_2 → *NH_3 (ΔG2).

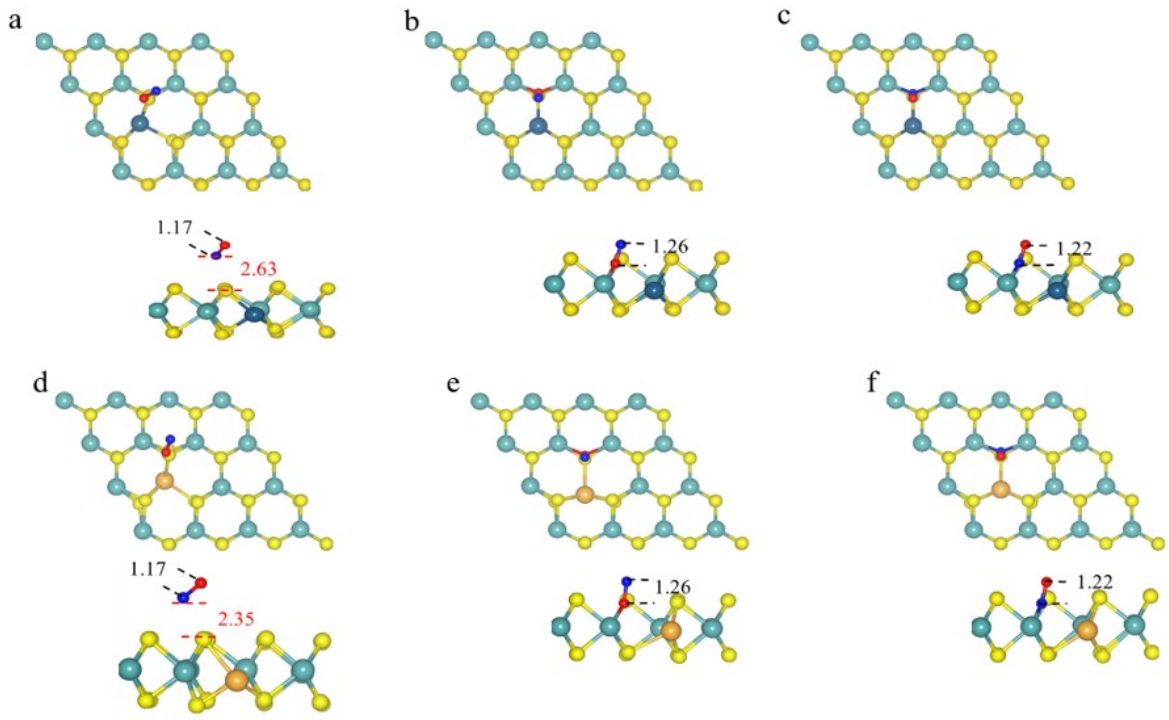


Fig. S6 The optimized geometric structures NO absorbed on Pt-MoS_2 and Au-MoS_2;

(a)NO absorbed on Pristine Pt-MoS_2; (b) NO absorbed on Pt-MoS_2@ Vs via O atom; (c) NO absorbed on on Pt-MoS_2@V_S via N atom; (d) NO absorbed on Pristine Au-MoS_2; (e) NO absorbed on Au-MoS_2@V_S via O atom; (f) NO absorbed on Au-MoS_2@V_S via N atom; NO bond lengths (Å) are labeled.

