Supporting information

Efficient nitrogen fixation to ammonia on MXenes

Mengmeng Shao,[a] Yangfan Shao,[ab] Wenzhou Chen,[a] Kin Long Ao,[a] Rui Tong,[a] Qing Zhu,[a] Iat Neng Chan,[a] Weng Fai Ip,[c] Xingqiang Shi[b] and Hui Pan*[a]

[a] Institute of Applied Physics and Materials Engineering, University of Macau, Macao, P. R. China

[b] Department of Physics, Southern University of Science and Technology, Shenzhen, Guangdong, P. R. China

[c] Chemistry Supporting Group, Faculty of Science and Technology, University of Macau, Macao, P. R. China

* H. Pan (huipan@umac.mo); Tel: 853-88224427; Fax: 853-88222426

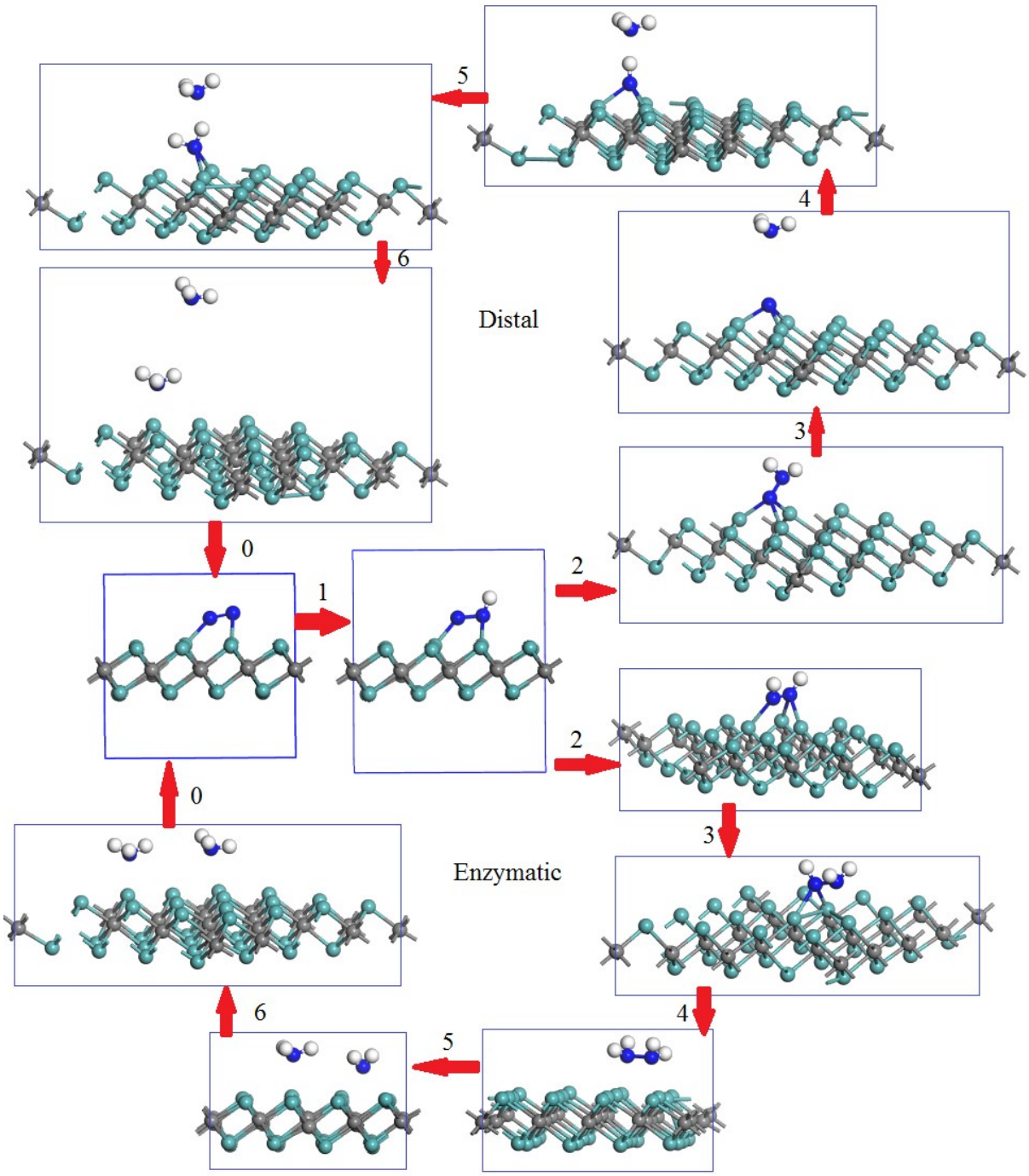

Fig. S1 The two possible pathways for N_2-fixation to NH_3 on M_2X.

