Design of MoS₂ Edge-Anchored Single-Atom Catalysts for Propane Dehydrogenation Driven by DFT and Microkinetic Model

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Table S1. Converge Test of k-points sampling using Sc_1-S_4/edge as an example

k-mesh	E /eV
1×2×1	−257.42
1×3×1	−257.44
1×4×1	−257.43
1×5×1	−257.44
1×10×1	−257.44
1×20×1	−257.44

Table S2. The values of $U - J$ parameters for DFT/PBE+U calculations

3d element	$U - J$ /eV
Sc	2.11
Ti	2.58
V	2.72
Cr	2.79
Mn	3.06
Fe	3.29
Co	3.42
Ni	3.40

Supplementary Note 1

The anchoring site on the basal plane of MoS_2 is the hollow site coordinated by three S atoms. These hollow sites can be divided in two categories according to their geometry, known as the hollow-1 and hollow-2, respectively (Fig. S1a). In top view, hollow-1 site is positioned at the center of three adjacent Mo atoms, whereas the hollow-2 site is located directly above the Mo atom. The cohesive energies of each TM elements were adopted from experimental data.[1]
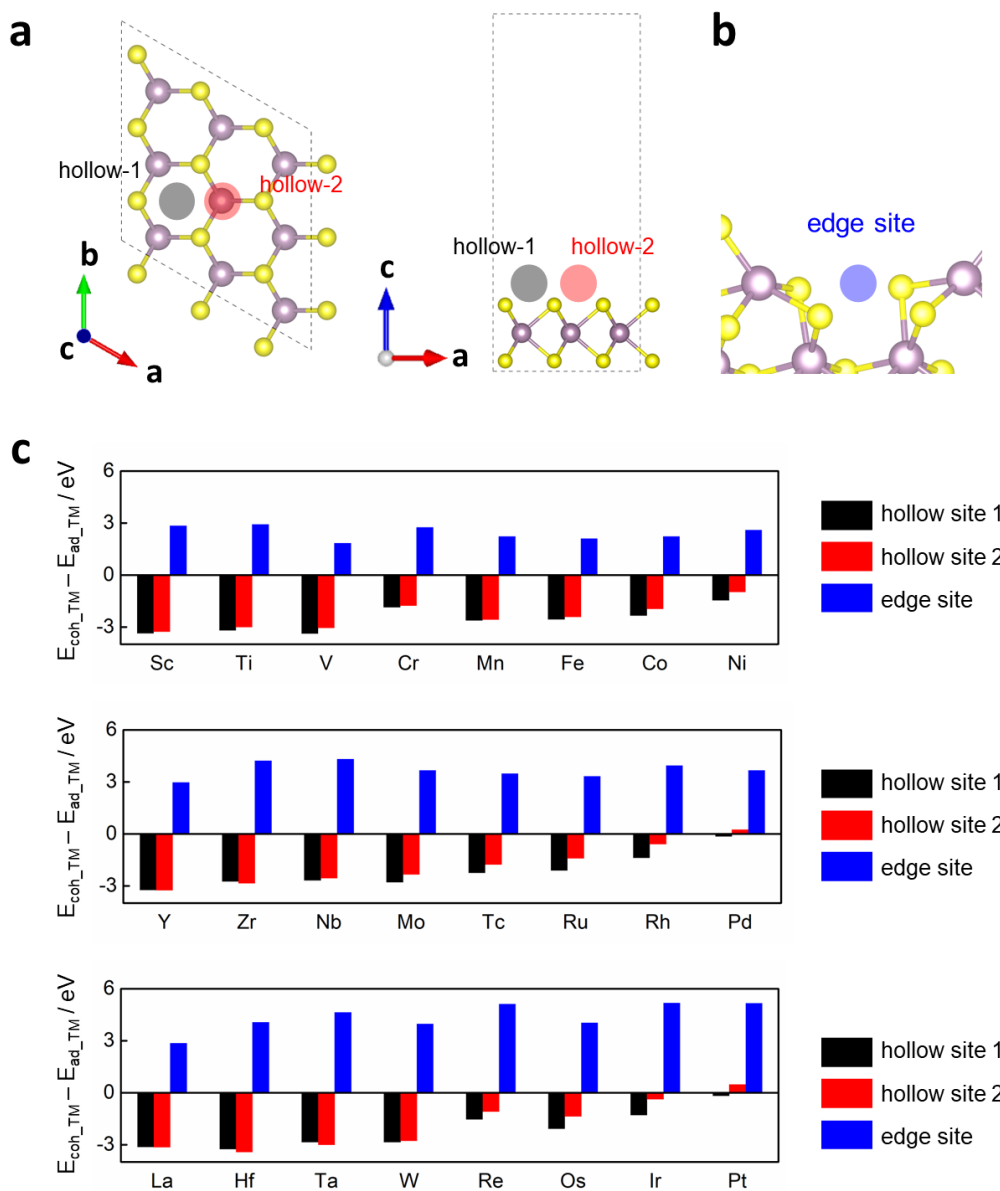
Fig. S1. Illustration of the structural configuration for hollow site (a) and edge site (b). (c) Thermodynamic stability ($E_{coh\_TM} - E_{ad\_TM}$) of the transition metal anchored on the basal plane and edge of the monolayer MoS_2, where the cohesive energies E_{coh_TM} are obtained from experimental data.[1]
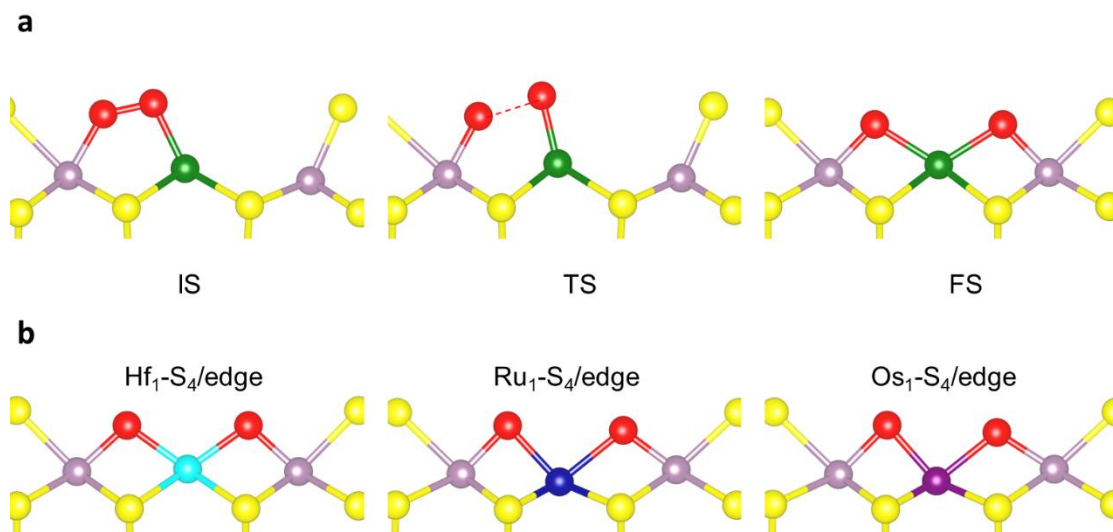
Fig. S2. (a) Structures of the initial state, transition state, and final state of the dissociative adsorption of an O_2 molecule on the TM_1-S_4/edge (using Sc_1-S_4/edge catalyst as an example). (b) Final states of dissociative adsorption of an O_2 molecule on the TM_1-S_4/edge (TM=Hf, Ru, Os) catalysts.

