Supporting Information

Anisotropic N-Modification of the Mo_4 Ensemble for Efficient Ammonia Synthesis on Molybdenum Nitrides

Jiankang Zhao[a], Chaonan Cui[a,b], Hua Wang[a], Jinyu Han[a], Xinli Zhu*[,a], Qingfeng Ge*[,a,c]

[a]*Collaborative Innovation Centre of Chemical Science and Engineering*, *School of Chemical Engineering and Technology*, *Tianjin University*, *Tianjin* 300072, *China*

[b]*State Key Laboratory for Structural Chemistry of Unstable and Stable Species, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China*

[c]*Department of Chemistry and Biochemistry, Southern Illinois University, Carbondale, IL 62901, United States*

1. Optimized structures

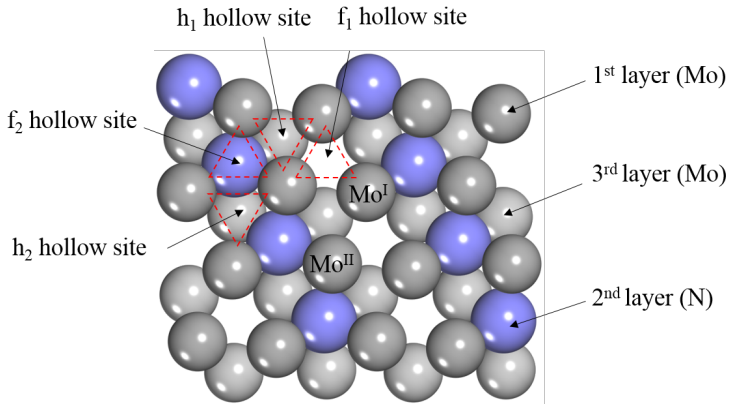

Figure S1. Top view of the Mo-terminated $Mo_2N(111)$ surface. h and f represent the hcp and fcc hollow sites, respectively. Gray = Mo and blue= N.

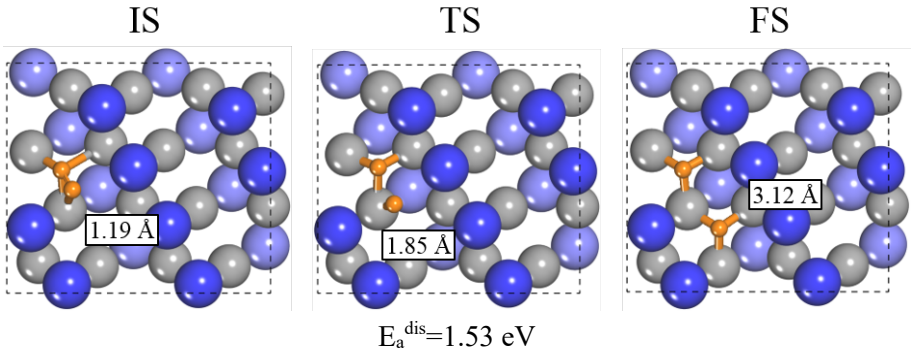

Figure S2. Adsorption and dissociation of N_2 on the N-terminated $Mo_2N(111)$ surface.

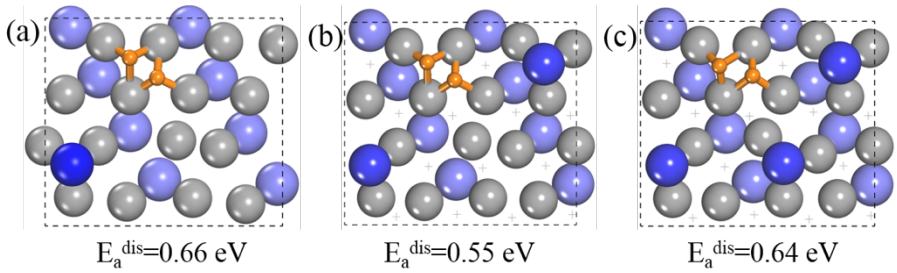

Figure S3. Top view of the TSs for N_2 activation with one (a), two (b) and three N_s atoms (c) on the surface but away from the Mo_4 active sites on the Mo-terminated $Mo_2N(111)$ surface. The corresponding activation barriers for dissociation are provided.