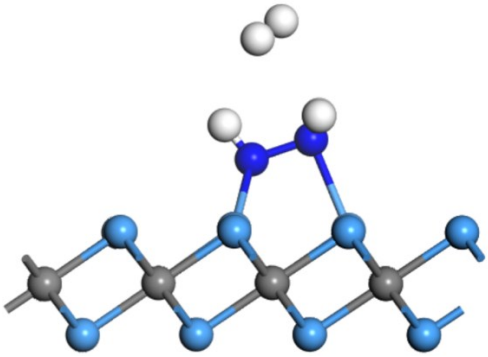

Fig. S2 The 5th step in "Enzymatic" pathway on Ta_2C.

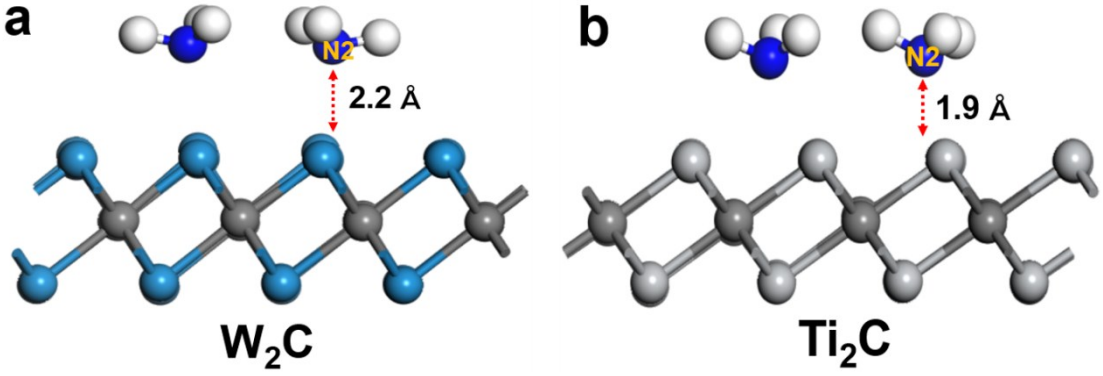

Fig. S3 The 6th step in "Enzymatic" pathway on W_2C (a) and Ti_2C (b).

Table S1. The energies (eV) in each step of the distal and enzymatic reaction pathway, as shown in Fig. 4.

Reaction	**Distal**						**Enzymatic**					
step	Mo_2C	W_2C	Ta_2C	Ta_2N	Ti_2C	Ti_2N	Mo_2C	W_2C	Ta_2C	Ta_2N	Ti_2C	Ti_2N
0	-476.65	-532.82	-530.55	-518.91	-420.54	-434.01	-476.65	-532.82	-530.55	-518.91	-420.54	-434.01
1	-480.29	-536.96	-534.31	-522.56	-424.20	-437.52	-480.29	-536.96	-534.31	-522.56	-424.20	-437.52
2	-484.21	-540.78	-537.89	-525.19	-426.43	-440.74	-484.31	-540.40	-537.73	-529.55	-427.59	-440.98
3	-489.09	-546.04	-543.04	-531.87	-432.03	-445.39	-487.56	-544.19	-540.97	-532.12	-429.93	-443.65
4	-493.11	-549.71	-546.69	-535.56	-436.04	-449.08	-490.53	-547.03	-543.38	-534.91	-436.34	-450.18
5	-496.04	-552.08	-549.76	-538.41	-438.92	-452.34	-496.56	-552.81	--	-538.46	-439.11	-452.74
6	-499.74	-555.82	-552.19	-541.82	-441.51	-454.62	-499.72	-556.31	--	-541.70	-441.67	-455.09

Note:

H_2= -6.77 eV

The step 0 means the adsorption of N_2 on MXenes (M_2X), the steps 1-6 correspond to different states along the N_2 conversion mechanism (Fig. 3). And the reaction energy at each step (shown in Fig. 4) is calculated as follows:

$$E_{re} = E(M_2X + N_2H_m) - E(M_2X + N_2H_{m-1}) - \frac{1}{2}E(H_2)$$

Table S2. The N-N bond length (Å) of the adsorbed N_2 in each step of the distal and enzymatic reaction pathway, as shown in Fig. 5.

