Oxidation of the hexagonal Mo_2C(101) Surface by H_2O dissociative adsorption

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Table S1. Dissociation barriers (E_a, eV) and reaction energies (E_r, eV) of $n$$H_2O$ and nOH on the Mo_2C(101) surface (the values without ZPE correction are given in square brackets for comparison)

	N	$nH_2O \rightarrow nOH + nH$	E_a	E_r	N	$nOH \rightarrow nO + nH$	E_a	E_r
$1H_2O$	1	$H_2O \rightarrow OH + H$	0.22	-0.96	2	$OH \rightarrow O + H$	0.74	-0.16
(1/8ML)			[0.39]	[-0.90]			[0.90]	[-0.09]
$O+H_2O$	3	$O+H_2O \rightarrow O + OH + H$	0.54	-0.57	5	$2OH(\text{Ⅰ}) \rightarrow OH + O + H$	0.79	0.02
			[0.71]	[-0.52]			[0.95]	[0.08]
	4	$O+H_2O \rightarrow 2OH$	0.15	-0.51	6	$OH + O \rightarrow 2O + H$	0.78	-0.19
			[0.26]	[-0.52]			[0.95]	[-0.12]
$2H_2O$	7	$2H_2O \rightarrow H_2O\text{--}OH + H$	-0.11	-0.94	9	$2OH(\text{Ⅱ}) \rightarrow OH + O + H$	0.78	-0.14
(1/4ML)			[0.05]	[-0.82]			[0.94]	[-0.08]
	8	$H_2O\text{--}OH \rightarrow 2OH + H$	0.59	-0.91	10	$OH + O \rightarrow 2O + H$	0.78	-0.19
			[0.74]	[-0.89]			[0.95]	[-0.12]
$3H_2O$	11	$3H_2O \rightarrow 2H_2O + OH + H$	-0.07	-1.07	14	$3OH \rightarrow 2OH + O + H$	0.83	0.06
(3/8ML)			[0.09]	[-1.02]			[0.98]	[0.13]
	12	$2H_2O + OH \rightarrow H_2O + 2OH$	0.45	-0.30	15	$2OH + O \rightarrow OH + 2O$	0.81	0.13
			[0.64]	[-0.21]			[0.97]	[0.20]
	13	$H_2O + 2OH \rightarrow 3OH + H$	0.58	-0.17	16	$OH + 2O \rightarrow 3O + H$	0.99	0.25
			[0.74]	[-0.09]			[1.15]	[0.32]
$4H_2O$	17	$4H_2O \rightarrow 3H_2O + OH + H$	0.00	-0.86	21	$4OH \rightarrow 3OH + O + H$	0.81	0.06
(1/2ML)			[0.15]	[-0.75]			[0.96]	[0.13]
	18	$3H_2O + OH \rightarrow 2H_2O + 2OH$	0.03	-0.77	22	$3OH + O \rightarrow 2OH + 2O + H$	0.87	0.17
			[0.19]	[-0.65]			[1.03]	[0.24]
	19	$2H_2O + 2OH \rightarrow H_2O + 3OH$	0.45	-0.29	23	$2OH + 2O \rightarrow OH + 3O + H$	1.05	0.42
			[0.58]	[-0.24]			[1.20]	[0.49]
	20	$H_2O + 3OH \rightarrow 4OH + H$	0.35	-0.41	24	$OH + 3O \rightarrow 4O + H$	1.08	0.46
			[0.51]	[-0.33]			[1.23]	[0.53]

N: the numbering of elementary reaction in this work.

