ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

Single atom supported MXene: How single-atomic-site catalysts tune high activity and selectivity of electrochemical nitrogen fixation

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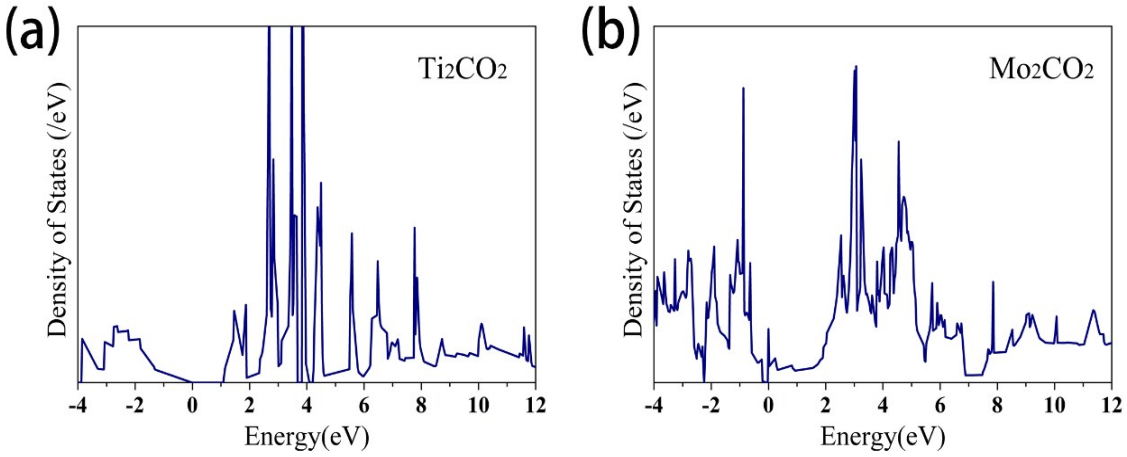


Figure S1. The calculated Density of States (DOS) of (a) Ti_2CO_2 and (b) Mo_2CO_2 at HSE06 level. The Fermi energy level is set to zero.

