Supporting Information

Construction of Frustrated Lewis Pairs on Carbon Nitride Nanosheet for Catalytic Hydrogenation of Acetylene

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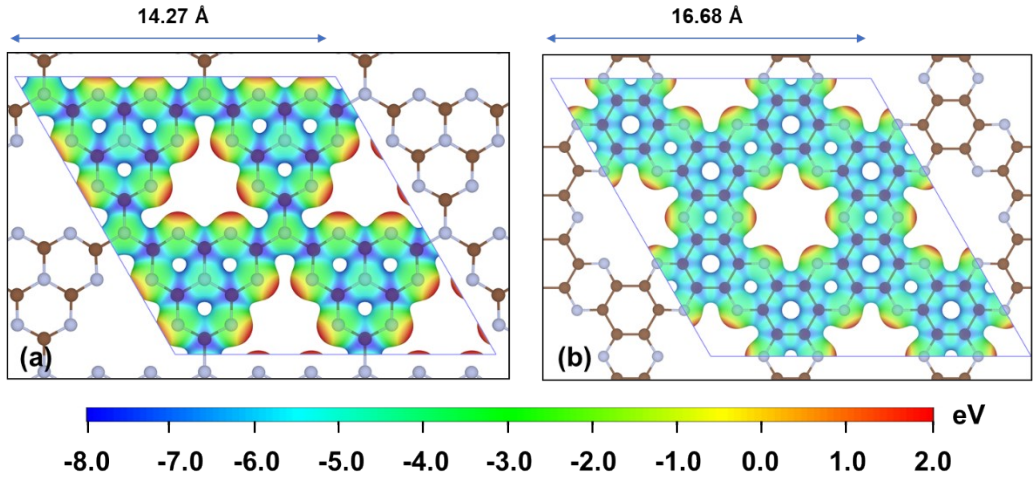

Figure S1. Optimized structures with charge density colored by local potential (eV) of (a) *g*-C_3N_4 and (b) C_2N. Color code: C, brown; N, light blue. Isosurface level of charge density: 0.1 e $bohr^{-3}$.

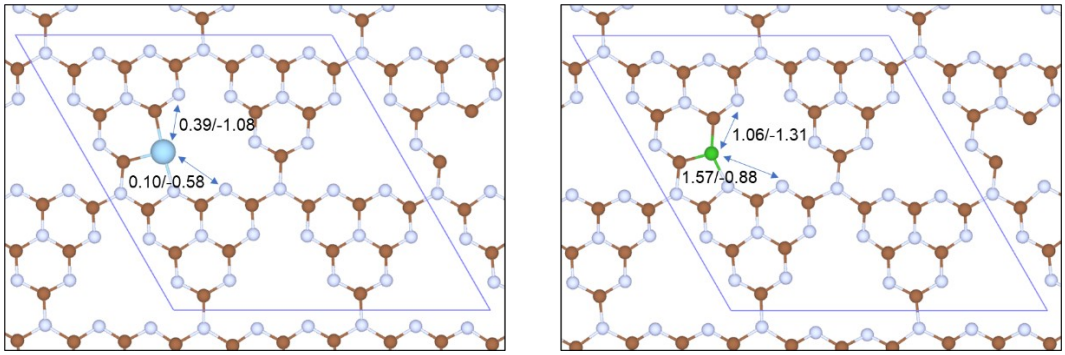

Figure S2. Comparison of H_2 dissociation on Al and B doped *g*-C_3N_4, with energy barrier/reaction energy.

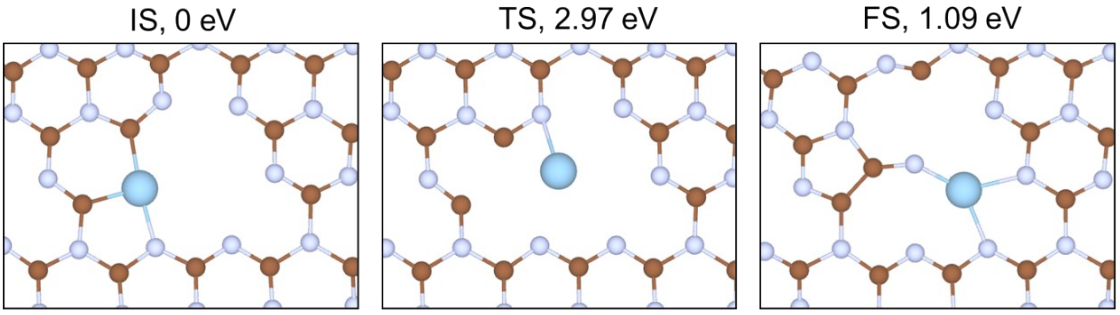

Figure S3. The initial, transition and final states of Al migration in the pore of the *g*-C_3N_4, related energies are also attached.