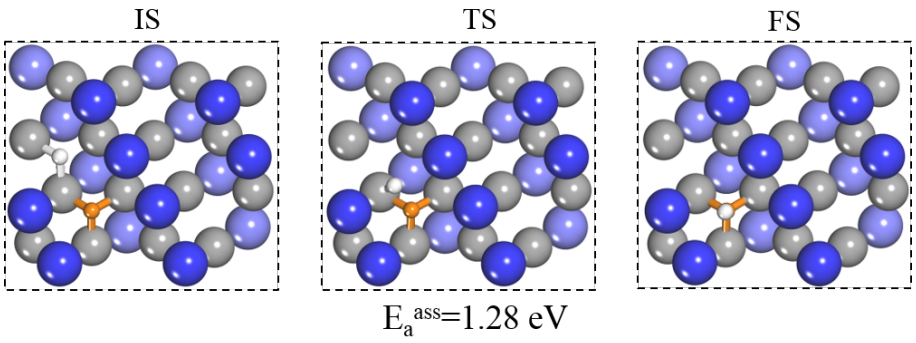

Figure S4. Hydrogenation of N on the N-terminated $Mo_2N(111)$ surface.

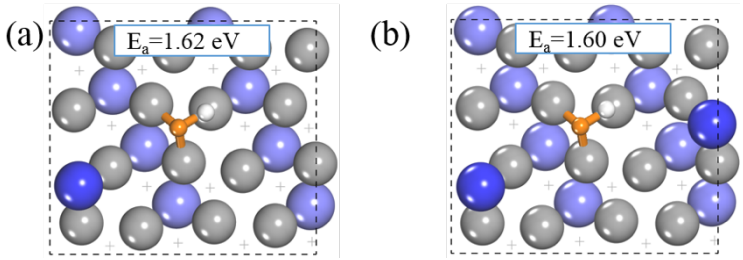

Figure S5. Top view of the TSs for N hydrogenation with one (a) and two N_s atoms (b) but away from the Mo_4 active sites. The corresponding activation barriers are shown in the figure.

2. Related structural parameters and energies during hydrogenation

Table S1. The N-N distance in TS for N_2 dissociation and ZPE-corrected activation barriers on different ensembles.

Ensembles	Domains	Label	d_{N-N}/ Å	E_{act} / eV
Mo_4N_s	D1	#1	1.71	0.33
		#2	1.69	0.41
		#3	1.70	0.60
		#8	1.70	0.66
		#9	1.68	0.68
		#10	1.76	0.60
	D2	#6	1.70	0.64
		#12	1.69	0.37
		#13	1.68	0.64
	D3	#4	1.85	1.55
Mo_4N_{2s}	D1	#2+#10	1.72	0.51
	D2	#6+#12	1.67	0.30
	D1+D2	#6+#10	1.72	0.56
	D1+D2	#2+#12	1.67	0.35
Mo_4N_{3s}	D1	#8+#10	1.69	0.65
	D1+D2	#2+#6+#10	1.70	0.46
	D1+D2	#2+#10+#12	1.68	0.27
Mo_4N_{4s}	D1+D2	#2+#6+#10+#12	1.67	0.26

Table S2. The N-H distance at the 3-centered TS with H atop Mo(4) for N hydrogenation and the activation barriers (without ZPE correction) of N hydrogenation at different local active site environment.

Ensembles	Domains	Label	d_{N-H}/ Å	E_{act}/ eV
Mo_4N_s	D1	#2	1.47	1.38
		#9	1.45	1.61
	D2	#10	1.46	1.59
		#6	1.52	1.51
		#12	1.47	1.34
	D3	#4	1.47	1.44
Mo_4N_{2s}	D1	#2+#10	1.45	1.44
	D2	#6+#12	1.51	1.56
	D1+D2	#10+#12	1.44	1.49
	D1+D2	#2+#12	1.50	1.19
Mo_4N_{3s}	D1	#8+#10	1.47	1.68
	D1+D2	#6+#10+#12	1.40	1.61
	D1+D2	#2+#10+#12	1.46	1.48
Mo_4N_{4s}	D1+D2	#2+#6+#10+#12	1.45	1.52

Table S3. The N-H distance at the 3-centered TS with H atop Mo(4) for NH hydrogenation and the activation barriers (without ZPE correction) of NH hydrogenation at different local active site environment.