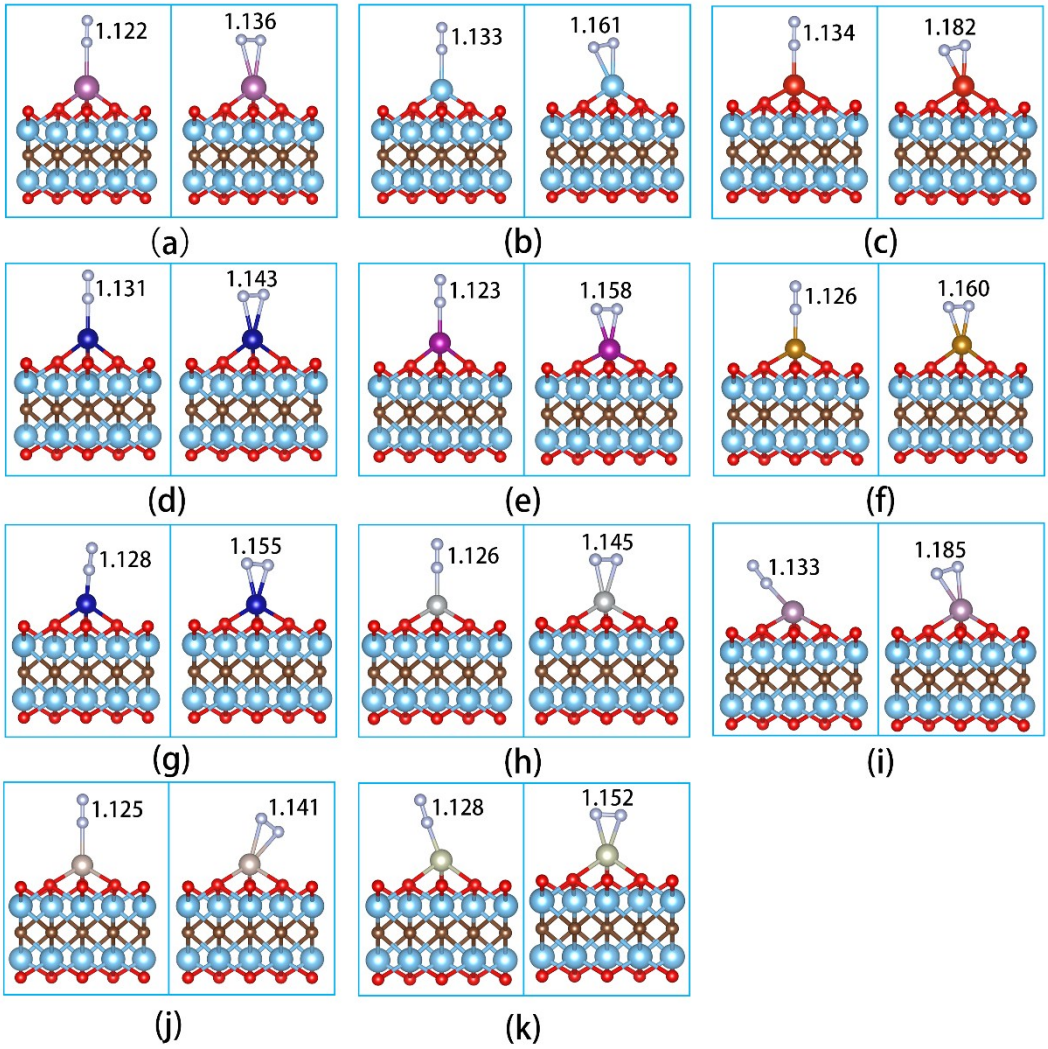
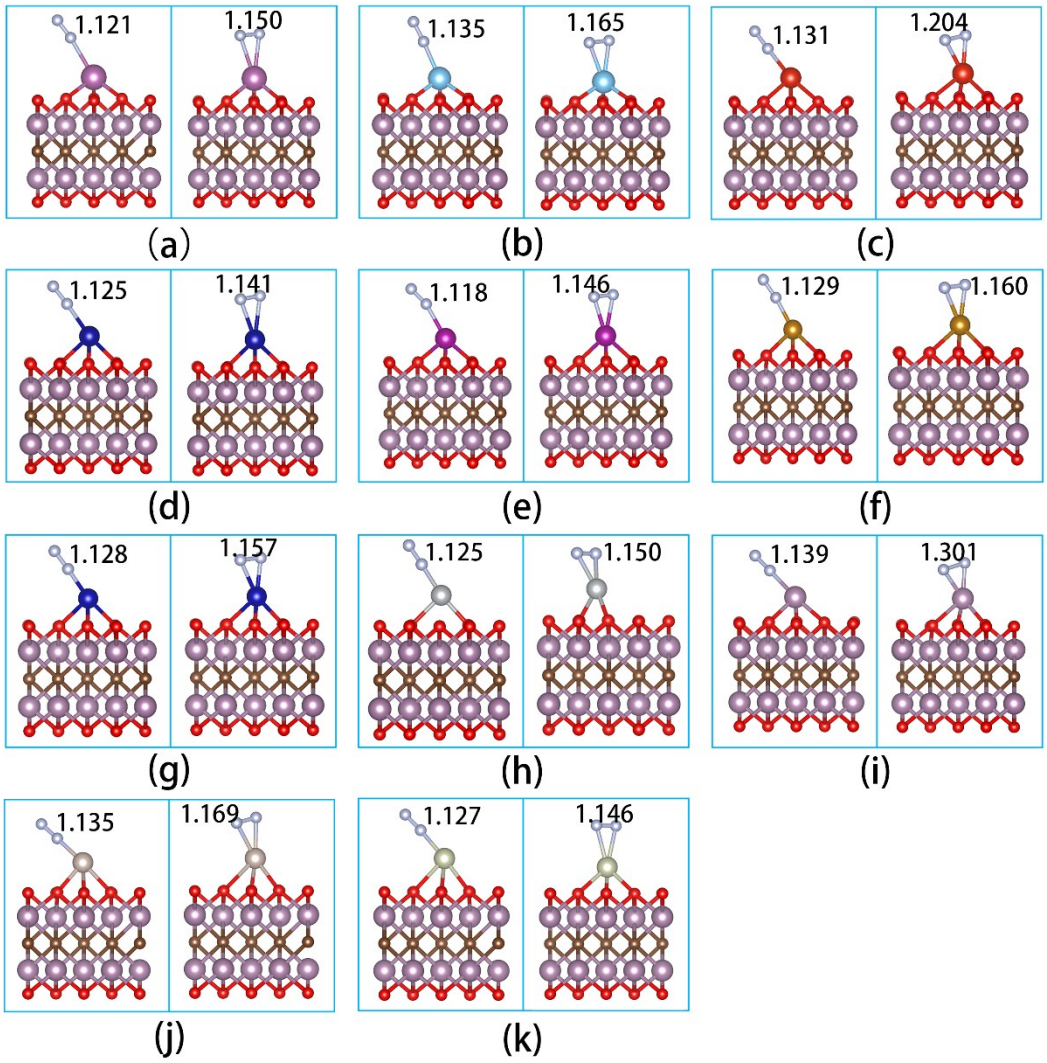


Figure S2. Side views of the adsorption of N_2 through the side-on and end-on patterns on (a) Sc, (b) Ti, (c) V, (d) Cr, (e) Mn, (f) Fe, (g) Co, (h) Ni, (i) Mo, (j) Ru, and (k) Rh @Ti_2CO_2.