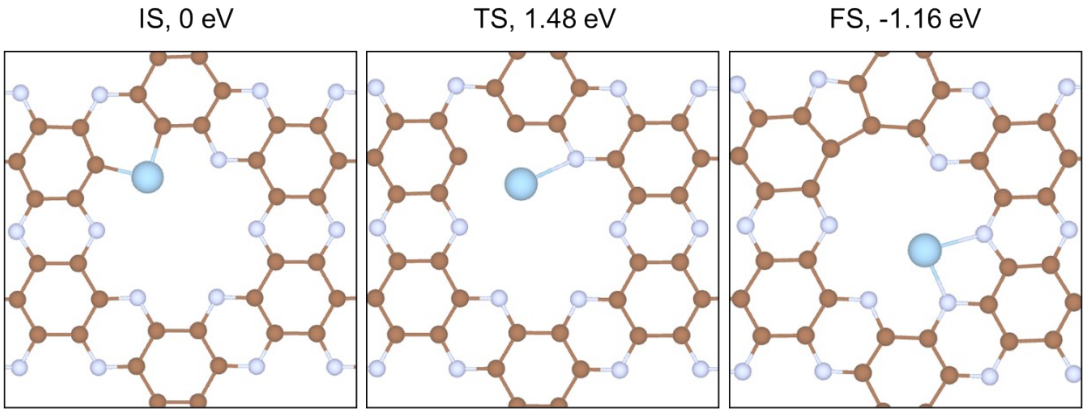

Figure S4. The initial, transition and final states of Al migration in the pore of the C_2N, related energies are also attached.

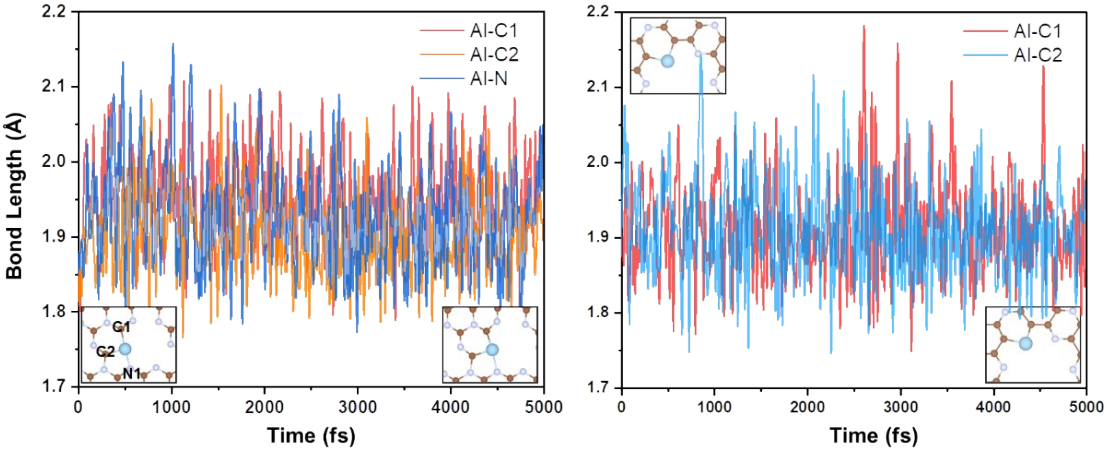

Figure S5. Bond length variation of Al–C/N bond in Al-doped *g*-C_3N_4 (left) and C_2N (right) AIMD simulations under 500 K for 5ps.