Ensembles	Domains	Label	d_{N-H}/ Å	E_{act}/ eV
Mo_4N_s	D1	#2	1.39	1.75
		#10	1.39	1.92
	D2	#6	1.41	1.81
		#12	1.38	1.76
	D3	#4	1.40	1.88
Mo_4N_{2s}	D1+D3	#4+#10	1.38	1.69
	D2+D2	#6+#12	1.37	1.61
	D1+D2	#2+#12	1.42	1.70
Mo_4N_{3s}	D1+D2	#2+#10+#12	1.39	1.61
	D1+D2	#6+#10+#12	1.33	1.60
Mo_4N_{4s}	D1+D2	#2+#6+#10+#12	1.28	1.39

3. Microkinetic analysis

The elementary reaction steps of ammonia synthesis on Mo_2N (111) include,

$$N_2(g) + * \leftrightarrows N_2* \quad (1)$$

$$N_2* + * \leftrightarrows 2N* \quad (2)$$

$$H_2(g) + 2* \leftrightarrows 2H* \quad (3)$$

$$N* + H* \leftrightarrows NH*+* \quad (4)$$

$$NH* + H* \leftrightarrows NH_2*+* \quad (5)$$

$$NH_2* + H* \leftrightarrows NH_3* +* \quad (6)$$

$$NH_3* \leftrightarrows NH_3(g)+ * \quad (7)$$

The adsorption of N_2, H_2 and NH_3 has been treated within the collision theory[1, 2] and the non-activated adsorption rate k_a can be expressed as,

$$k_a = \frac{S\sigma}{\sqrt{2\pi m k_B T}} \quad (8)$$

where m, k_B and T are the molecular mass, Boltzmann constant and temperature, respectively. The sticking coefficient σ was assumed to be 1. S is the average area of the adsorption site and is set to be $1.2\times10^{-18}\times$ 1/16 m^2 for each Mo_4 ensemble. The desorption was considered based on the adsorption/desorption equilibrium, i.e.

$$K = \frac{k_a}{k_d} = e^{-\frac{\Delta H - T\Delta S}{RT}} \quad (9)$$

The contribution of the elevated temperature to the reaction enthalpy was taken into account by including a $C_p\Delta T$ (C_p, heat capacity) term.

For the surface reactions, the forward rate constants were estimated using transition state theory,

$$k_f = \frac{k_B T}{h}\frac{q_{TS,vib}}{q_{IS,vib}} e^{-E_a/k_B T} \quad (10)$$

where k_B and h are the Boltzmann constant and Planck's constant. E_a is ZPE-corrected activation barrier for forward reaction. $q_{TS,vib}$ and $q_{IS,vib}$ are the vibrational partition functions for the

transition state and initial state, respectively.

The reaction rate of each elementary step is then,

$$r_1 = k_1 p_{N_2} \theta^* - k_{-1} \theta_{N_2} \tag{11}$$

$$r_2 = k_2 \theta_{N_2} \theta^* - k_{-2} \theta_N^2 \tag{12}$$

$$r_3 = k_3 P_{H_2} \theta^* - k_{-3} \theta_H^2 \tag{13}$$

$$r_4 = k_4 \theta_N \theta_H - k_{-4} \theta_{NH} \theta^* \tag{14}$$

$$r_5 = k_5 \theta_{NH} \theta_H - k_{-5} \theta_{NH_2} \theta^* \tag{15}$$

$$r_6 = k_6 \theta_{NH_2} \theta_H - k_{-6} \theta_{NH_3} \theta^* \tag{16}$$

$$r_7 = k_7 \theta_{NH_3} - k_{-7} P_{NH_3} \theta^* \tag{17}$$

where r_j is the rate of each step, k_j and k_{-j} the forward and backward rate constant, θ_i the coverage of each species, and θ^* the coverage of vacancies.

