Electronic supplementary information (ESI)

On-purpose design of dual active sites in single V atom anchored C_2N nanosheet for propane dehydrogenation catalysis

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Table S1. Adsorption energies of single TM atoms on C_2N.

TM	E_{ads}(H1) (eV)	E_{ads}(H2) (eV)	E_{ads}(H3) (eV)	E_{ads}(B1) (eV)	E_{ads}(B2) (eV)	E_{ads}(h1) (eV)	E_{ads}(h2) (eV)	E_{cohe}[a] (eV)
Sc	-7.54	-7.54				-3.56	-1.79	-3.9
Ti	-6.77	-6.75				-3.61	-2.05	-4.85
V	-6.04				-1.21	-2.62	-1.50	-5.31
Cr	-7.93	-7.92	-7.45			-3.73	-4.01	-4.1
Mn	-4.46	-4.44	-4.22		-0.47	-0.50	-0.45	-2.92
Fe	-4.57					-1.50	-1.05	-4.28
Co	-4.52					-1.67	-1.57	-4.39
Ni	-4.94					-1.84	-2.21	-4.44
Cu	-3.38			-0.59	-0.55	-0.35	-0.50	-3.49
Zn	-1.46			-0.14	-0.14	-0.15	-0.16	-1.35

[a] Cohesion energy

Table S2. Adsorption energies of single and double TM atoms on C_2N.

TM	E_{ads}(TM1) (eV)	E_{ads}(TM2) (eV)	ΔE^* (eV)	TM	E_{ads}(TM1) (eV)	E_{ads}(TM2) (eV)	ΔE^* (eV)[a]
Sc	-7.54	-3.66	3.88	Fe	-4.57	-3.86	0.71
Ti	-6.77	-5.02	1.75	Co	-4.52	-4.47	0.05
V	-6.04	-4.35	1.70	Ni	-4.94	-4.30	0.64
Cr	-7.93	-5.87	2.06	Cu	-3.38	-2.66	0.72
Mn	-4.46	-1.01	3.45	Zn	-1.46	-1.94	-0.48

[a] $\Delta E^* = E_{ads}(TM2) - E_{ads}(TM1)$

Table S3. Summary of possible elementary reactions in PDH.

Reaction No.	Elementary Reaction
1	$CH_3CH_2CH_3^* \rightarrow CH_3CH_2CH_2^* + H^*$
2	$CH_3CH_2CH_3^* \rightarrow CH_3CHCH_3^* + H^*$
3	$CH_3CH_2CH_2^* + H^* \rightarrow CH_3CH_2CH^* + 2H^*$
4	$CH_3CH_2CH_2^* + H^* \rightarrow CH_3CH{=}CH_2^* + H_2$
5	$CH_3CHCH_3^* + H^* \rightarrow CH_3CH{=}CH_2^* + H_2$
6	$CH_3CHCH_3^* + H^* \rightarrow CH_3CCH_3^* + 2H^*$
7	$CH_3CH{=}CH_2^* \rightarrow CH_3CH{=}CH^* + H^*$
8	$CH_3CH{=}CH_2^* \rightarrow CH_3C{=}CH_2^* + H^*$
9	$CH_3CH_2CH_3^* \rightarrow CH_3^* + CHCH_3^*$
10	$CH_3CH_2CH_2^* + H^* \rightarrow CH_3CH_2^* + CH_2^* + H^*$
11	$CH_3CHCH_3^* + H^* \rightarrow CH_3CH^* + CH_3^* + H^*$
12	$CH_3CH{=}CH_2^* \rightarrow CH_3CH + CH_2^*$

Table S4. The reaction energies of the first and second dehydrogenations of propane on TM_1/C_2N.

TM_1/C_2N	C_3H_8*	C_3H_7*(TM) + H*(N)		C_3H_6*(TM) + 2H*(N)	
	E_{ads} *(eV)	ΔE (eV)	E_b (eV)	ΔE (eV)	E_b (eV)
Sc_1/C_2N	-0.65	0.56	1.00	0.57	1.58
Ti_1/C_2N	-0.86	0.28	0.97	0.53	0.86
V_1/C_2N	-0.39	0.10	1.12	0.31	0.91
Cr_1/C_2N	-0.34	0.30	1.38	0.26	1.08
Mn_1/C_2N	-0.47	0.36	1.71	0.19	1.27

Table S5. The activation barriers (E_b) and reaction energies (E_{r1}) of dehydrogenation, the energies required for propylene desorption (E_{r2}) on TM_1/C_2N, as well as the energy difference between dehydrogenation and desorption process of propylene ($\Delta E = E_b - E_{r2}$).