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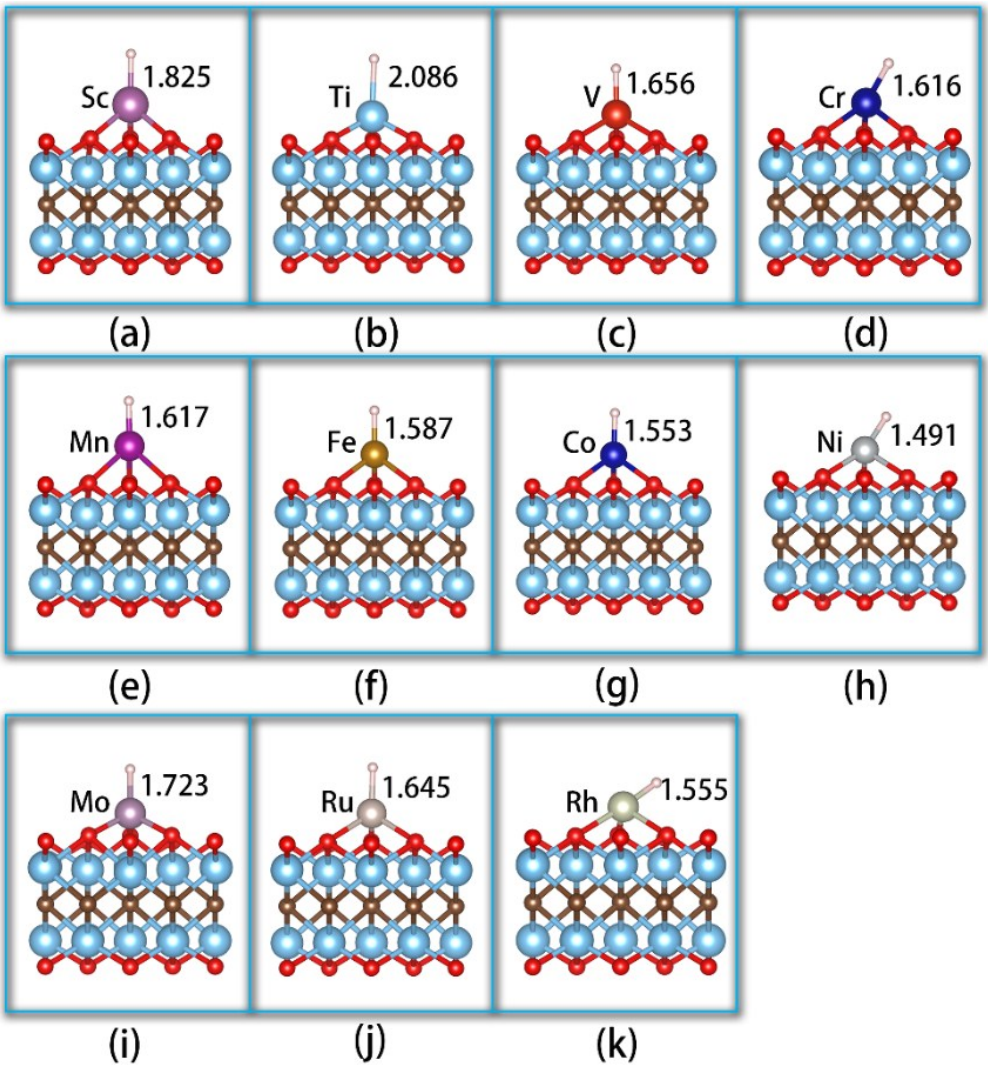


Figure S4. The optimized structures of H adsorption on TM@Ti_2CO_2.

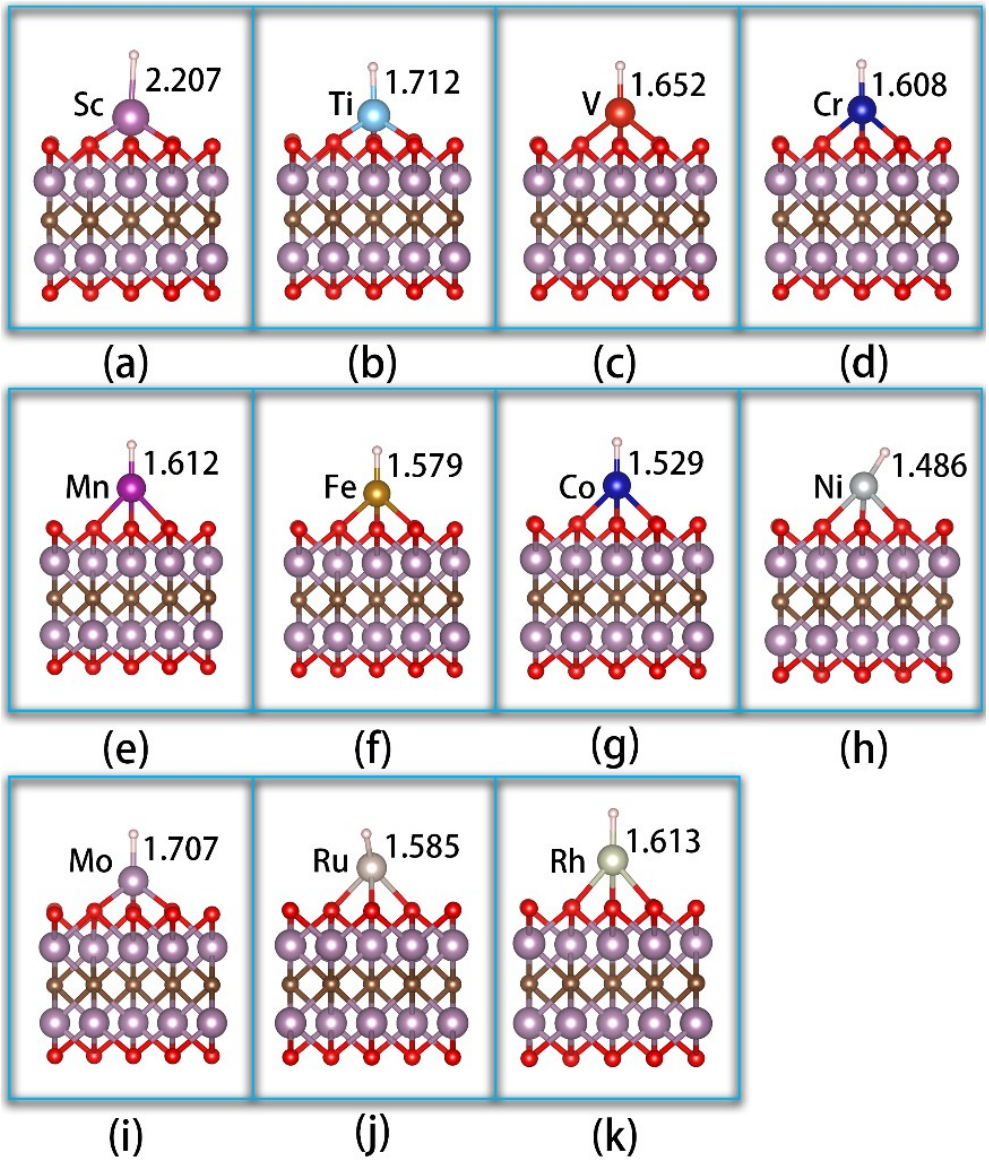


Figure S5. The optimized structures of H adsorption on TM@Mo_2CO_2.