Table S2. Stepwise adsorption energies (in eV) of OH and O at different coverage on the $Mo_2C(101)$ surface on the basis of H_2O dissociation and gaseous H_2 formation (the values without ZPE correction are given in square brackets for comparison)

θ	ΔE_{ads}(OH)	ΔE_{ads}(O)
1/8 ML	-1.10 [-1.05]	-0.69 [-0.47]
1/4 ML	-1.06 [-1.01]	-0.60 [-0.37]
3/8 ML	-0.92 [-0.86]	-0.26 [-0.04]
1/2 ML	-0.79 [-0.74]	-0.21 [0.01]
5/8 ML	-0.07 [0.00]	-0.04 [0.15]
3/4 ML	-0.05 [0.02]	0.09 [0.30]
7/8 ML	0.04 [0.08]	0.47 [0.70]
1 ML	0.43 [0.56]	0.24 [0.44]

Fig. S1. The detailed H-bonding arrangement on the Mo_2C(101) surface at different H_2O coverages

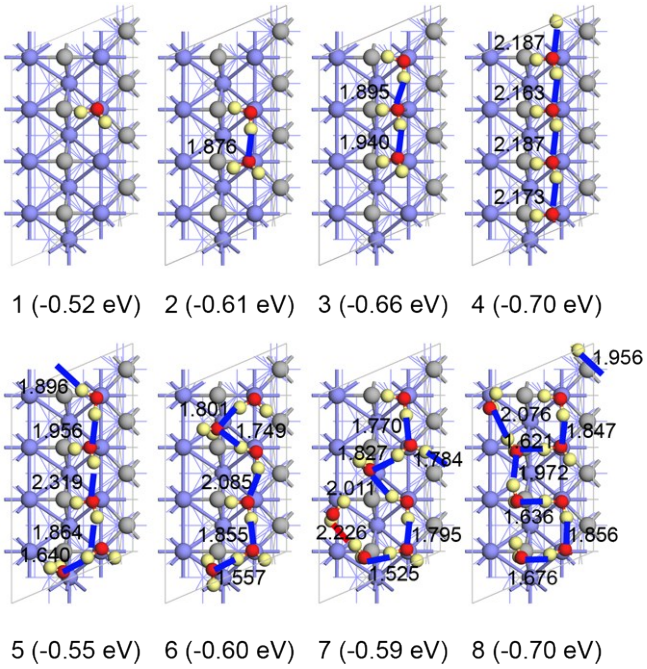

Fig. S2. Structures of initial state (IS), transition state (TS) and final state (FS) of H_2O dissociation on the Mo_2C (101) surface

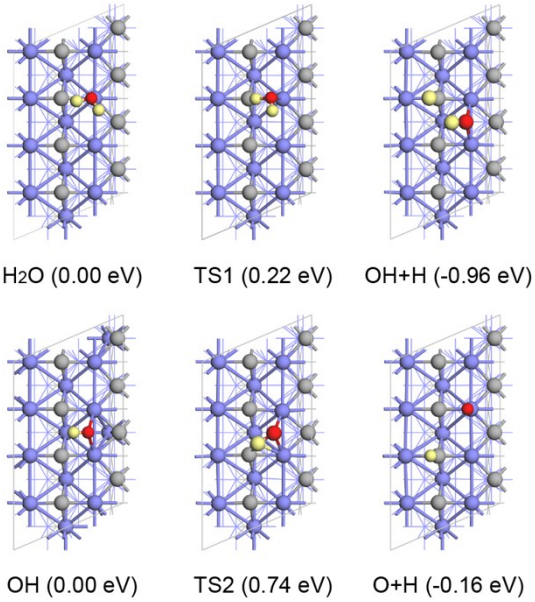

Fig. S3. Structures of initial state (IS), transition state (TS) and final state (FS) of O+H_2O dissociation on the Mo_2C (101) surface