TM_1/C_2N	C_3H_6*→C_3H_5*(TM) + H*(N)		C_3H_6*→C_3H_6(g)+*	ΔE (eV)
	E_b (eV)	E_{r1} (eV)	E_{r2} (eV)	
Sc_1/C_2N	1.25	0.97	1.42	-0.17
Ti_1/C_2N	1.38	1.03	1.43	-0.05
V_1/C_2N	1.53	1.06	1.10	+0.43
Cr_1/C_2N	1.97	0.68	1.07	+0.90
Mn_1/C_2N	1.83	0.83	1.32	+0.51

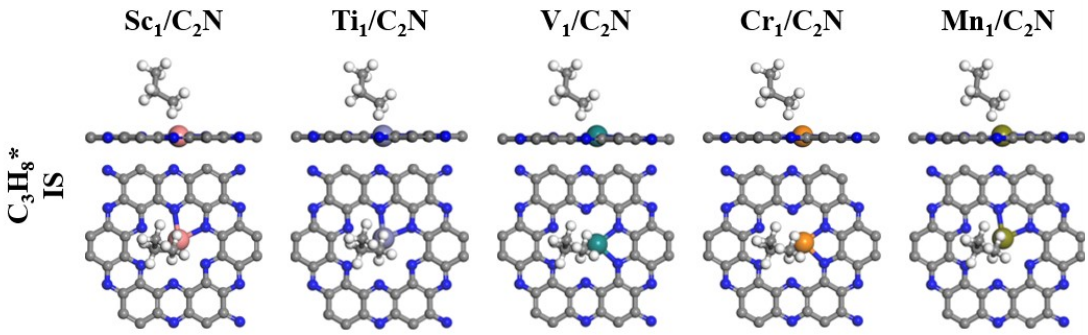

Fig. S1 Adsorption configurations of propane on TM_1/C_2N.

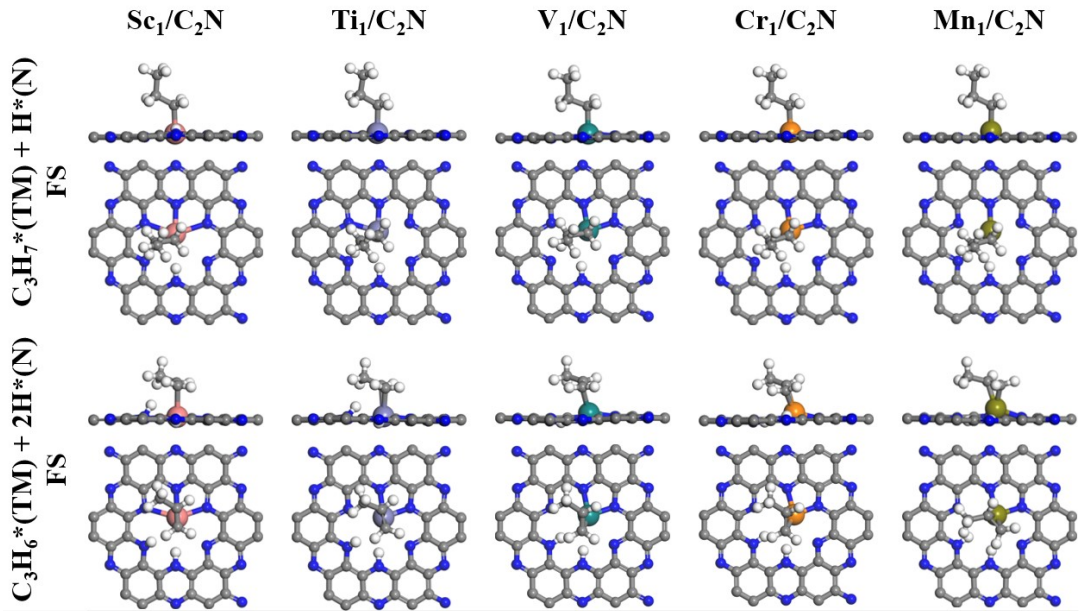

Fig. S2 Adsorption configurations of propyl, propylene and dissociated H atoms in the first and second dehydrogenations of propane on TM_1/C_2N.