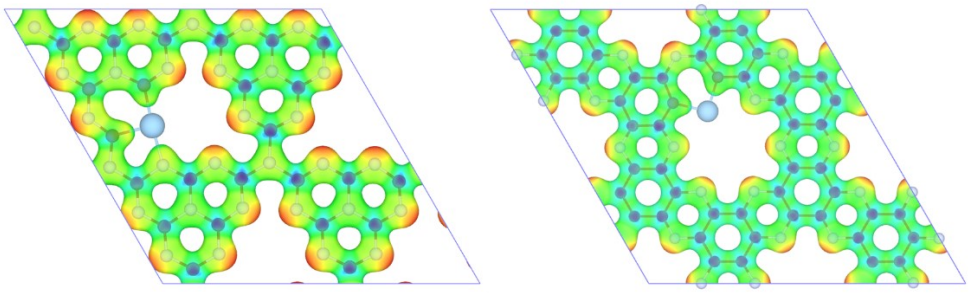

Figure S6. Electrostatic potential colored electron density Al doped *g*-C_3N_4 and C_2N.

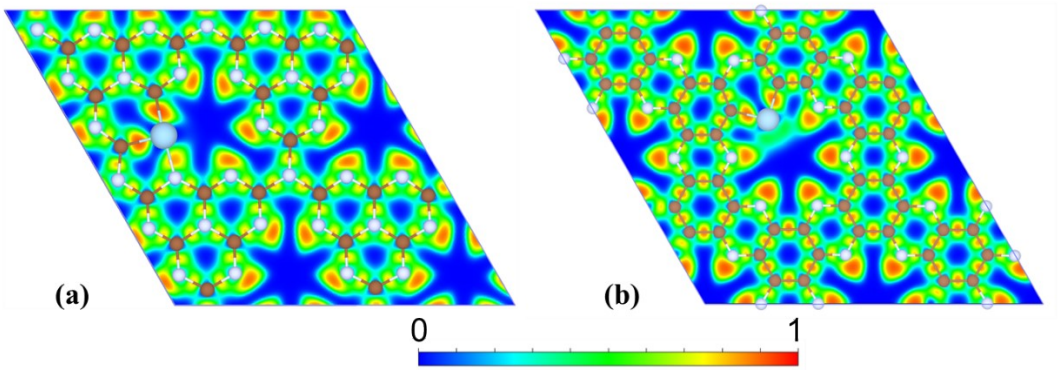

Figure S7. Electron localization function maps of Al-doped (a) *g*-C_3N_4 and (b) C_2N

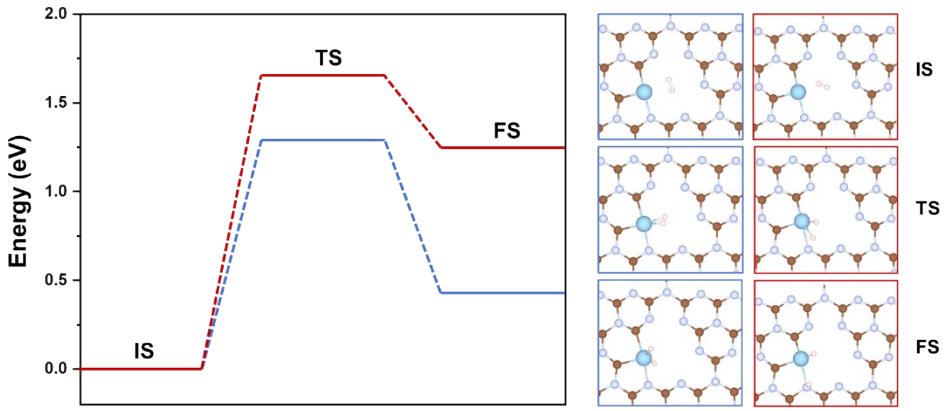

Figure S8. Comparison between the homolytic H_2 dissociation on Al site (blue) and heterolytic H_2 dissociation on CLP (red).