Table S3. Energy barriers (E_a), enthalpy changes (ΔH), entropy-corrected energy barriers (G_a) and Gibbs energy changes (ΔG) of each elementary step for the PDH reaction on the Sc_1-S_4/edge catalyst. (unit: eV)

Elementary reactions	E_a	ΔH	G_a	ΔG
C_3H_8 + * → [$C_3H_7\_H$]*	2.04	1.83	3.42	3.21
[$C_3H_7\_H$]* → [C_3H_6]* + H_2	0.48	−1.47	0.48	−2.81
[$MoH\_SH\_C_3H_6$]* → [C_3H_6]* + H_2	0.36	−0.19	0.36	−1.53
C_3H_8 + * → [$MoH\_C_3H_7$]*	0.76	0.59	2.14	1.97
[$MoH\_C_3H_7$]* → [$MoH\_SH\_C_3H_6$]*	0.62	−0.03	0.62	−0.03
[$MoH\_C_3H_7$]* → [$2MoH\_C_3H_6$]*	0.71	−0.32	0.71	−0.32
[$C_3H_7\_H$]* → [$MoH\_C_3H_7$]*	0.10	−1.24	0.10	−1.24
[MoH_SH]* → * + H_2	0.36	0.04	0.36	−0.67
[C_3H_6]* → * + C_3H_6	1.22	1.22	0.03	−0.09
[$MoH\_SH\_C_3H_6$]* → [MoH_SH]* + C_3H_6	1.00	1.00	0	−0.94
[$2MoH\_C_3H_6$]* → [$2MoH$]* + C_3H_6	0.88	0.88	0	−1.06
[$2MoH$]* → * + H_2	0.44	0.44	0	−0.27

Table S4. Key kinetic data for PDH reaction on Sc_1-S_4/edge catalyst along all pathways: the reaction rates, reversibilities and degree of rate control for each elementary step.

Elementary reactions	Reaction rate	Reversibility	Degree of rate control
C_3H_8 + * → [$C_3H_7\_H$]*	3.62×10^{-9}	3.94×10^{-7}	1.43×10^{-9}
[$C_3H_7\_H$]* → [C_3H_6]* + H_2	1.21×10^{-8}	5.08×10^{-7}	5.20×10^{-7}
[$MoH\_SH\_C_3H_6$]* → [C_3H_6]* + H_2	1.68×10^{-4}	2.53×10^{-3}	1.64×10^{-6}
C_3H_8 + * → [$MoH\_C_3H_7$]*	2.31×10^{-2}	9.96×10^{-1}	3.95×10^{-3}
[$MoH\_C_3H_7$]* → [$MoH\_SH\_C_3H_6$]*	1.76×10^{-2}	2.28×10^{-4}	7.58×10^{-1}
[$MoH\_C_3H_7$]* → [$2MoH\_C_3H_6$]*	5.51×10^{-3}	2.25×10^{-6}	2.38×10^{-1}
[$C_3H_7\_H$]* → [$MoH\_C_3H_7$]*	-8.48×10^{-9}	1.00	1.90×10^{-9}
[MoH_SH]* → * + H_2	1.74×10^{-2}	1.00	5.01×10^{-12}
[C_3H_6]* → * + C_3H_6	1.68×10^{-4}	1.00	8.95×10^{-18}
[$MoH\_SH\_C_3H_6$]* → [MoH_SH]* + C_3H_6	1.74×10^{-2}	2.70×10^{-3}	1.74×10^{-4}
[$2MoH\_C_3H_6$]* → [$2MoH$]* + C_3H_6	5.51×10^{-3}	2.40×10^{-1}	4.06×10^{-7}
[$2MoH$]* → * + H_2	5.51×10^{-3}	1.00	3.18×10^{-6}

Table S5. Coverages of all intermediates on Sc_1-S_4/edge catalyst at the steady state.