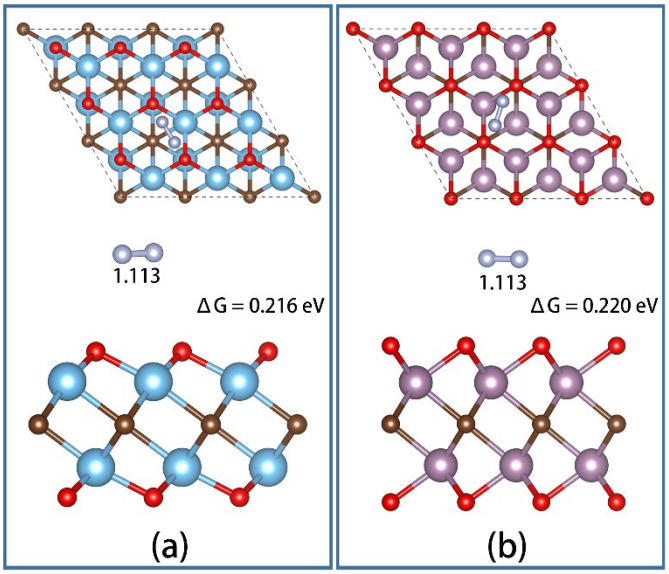


Figure S6. N_2 adsorption on (a) Ti_2CO_2 and (b) Mo_2CO_2 surface.

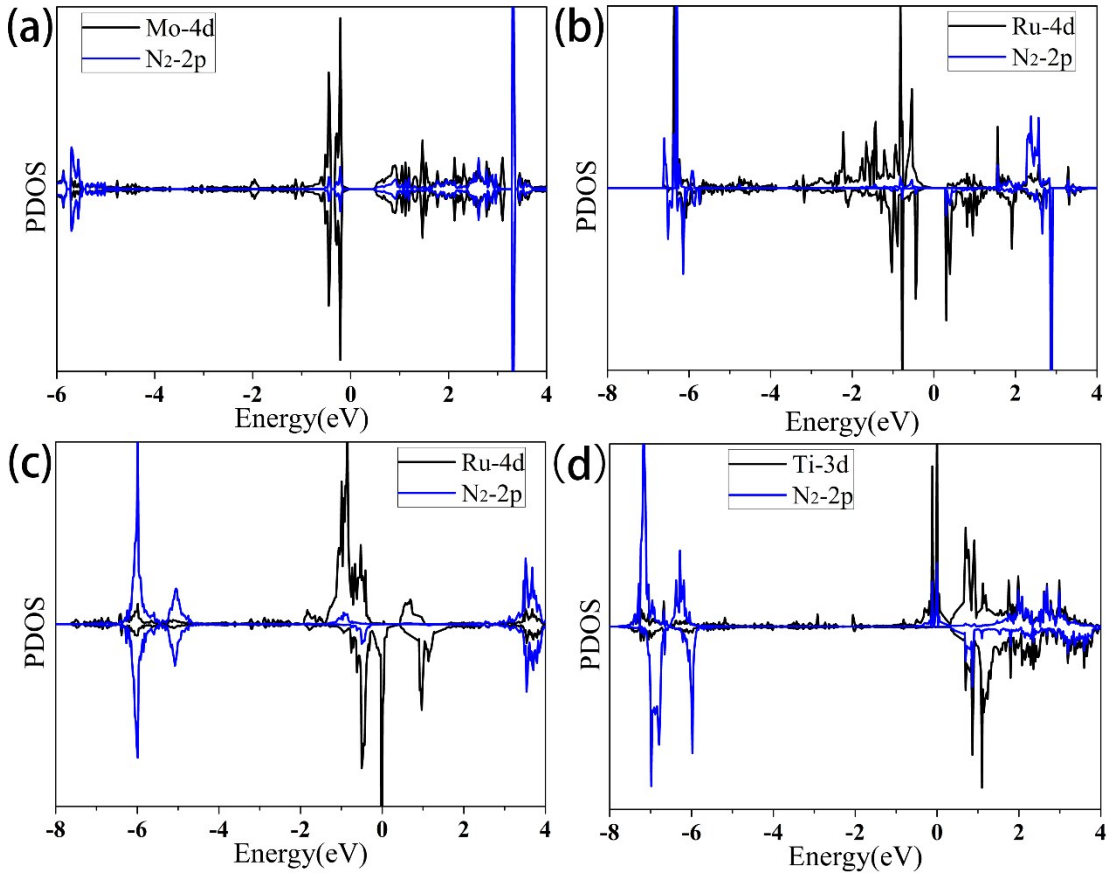
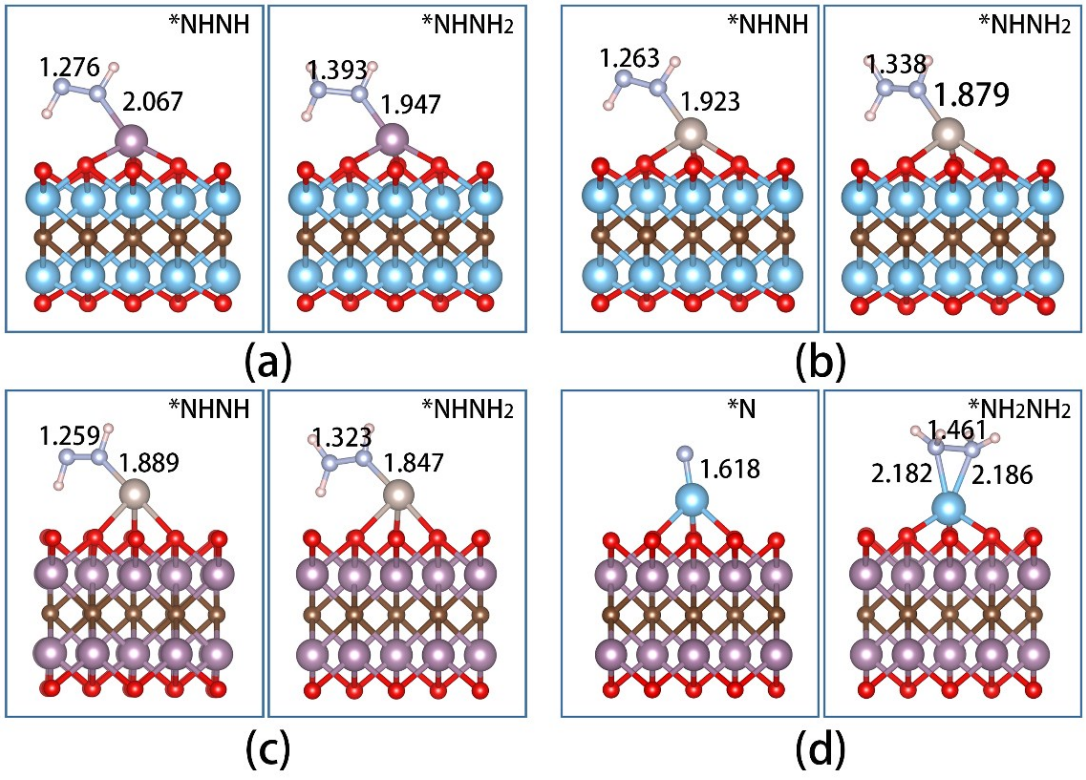