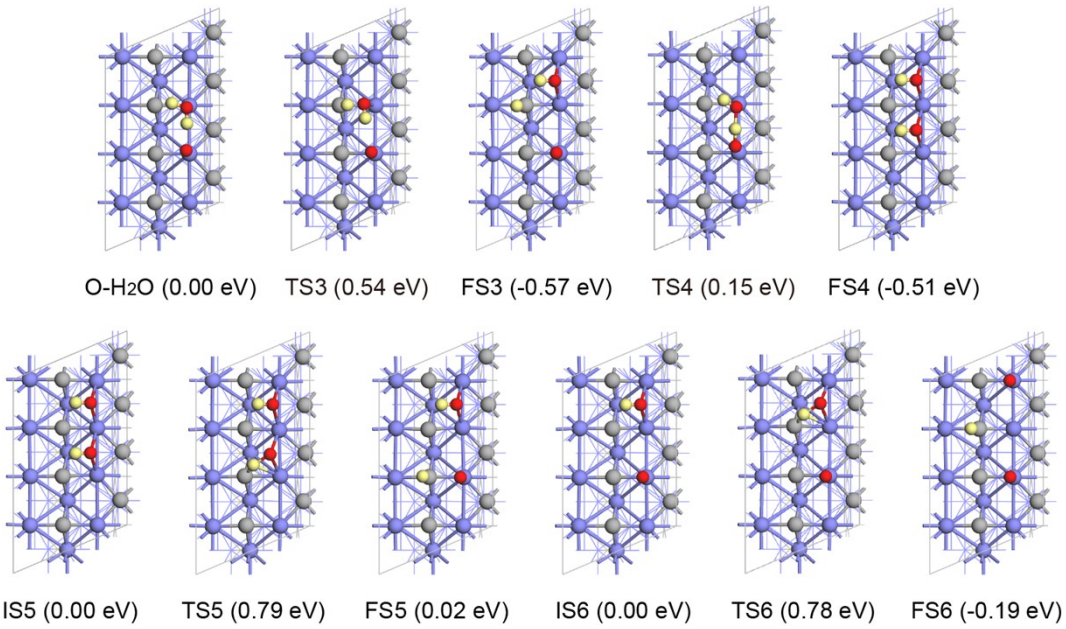

Fig. S4. Structures of initial state (IS), transition state (TS) and final state (FS) of 2H_2O dissociation on the Mo_2C (101) surface

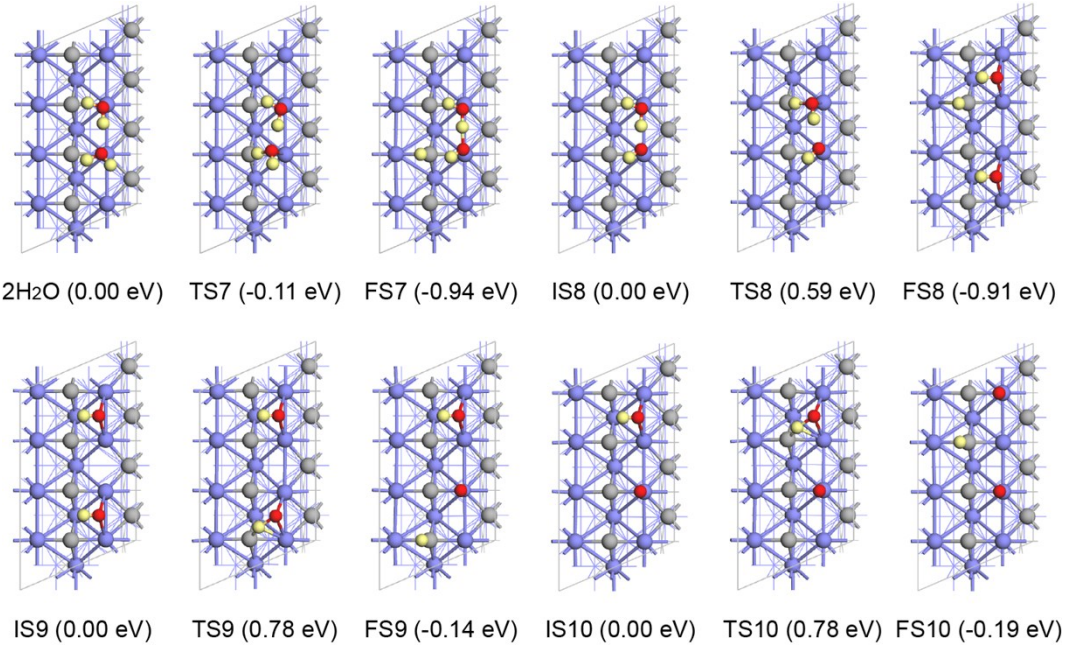

Fig. S5. Structures of initial state (IS), transition state (TS) and final state (FS) of $3H_2O$ dissociation on the Mo_2C (101) surface