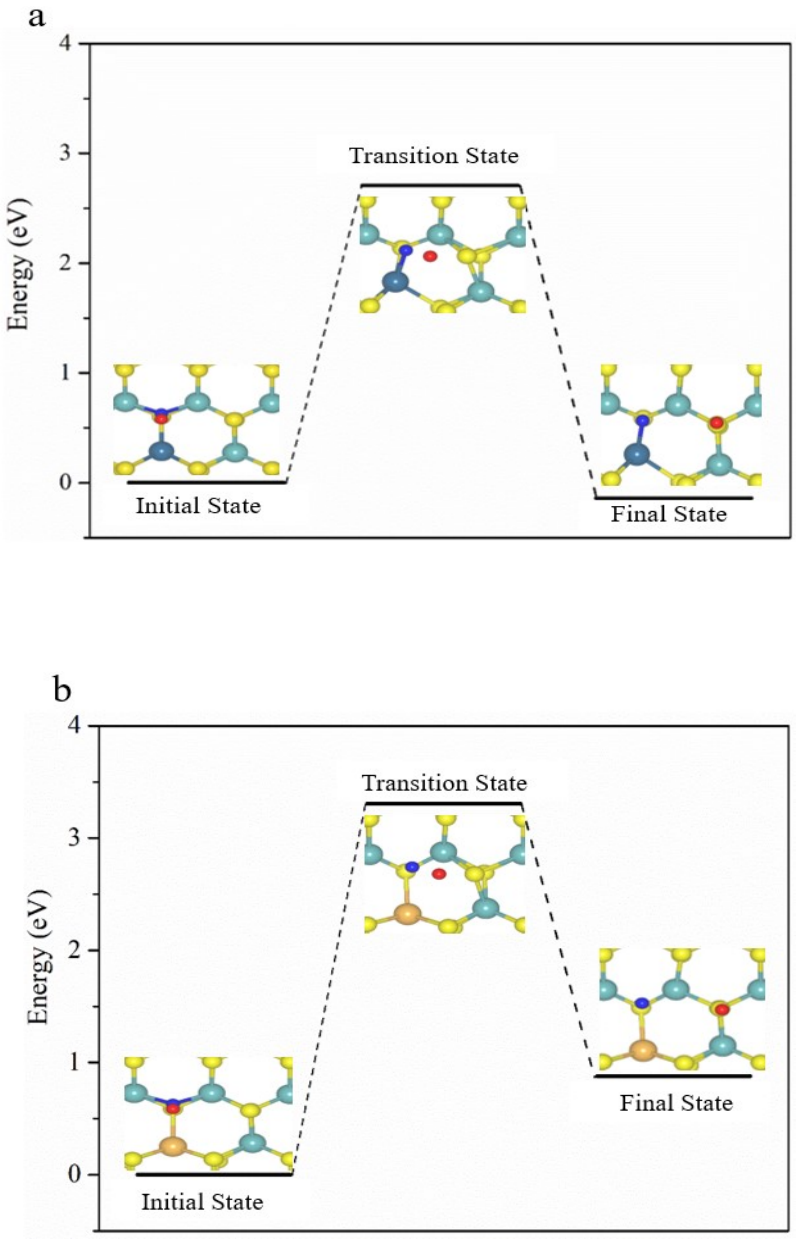


Fig. S7 Minimum energy path (MEP) of NO dissociation on the Pt-MoS_2@V_S (a) and Au-MoS_2@V_S (b)