Figure S7. PDOS of N_2 adsorption on (a) Mo, (b) Ru @ Ti_2CO_2 and (c) Ru, (d) Ti @Mo_2CO_2.



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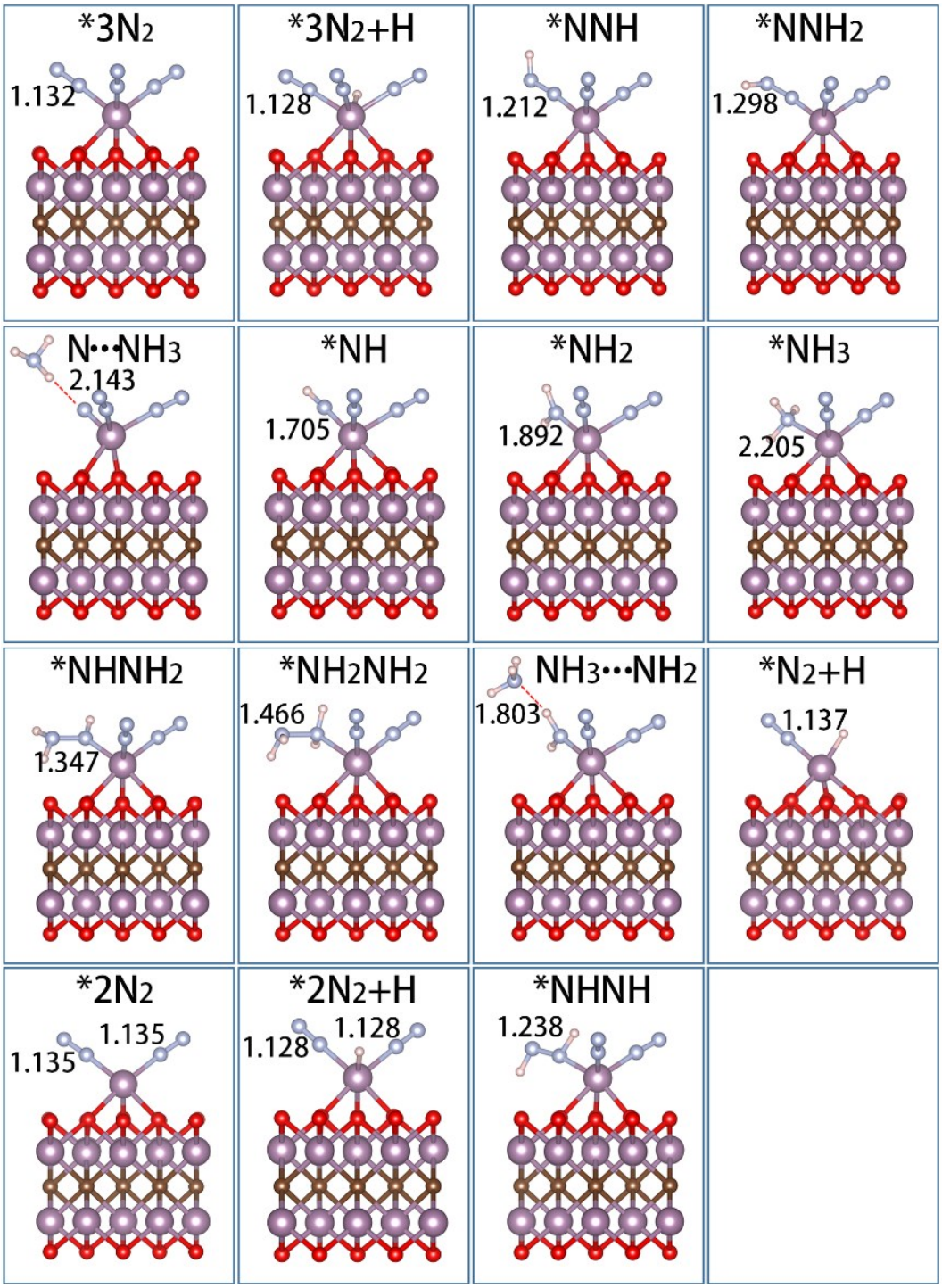

Figure S9. All intermediates coadsorbed on $Mo@Mo_2CO_2$.