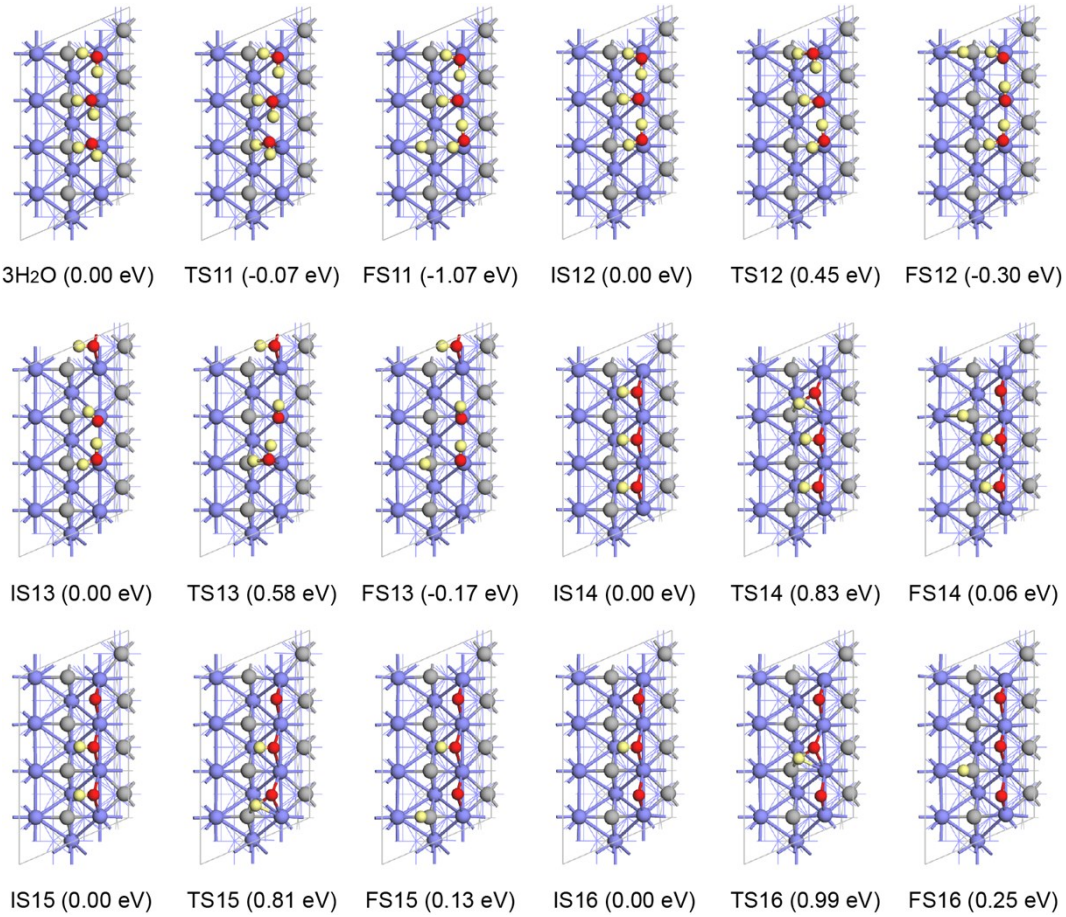

Fig. S6. Structures of initial state (IS), transition state (TS) and final state (FS) of $4H_2O$ dissociation on the Mo_2C (101) surface