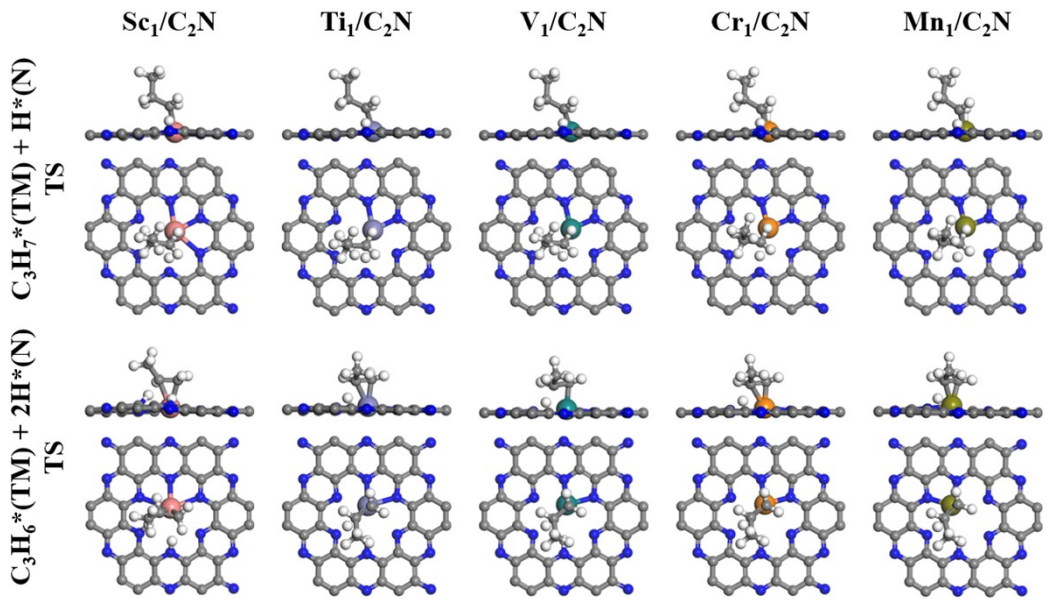

Fig. S3 Transition states of the first and second dehydrogenations of propane on TM_1/C_2N.

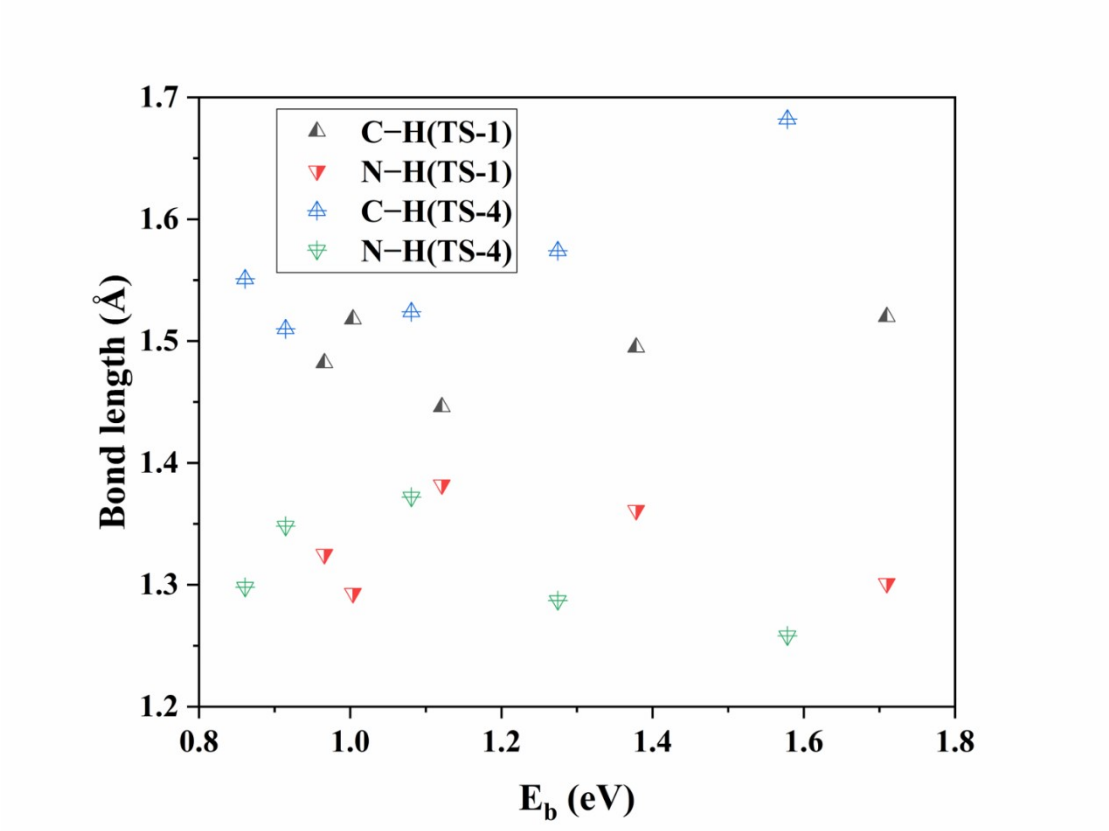

Fig. S4 Correspondence between the energy barrier and bond length of TS-1 and TS-4 on TM_1/C_2N.