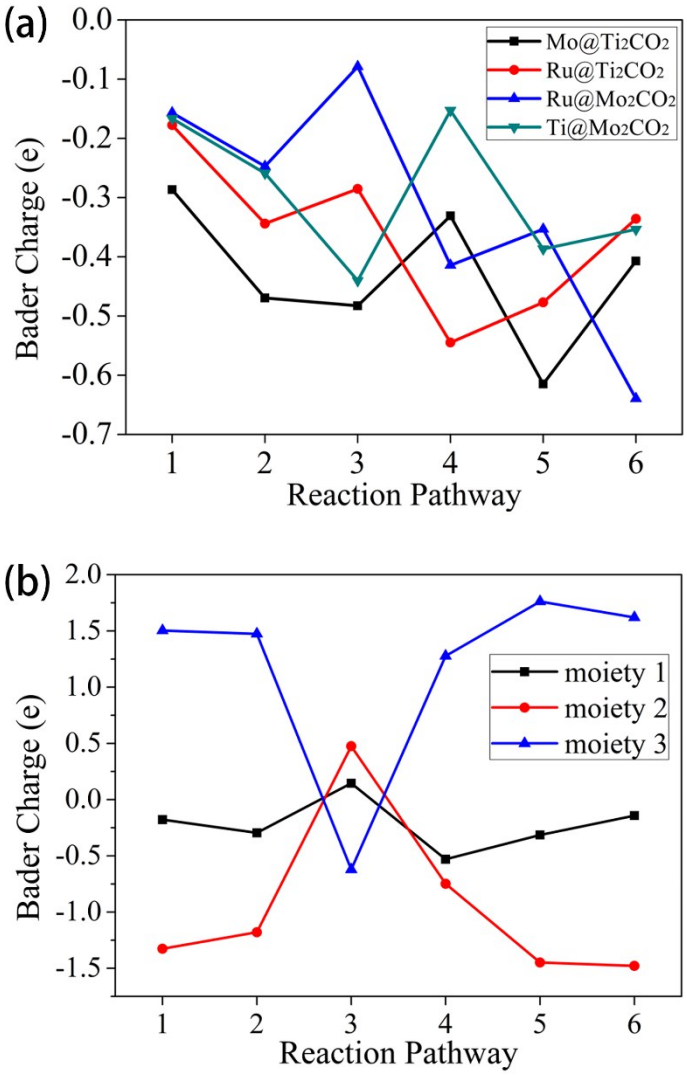

Figure S10. (a) The charge variations of $*N_xH_y$ on Mo, Ru@Ti_2CO_2 and Ru, Ti@Mo_2CO_2. (b) The charge variation of the three moieties along the distal pathway on Mo@Mo_2CO_2. Moieties 1, 2, and 3 represent the adsorbed N_xH_y species, two dinitrogen with the MoO_3 unit and MXene nanosheet, respectively. Here, 1, 2, 3, 4, 5 and 6 represent intermediates along the reaction pathway, as depicted in Figure 6 and Figure 7b, respectively.