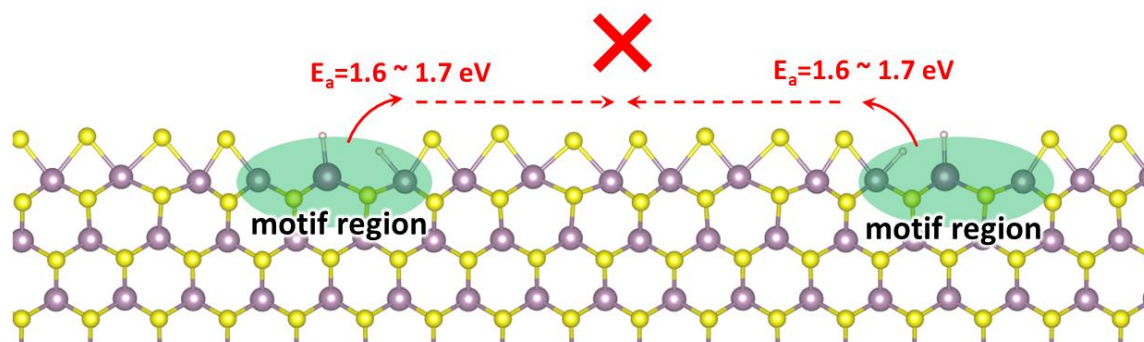| species	coverage
[C_3H_6]*	1.71×10^{-5}
[$C_3H_7\_H$]*	3.15×10^{-19}
[$MoH\_C_3H_7$]*	2.78×10^{-12}
[MoH_SH]*	9.03×10^{-9}
[$MoH\_SH\_C_3H_6$]*	9.31×10^{-16}
[$2MoH$]*	1.57×10^{-6}
[$2MoH\_C_3H_6$]*	3.87×10^{-16}
*	1.00

Fig. S3. Energy barriers of the H atom escaped from the motif region (using Sc_1-S_4/edge catalyst as an example).

Table S6. Energy barriers and enthalpy changes of each elementary reaction step along path 2 on six TM_1-S_4/edge. (unit: eV) The subscript i (i = 1-4) represents the process of the abstraction of α-H, the abstraction of β-H, the desorption of the propylene, and the formation of H_2, respectively.

TM_1-S_4/edge	E_{a1}	ΔH_1	E_{a2}	ΔH_2	ΔH_3	ΔH_4
Sc	0.76	0.59	0.62	-0.03	1.00	0.04
Ru	0	-0.09	0.71	0.38	1.04	0.26
Rh	0.56	0.56	0.99	0.51	0.87	-0.35
Os	0	-0.43	0.98	0.13	1.30	0.59
Ir	0.14	0.38	0.93	0.59	0.48	0.14
Pt	1.63	0.64	0.79	0.86	1.01	-0.92

Table S7. Key kinetic data for PDH reaction on TM_1-S_4/edge (TM= Pt, Rh, Ir, Os, Ru) catalysts along the dominant pathways: the energy barriers of the two dehydrogenation steps, the TOF, the energy barrier of first dehydrogenation process on TM_1'-S_4/edge catalysts (E_a'), and the corrected TOF (TOF') on TM_1'-S_4/edge (TM= Rh, Ir, Os, Ru). Note that DHS represents "dehydrogenation step".

	Pt_1-S_4/edge	Rh_1-S_4/edge	Ir_1-S_4/edge	Os_1-S_4/edge	Ru_1-S_4/edge
E_a of 1st DHS/eV	1.63	0.56	0.14	0	0
E_a of 2nd DHS/eV	0.79	0.99	0.93	0.63	0.71
TOF/site^{-1} s^{-1}	6.22×10^{-5}	2.20×10^{-4}	4.80×10^{-3}	23.5	18.4
E_a' of 1st DHS/eV	\	0.84	0.05	0.90	1.06
TOF'/site^{-1} s^{-1}	\	1.05×10^{-2}	1.98×10^{-2}	2.52×10^{-2}	1.21×10^{-1}

Table S8. Enthalpy changes of six screened TM_1-S_4/edge catalysts between two different motif configuration states (ΔE = $E(TM_1$'-S_4/edge SACs) − $E(TM_1$-S_4/edge SACs)).