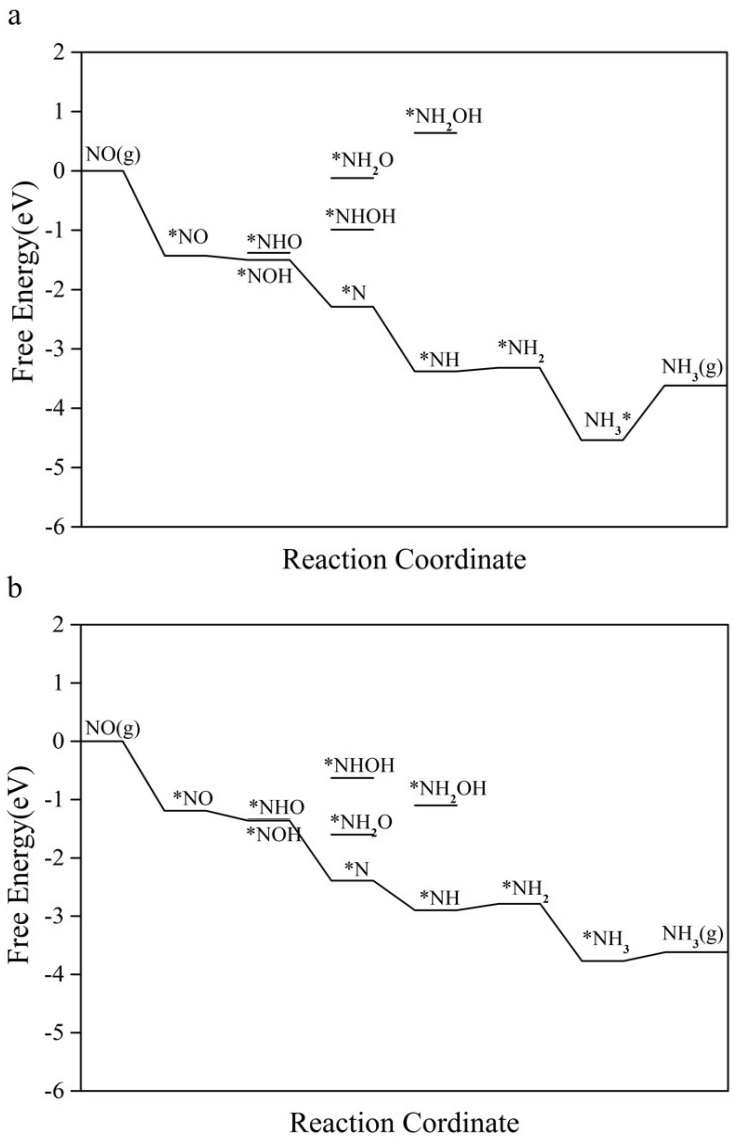


Fig. S8 Gibbs free adsorption energies of all species on the Pt-MoS_2@V_S (a) and Au-MoS_2@V_S (b); The connected line is the most preferable pathway.