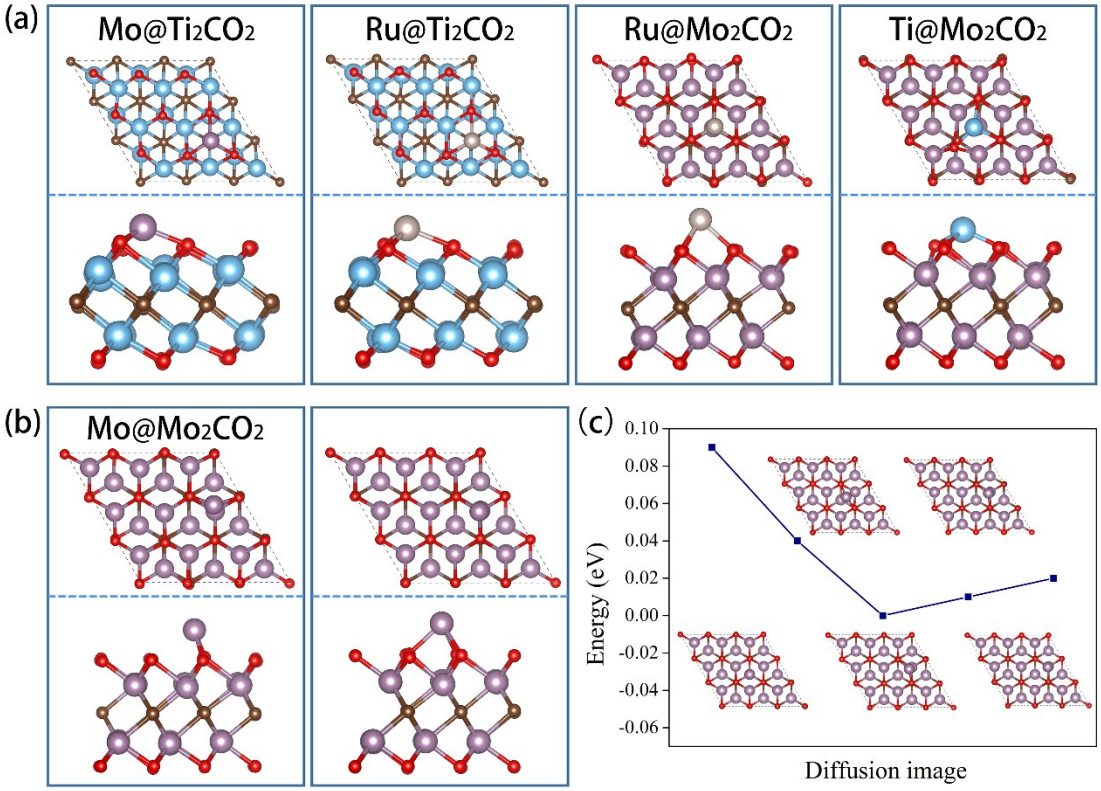

Figure S11. Configurations of (a)Mo@Ti_2CO_2, Ru@Ti_2CO_2, Ru@Mo_2CO_2, and Ti@Mo_2CO_2 after 2 ps of MD simulations, (b) two configurations of Mo@Mo_2CO_2 after MD simulations (left: Mo atom locating proximate bridge site, right: Mo atom locating hollow site). (c) The energy change of diffusion image from hollow site of Mo atom to other hollow site on Mo_2CO_2 surface.

Table S1. The calculated zero point energies (ZPE) and entropy of different gas molecules from NIST database (T= 298.15 K and f= 101,325 Pa, Unit eV).

Gas Molecule	$H^0 + D$	ZPE	-TS	G
N_2	-16.635	0.16	-0.58	-17.055
H_2	-6.77	0.27	-0.4	-6.9
NH_3	-19.54	0.93	-0.562	-19.172

Table S2. The calculated binding energy (E_b) of various metal atoms anchored on MXene (Unit eV).

Metal	Metal@Ti_2CO_2	Metal@Mo_2CO_2
Sc	6.78	7.85
Ti	6.51	7.07
V	5.04	5.59
Cr	4.08	4.77
Mn	3.06	4.29
Fe	3.54	4.13
Co	3.35	3.75
Ni	3.65	3.91
Cu	1.98	2.88
Mo	4.40	3.47
Ru	3.70	3.19
Rh	3.23	3.37
Pd	1.86	2.01
Ag	1.39	2.35
Ir	2.97	2.45
Pt	2.10	2.14

Table S3. The calculated thermodynamic quantities for H and N_2 adsorption on different kinds SAC (Unit eV, T=298.15 K).

Metal	Metal@Ti_2CO_2	ZPE	-TS	Metal@Mo_2CO_2	ZPE	-TS
Sc	*H	0.195	-0.02	*H	0.231	-0.01
	$*N_{2\text{-end-on}}$	0.181	-0.211	$*N_{2\text{-end-on}}$	0.164	-0.116
	$*N_{2\text{-side-on}}$	0.151	-0.246	$*N_{2\text{-side-on}}$	0.16	-0.186
Ti	*H	0.171	-0.02	*H	0.154	-0.03
	$*N_{2\text{-end-on}}$	0.181	-0.204	$*N_{2\text{-end-on}}$	0.185	-0.217
	$*N_{2\text{-side-on}}$	0.177	-0.193	$*N_{2\text{-side-on}}$	0.173	-0.139
V	*H	0.157	-0.025	*H	0.159	-0.03
	$*N_{2\text{-end-on}}$	0.177	-0.261	$*N_{2\text{-end-on}}$	0.199	-0.184
	$*N_{2\text{-side-on}}$	0.19	-0.149	$*N_{2\text{-side-on}}$	0.191	-0.144
Cr	*H	0.162	-0.024	*H	0.109	-0.01

	$*N_{2\text{-end-on}}$	0.192	-0.186	$*N_{2\text{-end-on}}$	0.195	-0.207
	$*N_{2\text{-side-on}}$	0.161	-0.184	$*N_{2\text{-side-on}}$	0.16	-0.223
Mn	*H	0.139	-0.044	*H	0.181	-0.01
	$*N_{2\text{-end-on}}$	0.191	-0.186	$*N_{2\text{-end-on}}$	0.185	-0.147
	$*N_{2\text{-side-on}}$	0.169	-0.248	$*N_{2\text{-side-on}}$	0.166	-0.169
Fe	*H	0.156	-0.03	*H	0.158	-0.03
	$*N_{2\text{-end-on}}$	0.189	-0.193	$*N_{2\text{-end-on}}$	0.197	-0.207
	$*N_{2\text{-side-on}}$	0.173	-0.224	$*N_{2\text{-side-on}}$	0.183	-0.198
Co	*H	0.127	-0.025	*H	0.157	-0.03
	$*N_{2\text{-end-on}}$	0.201	0.176	$*N_{2\text{-end-on}}$	0.208	-0.178
	$*N_{2\text{-side-on}}$	-0.189	-0.135	$*N_{2\text{-side-on}}$	0.181	-0.122
Ni	*H	0.175	-0.02	*H	0.169	-0.02
	$*N_{2\text{-end-on}}$	0.208	-0.171	$*N_{2\text{-end-on}}$	0.211	-0.175
	$*N_{2\text{-side-on}}$	0.178	-0.217	$*N_{2\text{-side-on}}$	0.182	-0.208
Mo	*H	0.175	-0.02	*H	0.156	-0.03
	$*N_{2\text{-end-on}}$	0.21	-0.149	$*N_{2\text{-end-on}}$	0.208	-0.161
	$*N_{2\text{-side-on}}$	0.185	-0.174	$*N_{2\text{-side-on}}$	0.187	-0.114
Ru	*H	0.112	-0.01	*H	0.163	-0.05
	$*N_{2\text{-end-on}}$	0.181	-0.214	$*N_{2\text{-end-on}}$	0.225	-0.139
	$*N_{2\text{-side-on}}$	0.163	-0.166	$*N_{2\text{-side-on}}$	0.177	-0.125
Rh	*H	0.222	-0.01	*H	0.146	-0.04
	$*N_{2\text{-end-on}}$	0.196	-0.196	$*N_{2\text{-end-on}}$	0.211	-0.166
	$*N_{2\text{-side-on}}$	0.186	-0.179	$*N_{2\text{-side-on}}$	0.213	-0.164

Table S4. The calculated ZPE and TS of the adsorbed *NNH on different kinds SAC (T=298.15 K).