TM_1-S_4/edge	Sc	Pt	Rh	Ir	Os	Ru
ΔE /eV	0.32	0.72	0.30	0.11	−0.63	−0.11

Table S9. The Gibbs free energy change (ΔG) of the reaction between fluttered S atom and H_2 forming H_2S at 900 K. Note that the Gibbs free energies of H_2, and H_2S are taken from handbook.[2]

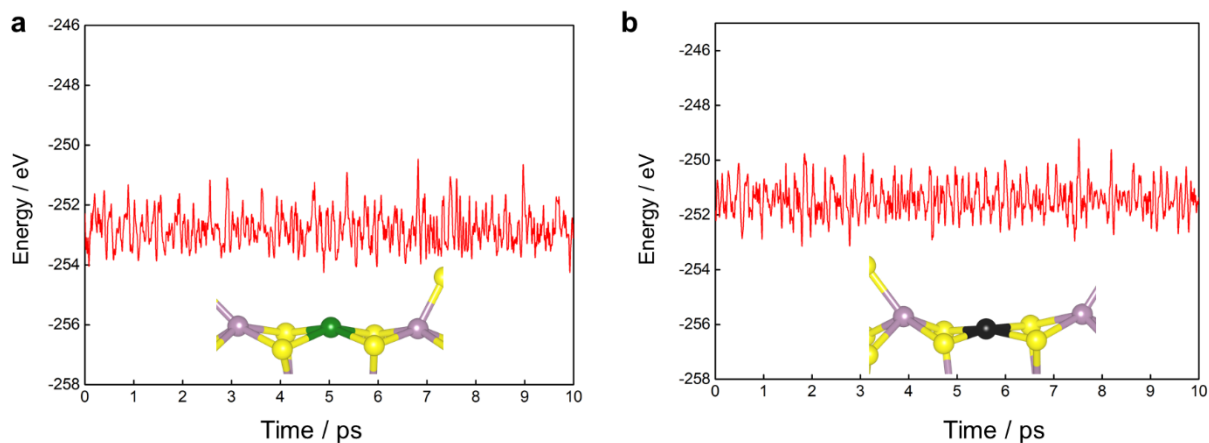| TM_1-S_4/edge	ΔG /eV
Ir	1.70
Rh	1.19
Os	2.14
Ru	1.71