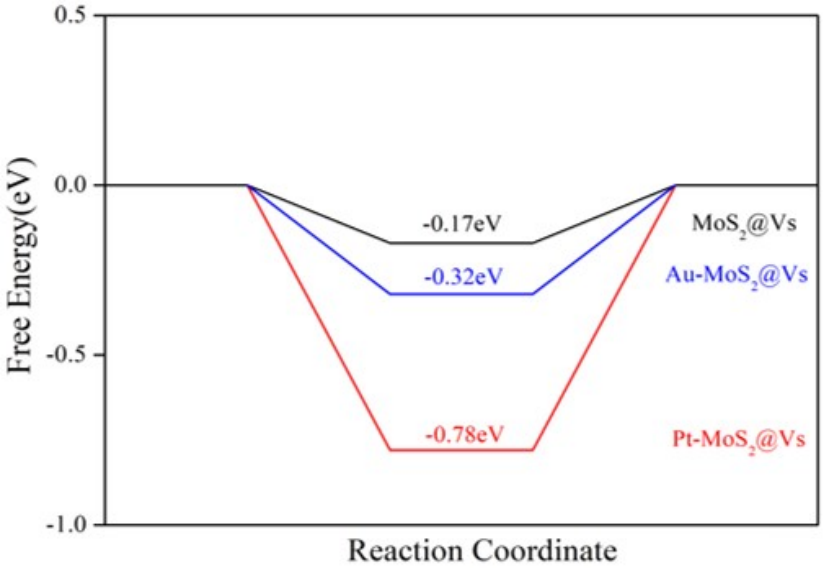


Fig. S9 Gibbs free energy diagrams for HER

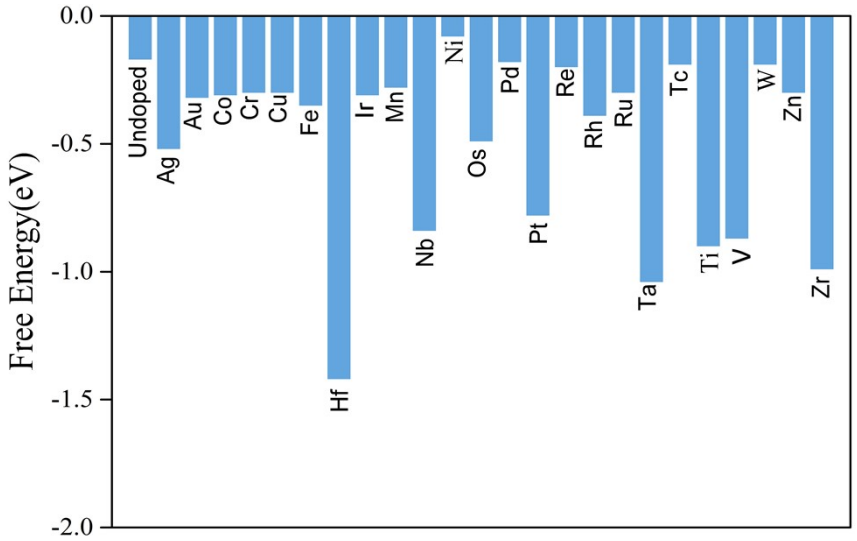


Fig. S10 Gibbs free energies of $^{*}H$ for all dopants on $MoS_2@V_S$

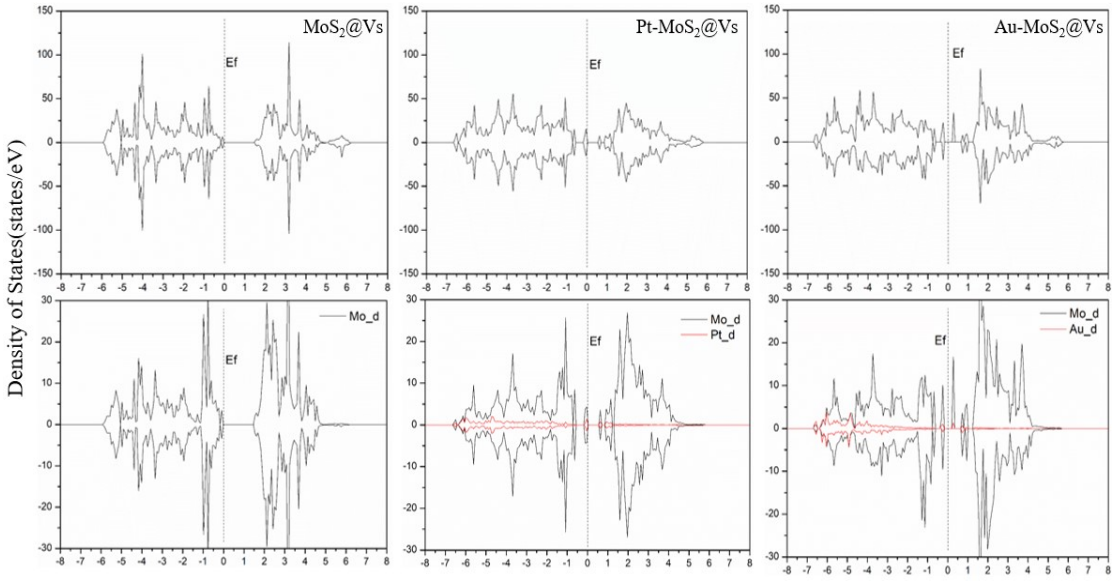


Fig. S11 Spin-polarized total density of states and Partial density of $MoS_2@V_S$, Pt-$MoS_2@V_S$ and Au-MoS_2@Vs; The Fermi level is set to zero energy and indicated by the vertical dashed line.