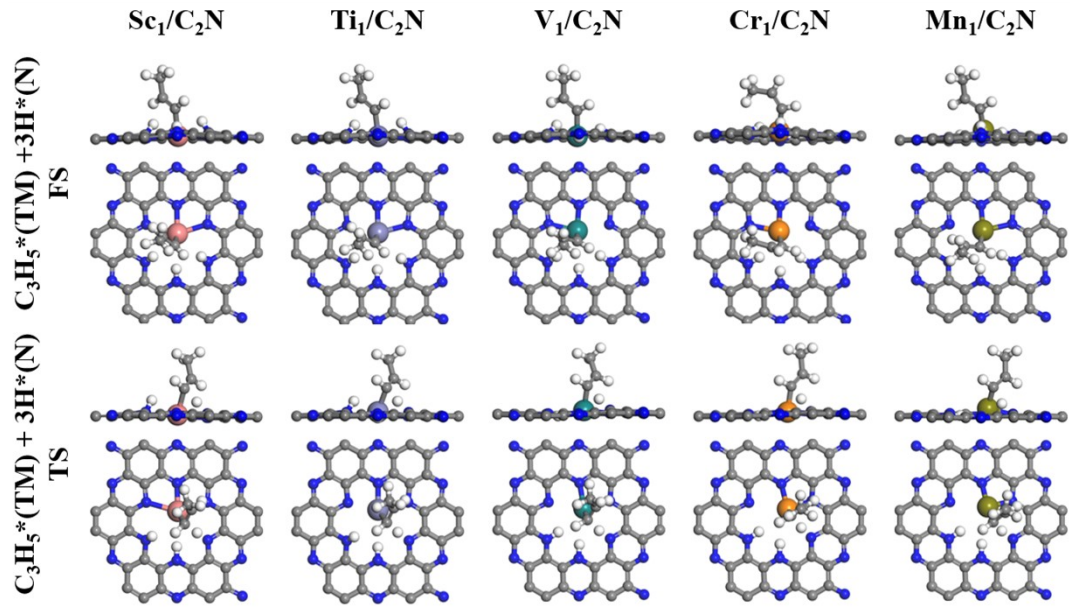

Fig. S5 Final states and transition states of propylene dehydrogenation on TM_1/C_2N.

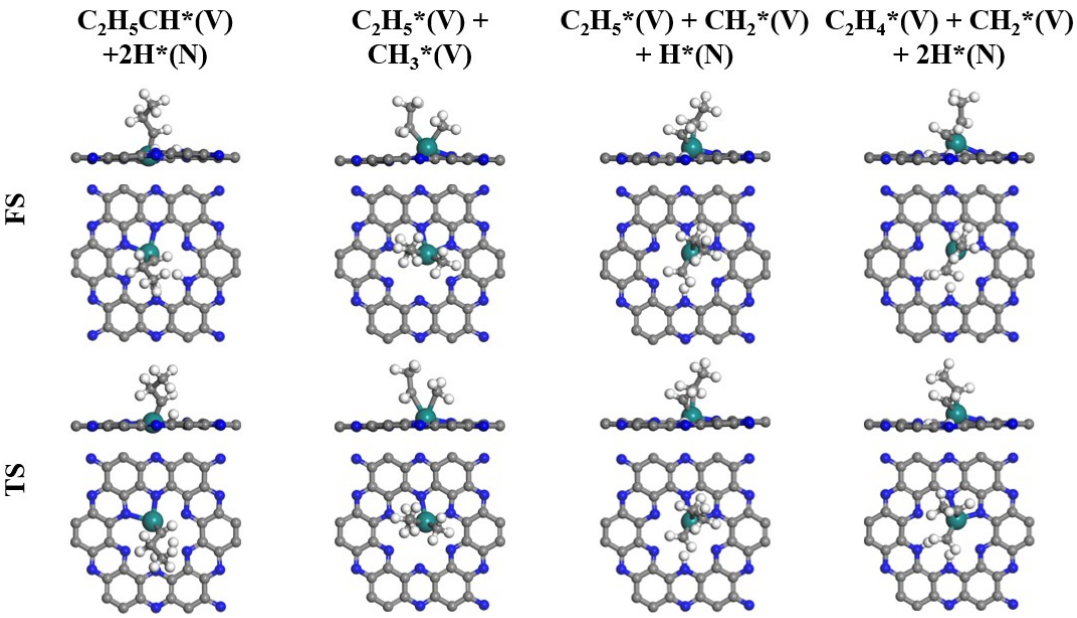

Fig. S6 Final states and transition states of over-dehydrogenation and C−C bond cracking of C3 species on V_1/C_2N.