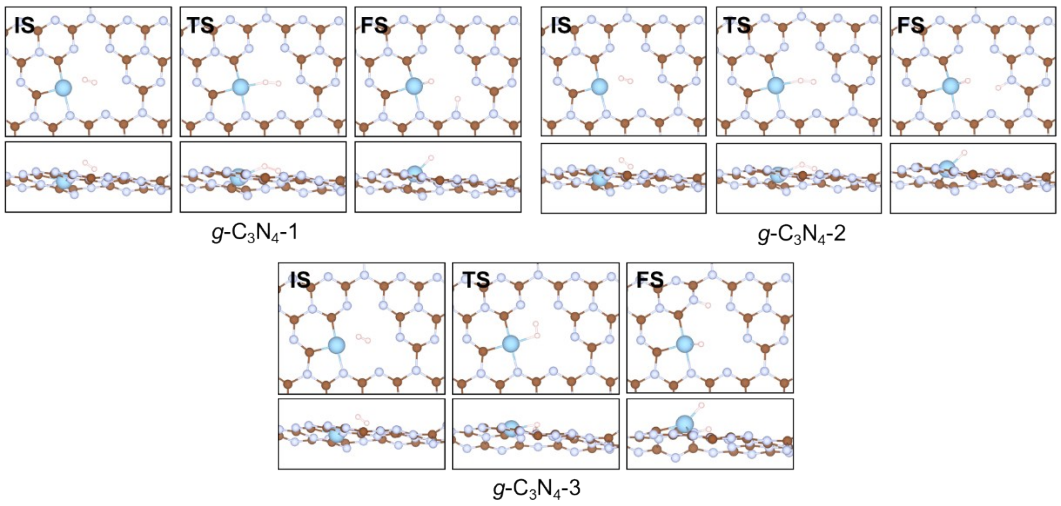

Figure S9. Initial (IS), transition (TS) and final states (TS) of H_2 dissociation catalyzed by FLPs in Al-doped *g*-C_3N_4.

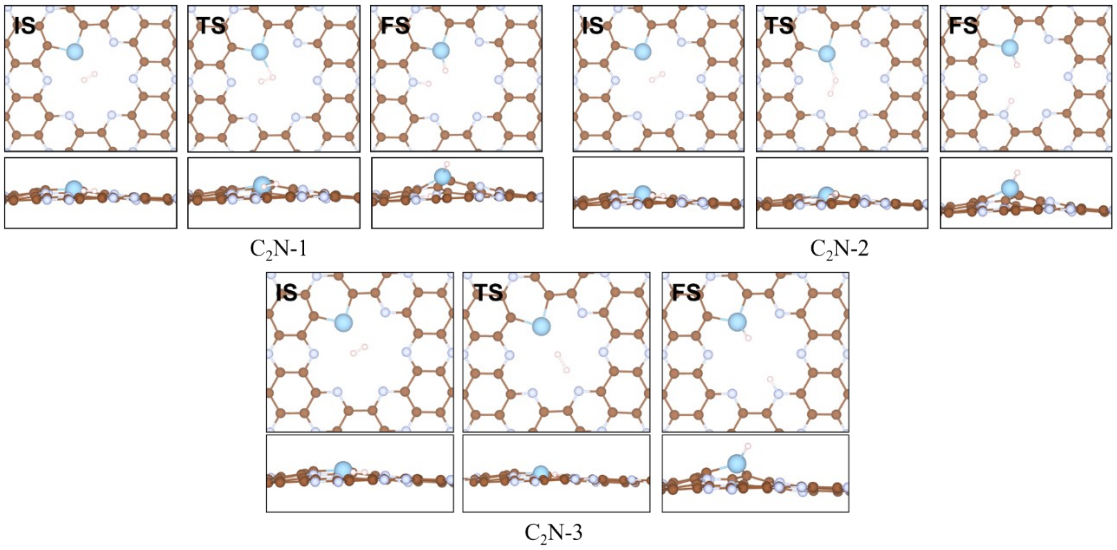

Figure S10. IS, TS and FS of H_2 dissociation catalyzed by FLPs in Al-doped C_2N.