Fig. S4. AIMD simulation of (a) Sc_1-S_4/edge and (b) Pt_1-S_4/edge catalysts at the temperature of 900 K.
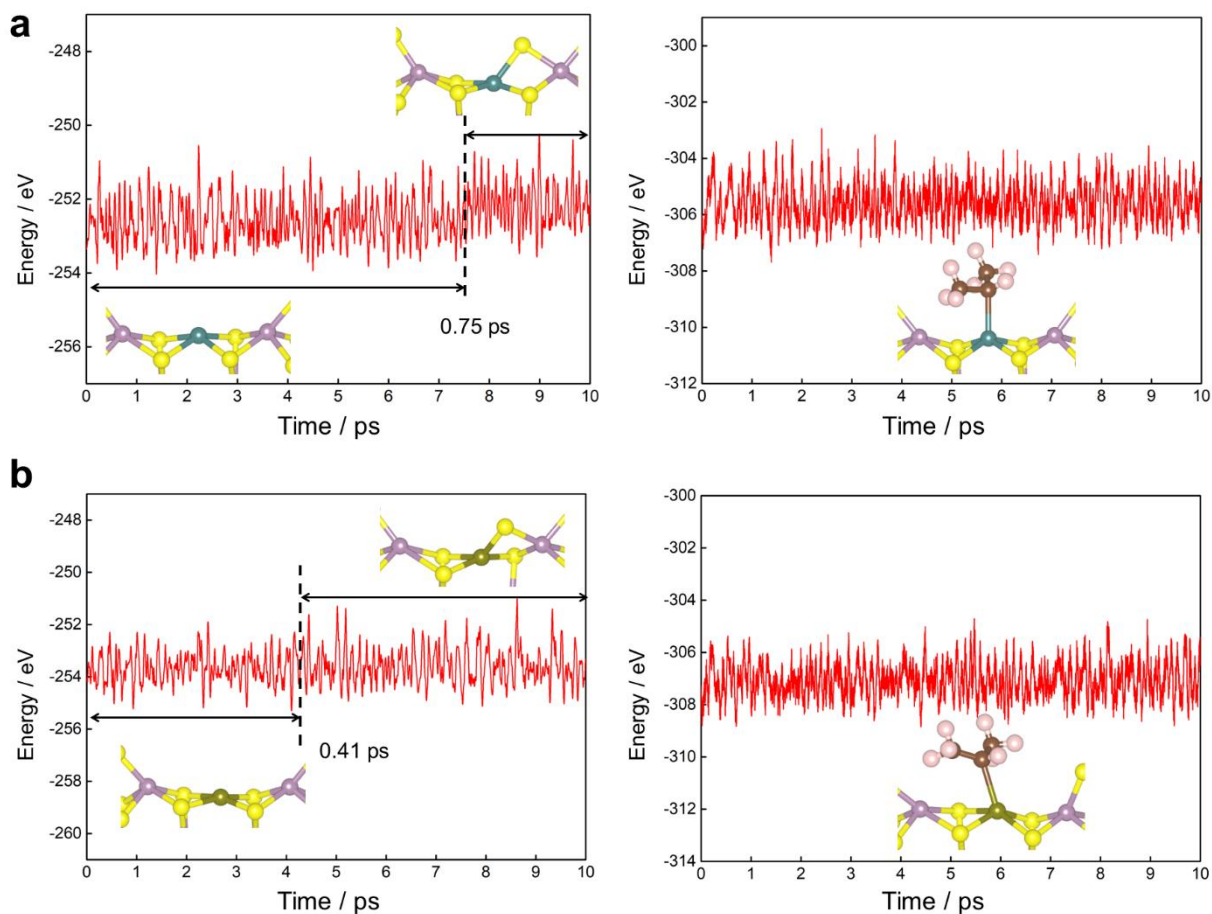