Table S1. Formation energies of TM- MoS_2.

dopants	formation energy（eV）	
	Mo-rich	S-rich
Ag	6.05	3.34
Au	6.04	3.34
Co	3.55	0.84
Cr	0.22	-2.49
Cu	5.33	2.62
Fe	2.67	-0.15
Hf	-0.91	-3.62
Ir	3.53	0.82
Mn	1.45	-1.26
Nb	-1.13	-3.84
Ni	4.02	1.31
Os	2.62	-0.10
Pd	4.21	1.5
Pt	3.98	1.27
Re	1.23	-1.48
Rh	3.24	0.53
Ru	2.22	-0.49
Ta	-3.03	-5.74
Tc	0.92	-1.80
Ti	-0.80	-3.5
V	-0.43	-3.14
W	-0.58	-3.29
Zn	4.85	2.14
Zr	-0.99	-3.70

Table S2. Formation energies of S vacancy in TM-MoS_2. A, B, C and D represents the first nearest neighbor position (1NN), the second nearest neighbor position (2NN), the third nearest neighbor position (3NN) and the fourth nearest neighbor position (4NN) according to the distance between the dopants and S vacancy.

dopants	S vacancy formation energy（eV）			
	A	B	C	D
Ag	1.43	3.14	2.81	3.25
Au	1.32	3.24	2.93	3.08
Co	1.25	3.23	3.10	3.15
Cr	3.07	3.24	3.25	3.25
Cu	1.35	3.07	2.79	3.28
Fe	1.82	3.35	3.18	3.14
Hf	2.97	3.19	3.00	3.16
Ir	1.16	3.05	2.73	2.93
Mn	1.45	3.16	3.19	3.17
Nb	3.07	3.18	3.12	3.17
Ni	1.19	3.52	2.92	3.51
Os	1.96	3.11	3.26	3.03
Pd	1.28	3.11	2.90	3.24
Pt	1.92	3.41	2.93	3.23
Re	2.39	2.69	2.74	2.75
Rh	1.19	3.10	2.73	3.30
Ru	1.67	3.15	3.17	3.23
Ta	5.12	5.18	5.13	5.16
Tc	2.33	2.81	2.82	2.87
Ti	2.73	3.20	3.07	3.19
V	2.96	3.19	3.16	3.20
W	2.98	3.22	3.25	3.22
Zn	1.56	3.20	2.80	3.18
Zr	2.90	3.20	2.97	3.16
undoped	2.41	2.41	2.41	2.41

Table S3. Adsorption energy (E_{ad}) of NO adsorbed on Pt and Au doped MoS_2 (eV);

Species		MoS_2	Pt- MoS_2	Au- MoS_2
Pristine		- 0.14	- 0.20	- 0.38
S vacancy	O end on	- 0.23	- 0.11	- 0.39
	N end on	- 2.72	- 2.01	- 1.76

Table S4. Adsorption energy (E_{ad}) of various species adsorbed on $MoS_2@V_S$, Pt and Au doped $MoS_2@V_S$.

Species	MoS_2@Vs	Pt- MoS_2@Vs	Au- MoS_2@Vs
NO	- 2.72	- 2.01	- 1.76
NOH	- 4.04	- 2.38	- 2.25
N	- 4.56	- 2.85	- 2.95
NH	- 6.34	- 4.30	- 3.78
NH_2	- 5.21	- 4.5	- 5.40
NH_3	- 4.96	- 6.06	- 5.30
NHO	- 2.92	- 2.32	- 2.27
HNOH	- 2.42	- 2.24	- 1.81
H_2NO	- 2.5	- 1.36	- 2.88
H_2NOH	- 2.29	- 1.36	- 2.69
H	- 0.42	- 0.99	- 0.53

Table S5. Gibbs free adsorption energies of various species adsorbed on TM-MoS_2@V_S (eV). Adsorbed ta the first nearest neighbor position (1NN), the second nearest neighbor position (2NN).