Reaction	**Distal**						**Enzymatic**					
step	Mo_2C	W_2C	Ta_2C	Ta_2N	Ti_2C	Ti_2N	Mo_2C	W_2C	Ta_2C	Ta_2N	Ti_2C	Ti_2N
-1	1.113	1.113	1.113	1.113	1.113	1.113	1.113	1.113	1.113	1.113	1.113	1.113
0	1.272	1.39	1.394	1.395	1.342	1.343	1.272	1.390	1.394	1.395	1.342	1.343
1	1.359	1.415	1.396	1.395	1.409	1.406	1.359	1.415	1.396	1.395	1.409	1.406
2	1.410	1.434	1.437	1.436	1.426	1.412	1.407	1.413	1.432	3.099	1.456	1.453
3	2.663	2.591	2.715	2.695	3.256	2.714	1.455	1.460	1.472	3.049	1.482	1.465
4	2.74	2.690	3.681	3.933	3.355	2.989	1.468	1.471	1.470	3.952	3.284	3.115
5	2.822	3.431	4.370	4.160	3.347	2.911	4.494	2.882	--	4.734	3.339	3.238
6	3.571	2.962	2.977	5.408	4.012	5.278	3.658	3.365	--	3.492	3.723	3.547

Note:

The step -1 correspond to the N-N bond length of free N_2 which is about 1.113 Å. And the step 0 means the N-N bond length of the adsorbed N_2 on MXenes.

Table S3. The charge transfer (the charge difference of the present step from that of the previous step) of N atoms in the catalyst (W_2C and Ti_2C) of the distal reaction pathway, as shown in Fig. 6a&c.

Reaction step	**W_2C**				**Ti_2C**			
	N1		N2		N1		N2	
	Charge	**Charge Transfer**	Charge	**Charge Transfer**	Charge	**Charge Transfer**	Charge	**Charge Transfer**
0	5.833	**--**	5.498	**--**	5.815	**--**	5.914	**--**
1	5.870	**0.037**	5.708	**0.210**	5.968	**0.154**	5.999	**0.085**
2	5.895	**0.025**	5.806	**0.098**	5.991	**0.023**	5.969	**-0.030**
3	6.241	**0.346**	6.183	**0.377**	6.456	**0.466**	6.263	**0.294**
4	6.347	**0.106**	6.172	**-0.011**	6.560	**0.104**	6.258	**-0.006**
5	6.286	**-0.061**	--	**--**	6.505	**-0.056**	--	**--**
6	6.245	**-0.041**	--	**--**	6.306	**-0.199**	--	**--**

Note:

The charge transfer is the charge difference of the present step from that of the previous step, which is calculated as follows:

$$q(M_2X + N_2H_m) - q(M_2X + N_2H_{m-1})$$

Table S4. The charge transfer (the charge difference of the present step from that of the previous step) of N atoms in the catalyst (W_2C and Ti_2C) of the enzymatic reaction pathway, as shown in Fig. 6b&d.

Reaction step	**W_2C**				**Ti_2C**			
	N1		N2		N1		N2	
	Charge	**Charge Transfer**	Charge	**Charge Transfer**	Charge	**Charge Transfer**	Charge	**Charge Transfer**
0	5.833	**--**	5.498	**--**	5.815	**--**	5.914	**--**
1	5.870	**0.037**	5.708	**0.210**	5.968	**0.154**	5.999	**0.085**
2	5.857	**-0.013**	5.808	**0.100**	6.057	**0.089**	5.989	**-0.010**
3	5.886	**0.029**	5.844	**0.036**	6.045	**-0.012**	5.959	**-0.030**
4	5.825	**-0.061**	5.819	**-0.025**	6.490	**0.445**	6.492	**0.532**
5	6.247	**0.422**	6.253	**0.433**	6.492	**0.001**	6.313	**-0.179**
6	6.168	**-0.079**	6.208	**-0.045**	6.340	**-0.152**	6.332	**0.019**

Note:

The charge transfer is the charge difference of the present step from that of the previous step, which is calculated as follows:

$$q(M_2X + N_2H_m) - q(M_2X + N_2H_{m-1})$$

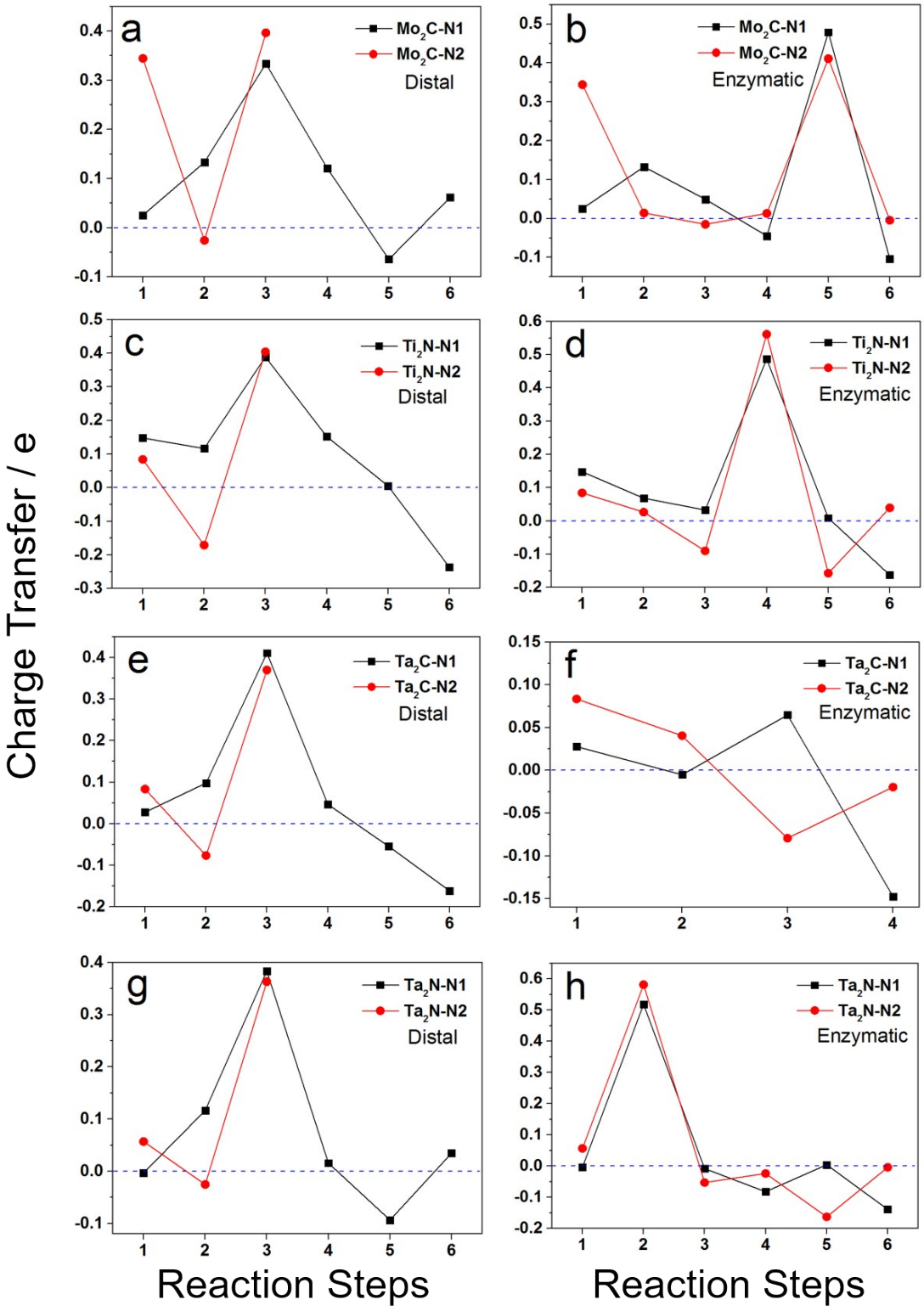

Fig. S4 Charge transfer at each step for N_2-fixation on Mo_2C, Ti_2N, Ta_2C and Ta_2N in Distal (a, c, e, g) and Enzymatic (b, d, f, h) pathways.

From the Fig. S4, we can see most of the formation energy at each step strongly depends on the value of transferred charge on each N atom. However, at the 2nd step on the "Distal" pathway of Mo_2C, the exothermic reaction corresponds to electron lose on N2 due to the extended N-N bond length (Fig. 5a) and charge transfer from N2 to N1.