Fig. S5. AIMD simulations of (a) Rh_1-S_4/edge and (b) Ir_1-S_4/edge catalysts without or with a propyl adsorbed on the single atom at 900 K.
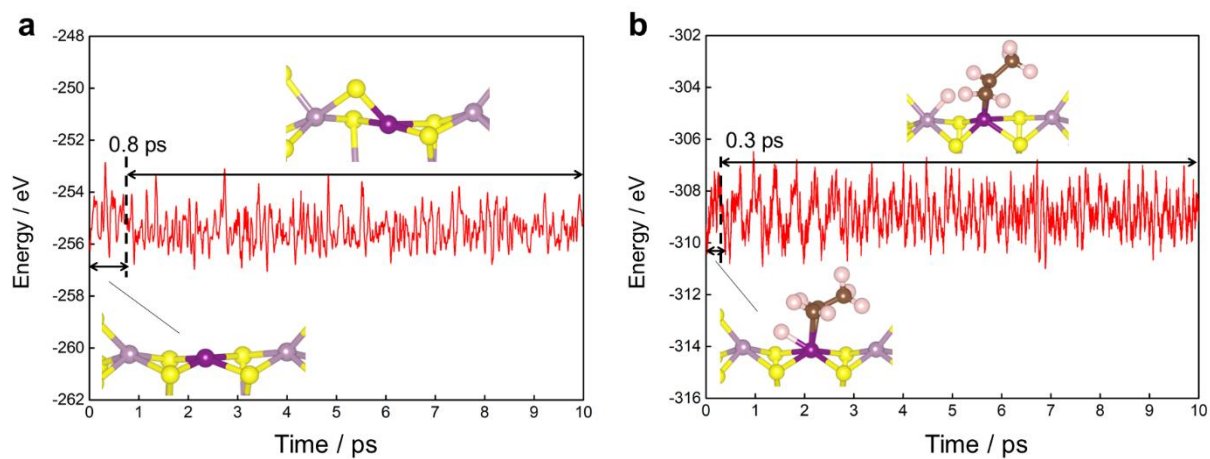
Fig. S6. AIMD simulations of Os_1-S_4/edge catalyst (a) without and (b) with a propyl adsorbed on the Os atom at 900 K.
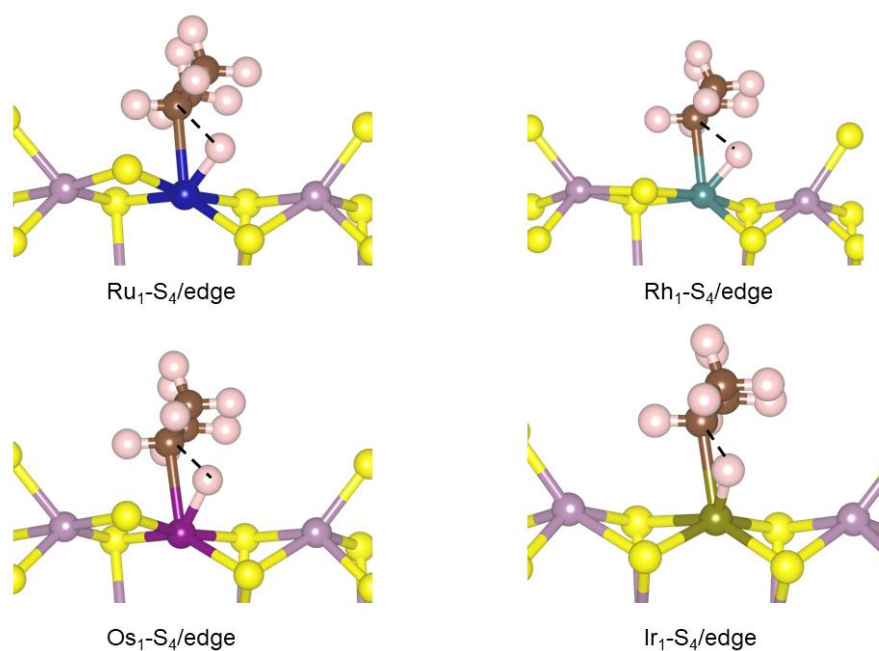