Metal	$*NNH@Ti_2CO_2$		$*NNH@Mo_2CO_2$	
	ZPE (eV)	-TS (eV)	ZPE (eV)	-TS (eV)
Sc	0.427	-0.251	0.431	-0.168
Ti	0.444	-0.201	0.445	-0.216
V	0.456	-0.19	0.451	-0.208
Cr	0.439	-0.231	0.442	-0.218
Mn	0.448	-0.15	0.434	-0.247
Fe	0.469	-0.118	0.467	-0.194
Co	0.477	-0.182	0.467	-0.129
Ni	0.475	-0.114	0.476	-0.117
Mo	0.488	-0.15	0.492	-0.158
Ru	0.481	-0.108	0.478	-0.189
Rh	0.478	-0.183	0.453	-0.103

Table S5. The calculated ZPE and TS of the different adsorbed intermediates on TM (Ru and Mo) @MXene (T=298.15 K).

Adsorbed species	$Mo@Ti_2CO_2$		$Ru@Ti_2CO_2$		$Ru@Mo_2CO_2$		$Ti@Mo_2CO_2$	
	ZPE (eV)	-TS (eV)	ZPE (eV)	-TS (eV)	ZPE (eV)	-TS (eV)	ZPE (eV)	-TS (eV)
$*NNH_2$	0.815	-0.176	0.828	-0.142	0.82	-0.136	0.794	-0.201
$*N...NH_3$ or *N	1.017	-0.256	1.025	-0.279	1.015	-0.294	0.067	-0.108
*NH	0.346	-0.094	0.312	-0.02	0.339	-0.098	0.344	-0.109
$*NH_2$	0.679	-0.103	0.679	-0.056	0.679	-0.056	0.637	-0.177
$*NH_3$	1.0	-0.157	1.01	-0.203	1.028	-0.172	1.032	-0.13
*NHNH	0.828	-0.172	0.839	-0.145	0.835	-0.179	-	-
$*NHNH_2$	1.144	-0.175	1.132	-0.162	1.146	-0.152	1.13	-0.158
$*NH_2NH_2$	-	-	-	-	-	-	1.451	-0.199

Table S6. The calculated free energies of the different adsorbed intermediates on TM (Ru, Mo, and Ti) @MXene (T=298.15 K).

Adsorbed species	$@Ti_2CO_2$		$@Mo_2CO_2$	
	Mo	Ru	Ru	Ti
*clean surface	-419.069	-416.284	-432.208	-435.978
*NNH	-439.201	-436.256	-453.144	-456.352
$*NNH_2$	-442.926	-440.169	-456.856	-460.395
$*N...NH_3$	-446.855	-443.899	-460.561	-443.351
	-431.901	-428.023	-444.673	-449.305
*NH	-435.645	-432.230	-448.685	-453.519
$*NH_2$	-438.579	-436.062	-452.487	-456.506
$*NH_3$	-442.248	-439.60	-456.096	–
*NHNH	-446.237	-443.216	-460.105	-464.624
$*NHNH_2$	–	–	–	-466.955
$*NH_2NH_2$				

Table S7. The calculated ZPE and TS for all coadsorbed species and all the possible surface intermediates along the NRR via different reaction mechanisms with two speculator dinitrogen molecules on $Mo@Mo_2CO_2$.

Adsorbed species	$*N_2$	$*2N_2$	$*3N_2$	$*N_2$-H	$*2N_2$-H	$*3N_2$-H
ZPE (eV)	0.208	0.428	0.623	0.386	0.585	0.868
-TS (eV)	-0.161	-0.294	-0.491	-0.167	-0.35	-0.437
Adsorbed species	$*N_2H$	$*N_2H_2$	$*NNH_3$	*NH	$*NH_2$	$*NH_3$
ZPE (eV)	0.925	1.263	1.457	0.814	1.116	1.477
-TS (eV)	-0.441	-0.397	-0.581	-0.36	-0.384	-0.401
Adsorbed species	$*NHNH_2$	$*NH_2NH_2$	NH_3NH_2	*NHNH		

ZPE (eV)	1.60	1.94	2.1	1.477
-TS (eV)	-0.432	-0.49	-0.572	-0.401

Table S8. The calculated Gibbs free energies at 298.15 K (in eV) with two speculator dinitrogen molecules on $Mo@Mo_2CO_2$.

Adsorbed species	$*N_2$	$*2N_2$	$*3N_2$	$*N_2$-H	$*2N_2$-H	$*3N_2$-H
G	-452.508	-470.432	-488.337	-455.944	-473.985	-491.249
Adsorbed species	$*N_2H$	$*N_2H_2$	$*NNH_3$	*NH	$*NH_2$	$*NH_3$
G	-491.469	-495.405	-498.818	-483.756	-487.296	-491.349
Adsorbed species	$*NHNH_2$	$*NH_2NH_2$	NH_3NH_2	*NHNH		
G	-498.503	-501.857	-506.620	-493.629		