A set of algebraic differential equations are then generated for each intermediate,

$$\frac{d\theta_i}{dt} = \sum_j \upsilon_{i,j} r_j \tag{18}$$

$$\sum_i \theta_i = 1 - \theta * \tag{19}$$

A steady-state is achieved when the change in the coverage of all intermediates approach zero. The surface coverage was obtained by solving the differential equations using the SciPy Python package. The reaction rate and TOF can be obtained.

Table S4. The calculated activation barriers, and the corresponding rate constants of forward and reverse reaction for each elementary step on the Mo-terminated surface with N/Mo ratio of 0.

Step no.	Reaction	Mo-terminated surface with N/Mo ratio = 0/16			
		$E_{a,f}$	$E_{a,r}$	k_f	k_r
1	N_2+*=N_2*	/	2.27(#)	1.44E+08	7.68E+00
2	N_2+*=2N*	0.58	1.64	2.26E+08	4.12E+02
3	H_2+2*=2H*	/	1.94(#)	5.39E+08	5.62E+00
4	N*+H*=NH*+*	1.43	1.14	6.06E+01	1.64E+03
5	NH*+H*=NH_2*+*	1.65	0.66	2.72E+00	5.51E+07
6	NH_2*+H*=NH_3*+*	1.75	0.87	1.52E+00	3.94E+05
7	NH_3*=NH_3+*	2.04(#)	/	1.62E+01	1.85E+08

Table S5. The calculated activation barriers, and the corresponding rate constants of forward and reverse reaction for each step on N-terminated surface with N/Mo ratio of 8/16.

Step no.	Reaction	N-terminated surface with N/Mo ratio = 8/16			
		$E_{a,f}$	$E_{a,r}$	k_f	k_r
1	N_2+*=N_2*	/	0.16(#)	1.44E+08	4.86E+16
2	N_2*+*=2N*	1.53	3.23	5.97E+00	1.96E-11
3	H_2+2*=2H*	/	1.62(#)	5.39E+08	1.40E+03
4	N*+H*=NH*+*	1.28	1.47	4.18E+03	1.33E+02
5	NH*+H*=NH_2*+*	1.39	0.41	2.73E+02	1.34E+09
6	NH_2*+H*=NH_3*+*	1.64	1.09	4.39E+01	7.40E+04
7	NH_3*=NH_3+*	0.87(#)	/	9.35E+09	1.85E+08

Table S6. The calculated activation barriers, and the corresponding rate constants of forward and reverse reaction for each step on N-rich surface with N/Mo ratio of 7/16.

Step no.	Reaction	N-rich surface with N/Mo = 7/16			
		$E_{a,f}$	$E_{a,r}$	k_f	k_r
1	N_2+*=N_2*	/	1.43(#)	1.44E+08	1.50E+07
2	N_2*+*=2N*	0.99	1.53	7.01E+05	1.01E+02
3	H_2+2*=2H*	/	1.62(#)	5.39E+08	1.40E+03
4	N*+H*=NH*+*	1.06	1.25	1.86E+05	5.91E+03
5	NH*+H*=NH_2*+*	1.32	0.26	9.13E+02	1.77E+10
6	NH_2*+H*=NH_3*+*	1.61	1.15	7.37E+01	2.63E+04
7	NH_3*=NH_3+*	1.25(#)	/	1.33E+07	1.85E+08

In Table S4-S6, "/" represent the non-activated adsorption process; (#) represents the activation barriers of desorption process are equal to the desorption energies.

1. Yuan, H.; Zhu, X.; Han, J.; Wang, H.; Ge, Q. Rhenium-Promoted Selective CO_2 Methanation on Ni-Based Catalyst. *J. CO_2 Util.* **2018**, *26*, 8-18.
2. Motagamwala, A. H.; Ball, M. R.; Dumesic, J. A. Microkinetic Analysis and Scaling Relations for Catalyst Design. *Annu. Rev. Chem. Biomol. Eng.* **2018**, *9*, 413-450.