Fig. S7. Transition states of first dehydrogenation step on TM_1'-S_4/edge (TM = Ru, Rh, Os, Ir) catalysts. Note that at the transition state on Ir_1-S_4/edge catalyst, the two-coordinated S atom returns to its original position.
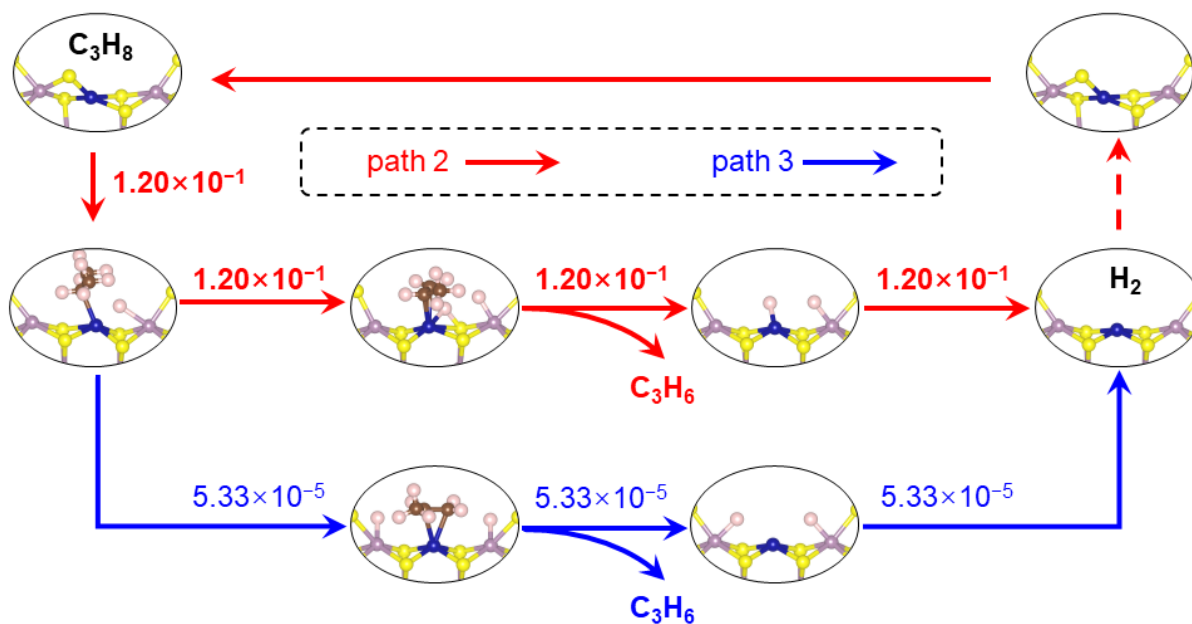
Fig. S8. PDH reaction network on the Ru_1'-S_4/edge catalyst and the TOF (s^{-1}) of each path at steady state. The reaction condition: T = 900 K, the initial partial pressures p_{C3H8} = 0.3 bar and $p_{C3H6} = p_{H2}$ = 0 bar.[3-6]

Table S10. Energy barriers and enthalpy changes of deep dehydrogenations of adsorbed propylene assisted by TM and the unsaturated Mo, respectively, on Ru_1-S_4/edge catalyst. (unit: eV)

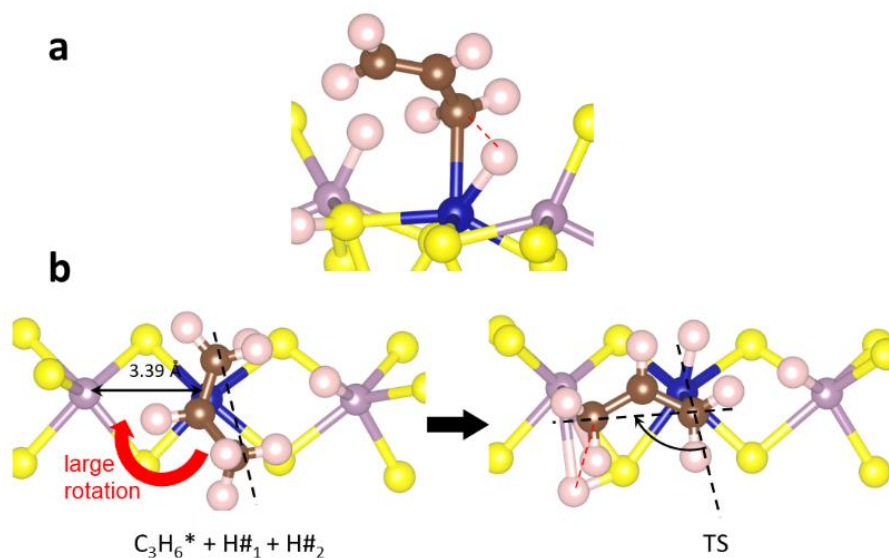|	Ru_1-S_4/edge catalyst
E_a (assisted by Mo)	1.38
ΔH (assisted by Mo)	1.38
E_a (assisted by TM)	1.19
ΔH (assisted by TM)	1.19

Fig. S9. (a) Transition state structures of the dehydrogenation of the methyl of the propylene on the Ru_1-

S_4/edge catalyst. (b) Initial and transition state structures of the dehydrogenation of the methyl assisted by the unsaturated Mo atom requiring a large angle of rotation for the adsorbed propylene on Ru_1-S_4/edge catalyst.

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