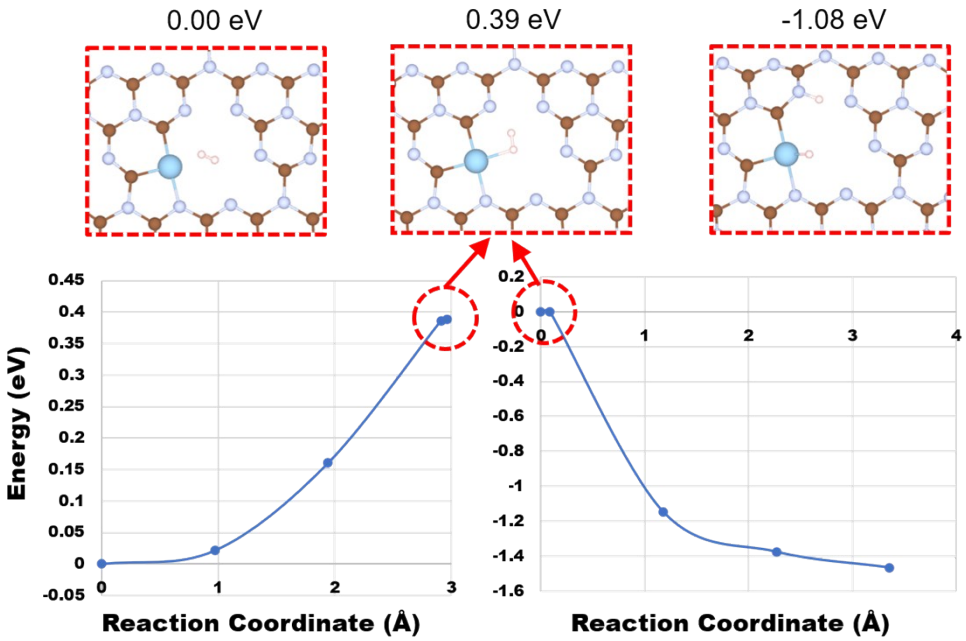

Figure S11. Reaction coordinate (split at metastable state) of H_2 activation catalyzed by Al-doped *g*-C_3N_4-3, owing to the existence of a metastable state in the process.

Different from the other two FLPs, the pathway of H_2 dissociation on *g*-C_3N_4-3 involved a metastable state (MS, $d_{H\text{-}H}$=0.85 Å, without image frequency), which can be considered as an intermediate. To verify this path, we split the process into two steps, IS to MS and MS to FS, which can represent the orientation transformation of H_2 and H_2 cleavage, respectively. Results show that the former one is pure energetic climbing while the latter is downhill, both two steps would not experience a transition state. These suggest that starting from the same initial state with the other two FLPs, the H_2 dissociation on *g*-C_3N_4-3 should overcome an energy of 0.39 eV.