			1NN				2NN		
Dopants	*NO	*NOH	*N	*NH	*NH_2	*NH_3	*NH	*NH_2	*NH_3
Ag	-1.61	-1.66	-2.55	-3.59	-2.76	-3.82	-5.31	-4.18	-3.64
Au	-1.19	-1.36	-2.39	-2.90	-4.15	-3.77	-5.31	-4.24	-3.52
Co	-0.98	-1.27	-2.27	-3.25	-4.39	-3.88	-5.43	-4.21	-3.78
Cr	-2.19	-3.10	-3.84	-5.27	-3.88	-3.76	-5.43	-4.00	-3.44
Cu	-1.45	-1.63	-2.29	-3.50	-4.51	-4.09	-5.29	-4.21	-3.60
Fe	-1.74	-1.81	-2.99	-3.89	-4.35	-3.71	-5.37	-4.05	-3.47
Hf	-2.75	-3.31	-4.11	-5.41	-5.20	-4.48	-5.37	-4.81	-4.07
Ir	-1.30	-1.29	-2.80	-3.35	-2.19	-3.77	-5.26	-3.80	-3.50
Mn	-2.13	-2.36	-3.52	-4.47	-4.28	-3.56	-5.33	-3.86	-3.45
Nb	-2.13	-2.91	-4.09	-5.17	-5.00	-3.75	-5.36	-4.92	-3.88
Ni	-1.32	-1.03	-1.90	-2.95	-4.35	-3.98	-5.35	-4.28	-3.51
Os	-1.91	-2.05	-3.52	-3.77	-2.73	-3.37	-5.31	-3.80	-3.46
Pd	-1.17	-0.87	-2.20	-2.78	-4.31	-3.89	-5.30	-4.02	-3.46
Pt	-1.43	-1.50	-2.19	-3.38	-3.32	-4.54	-5.63	-4.60	-3.79
Re	-2.56	-2.35	-4.49	-4.61	-3.56	-3.51	-4.93	-3.76	-3.41
Rh	-1.34	-1.33	-2.59	-2.98	-2.08	-3.68	-5.29	-4.06	-3.49
Ru	-1.66	-1.43	-3.08	-3.57	-2.60	-3.28	-2.25	-0.77	0.34
Ta	-2.36	-3.17	-4.35	-5.45	-5.16	-3.90	-5.37	-4.91	-3.90
Tc	-2.49	-2.35	-4.15	-4.51	-3.43	-3.60	-5.01	-3.74	-3.42
Ti	-2.39	-2.96	-3.79	-5.07	-4.94	-4.31	-5.39	-4.81	-4.03
V	-2.22	-3.00	-4.12	-5.19	-5.04	-3.98	-5.38	-4.85	-3.61
W	-2.15	-3.23	-4.07	-5.50	-4.02	-3.36	-5.42	-3.98	-3.41
Zn	-1.70	-1.91	-2.78	-3.36	-4.72	-4.11	-5.40	-4.53	-3.65
Zr	-2.74	-3.26	-4.03	-5.31	-5.16	-4.48	-5.38	-4.83	-4.09
Undoped	-2.16	-3.14	-3.99	-5.42	-3.98	-3.42		//	

Table S6. Solvation energy of various species for NOER. The values are adopted from the data reported by Clayborne *et. al* [1]

Species	Solvation Energy(eV)
N	-0.1
NH	-0.3
NH_2	-0.24
NH_3	-0.16
NOH	-0.31
HNO	-0.23
HNOH	-0.47
H_2NO	-0.24
H_2NOH	-0.41

Table S7. Bader charge variation of six species along the preferred pathway (e).

Species	$MoS_2@V_S$	Pt- $MoS_2@V_S$	Au- $MoS_2@V_S$
NO	0.83	0.65	0.61
NOH	0.78	0.64	0.61
N	1.05	0.92	0.91
NH	0.79	0.64	0.57
NH_2	0.4	0.35	0.14
NH_3	- 0.1	- 0.1	- 0.1

REFERENCES

1. A. Clayborne, H. J. Chun, R. B. Rankin and J. Greeley, *Angew Chem Int Edit*, 2015, **54**, 8255-8258.