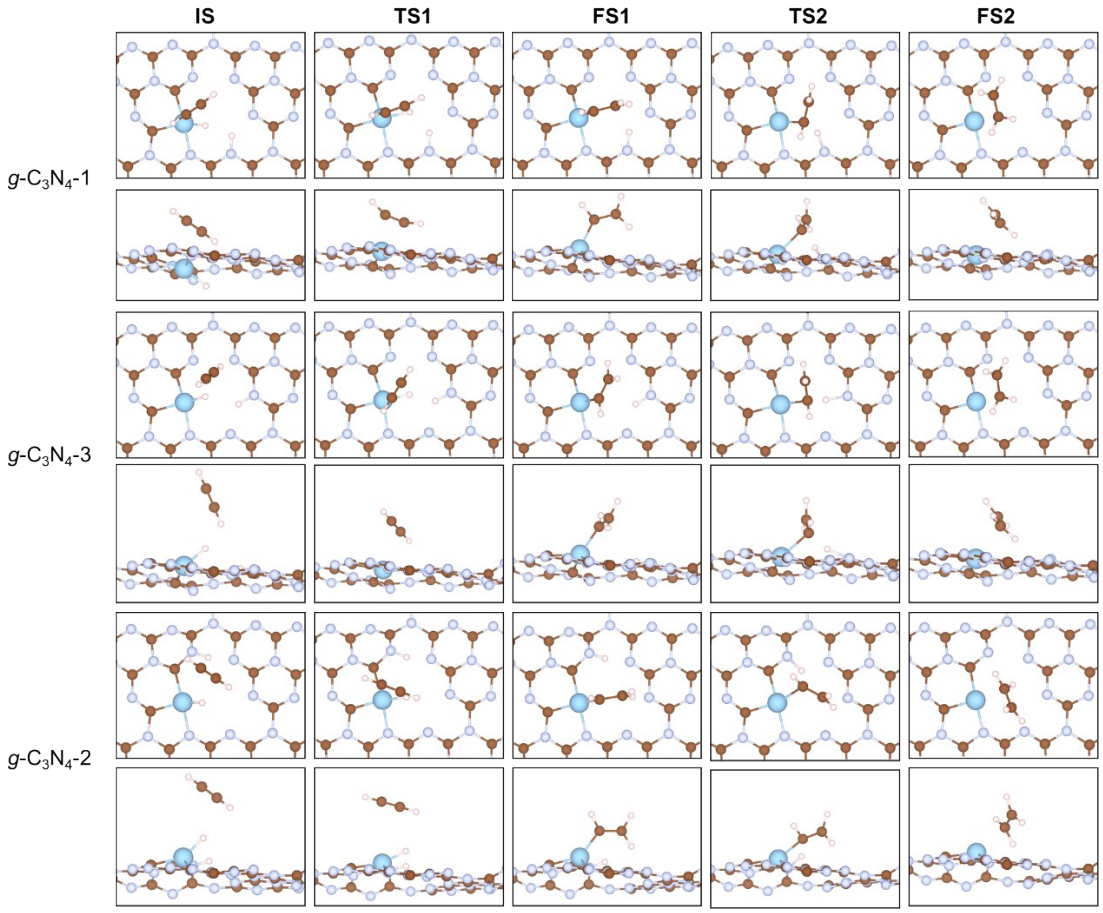

Figure S12. IS, TS and FS of acetylene hydrogenation catalyzed by FLPs in Al-doped *g*-C_3N_4.

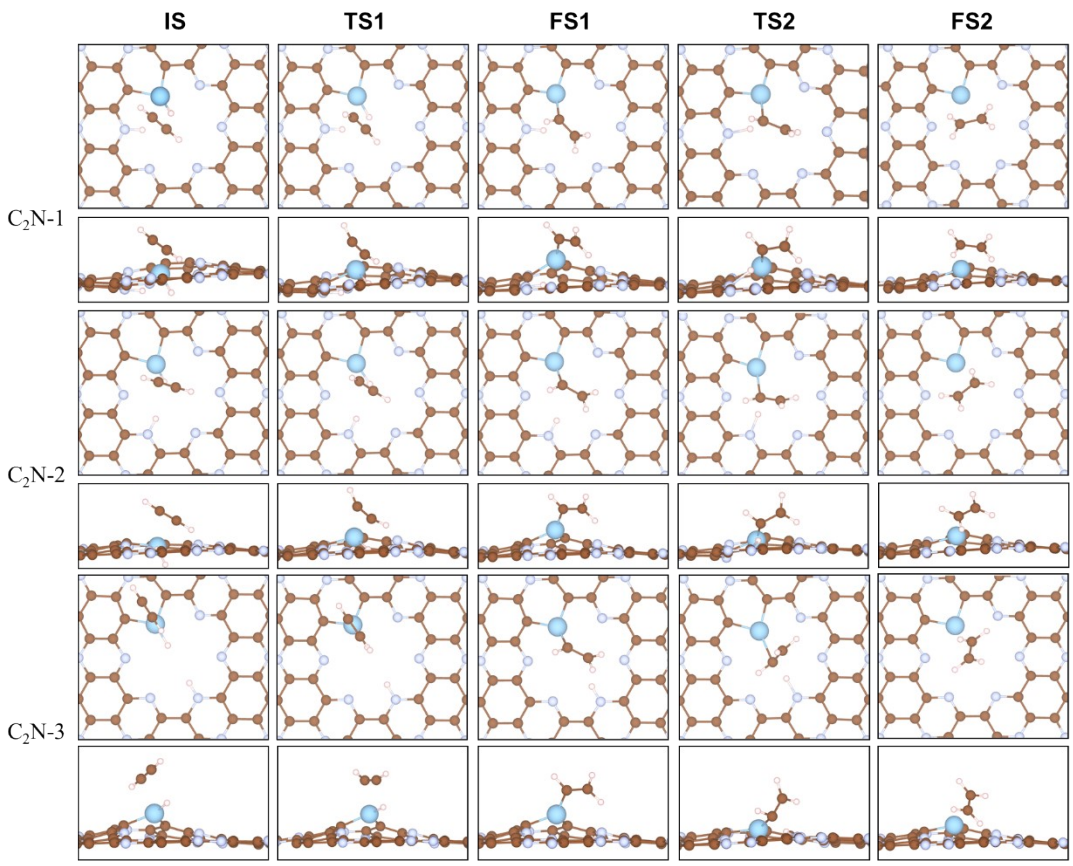

Figure S13. IS, TS and FS of acetylene hydrogenation catalyzed by FLPs in Al-doped C_2N.

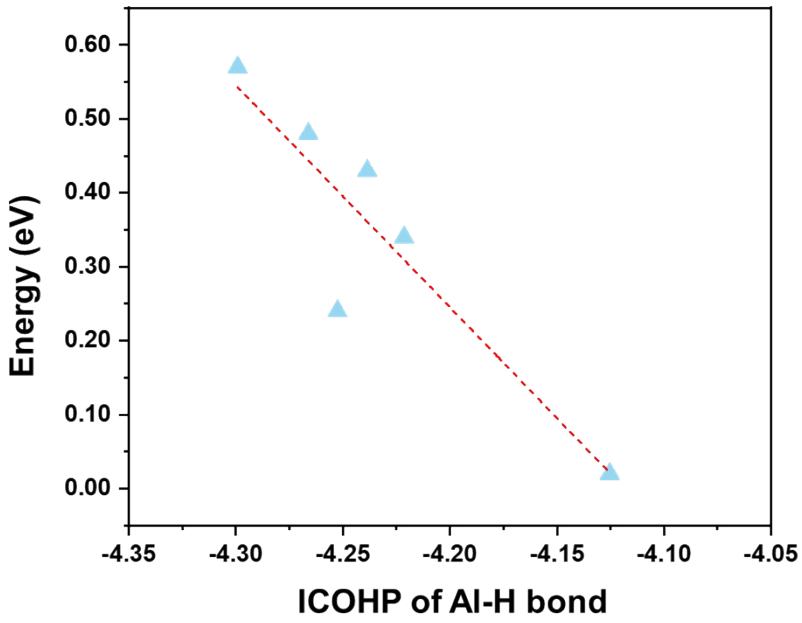

Figure S14. Correlation between the ICOHP of Al-H bond with the energy barrier of the first hydrogenation.

Table S1. Distance ($d_{N\text{-}LA}$) of N-Al and adsorption energy (E_{ads}) of LA for varying carbon nitride supporting LA. The cohesive energy of Al[1] and B[2] is 3.67 and 5.91 eV, respectively.

		Al		B	
		$d_{N\text{-}LA}$ (Å)	E_{ads} (eV)	$d_{N\text{-}LA}$ (Å)	E_{ads} (Å)
g-C_3N_4	adsorption	2.39-2.78	-2.86	2.67-3.52	-4.74
	substitution	3.29-4.16	-4.72	2.67-4.78	-10.92
C_2N	adsorption	2.87-3.61	-4.36	3.10-4.21	-5.17
	substitution	2.59-4.88	-4.18	2.87-5.60	-7.73

Table S2. Calculated distance between Al and N sites (d_{Al-N}), atomic charge (Q) of hydrogen in transition state (TS), and H-H bond lengths (d_{H-H}).

FLP sites	d_{Al-N}/Å	Q/e (TS)		d_{H-H}/Å
		H(Al)	H(N)	
g-C_3N_4-1	3.29	-0.47	0.36	0.91
g-C_3N_4-2	4.16	-0.47	0.35	0.90
g-C_3N_4-3	3.68	-0.37	0.30	0.85
C_2N-1	2.59	-0.19	0.14	0.82
C_2N-2	4.26	-0.48	0.36	0.99
C_2N-3	4.28	-0.48	0.36	1.10

References:

1. Sen, P.; Ciraci, S.; Buldum, A.; Batra, I. P., Structure of aluminum atomic chains. *Physical Review B* **2001,** *64* (19), 195420.
2. Hayami, W.; Otani, S., The Role of Surface Energy in the Growth of Boron Crystals. *The Journal of Physical Chemistry C* **2007,** *111* (2), 688-692.