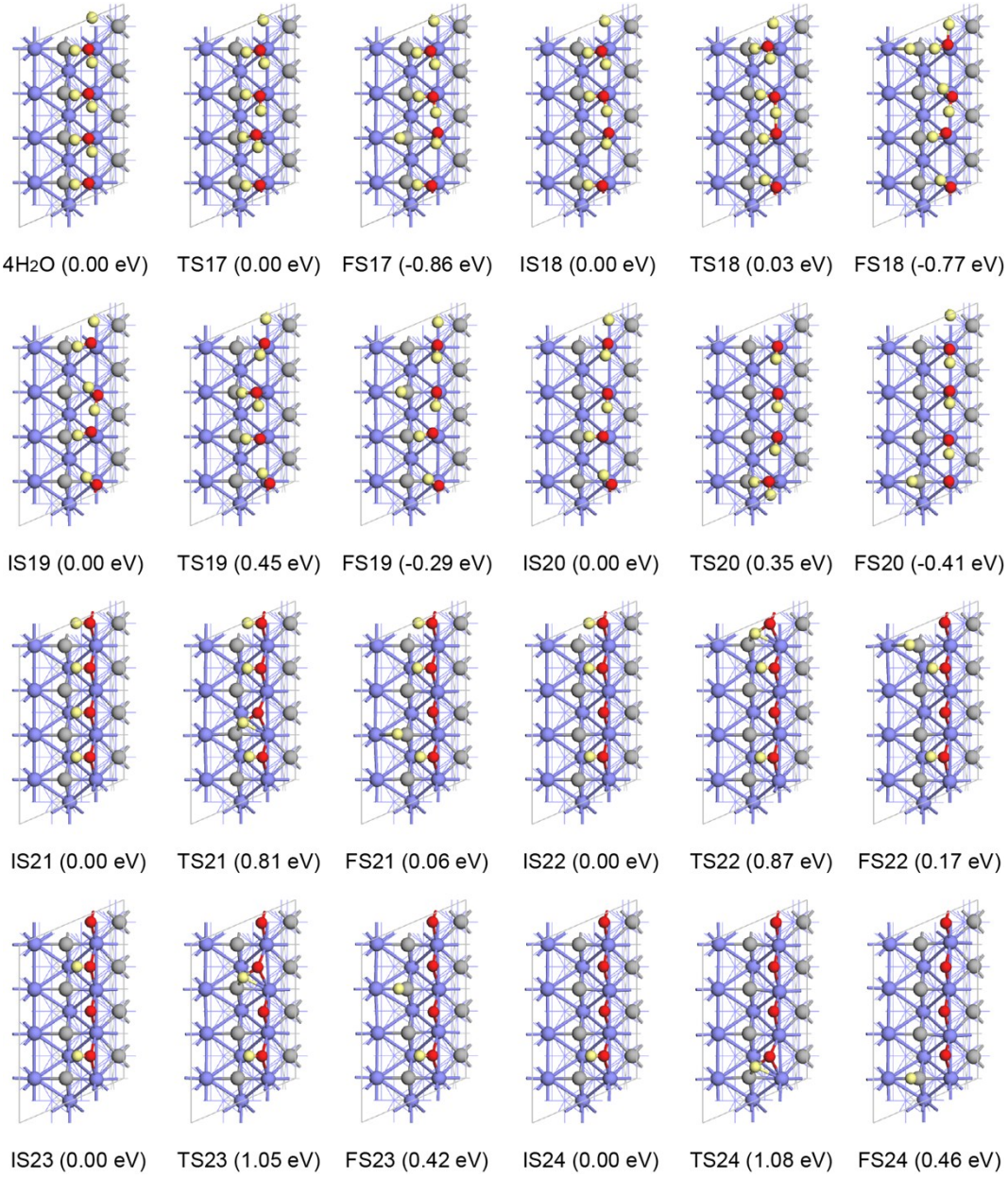

Fig. S7. Structures of initial state (IS), transition state (TS) and final state (FS) of $5H_2O$ dissociation on the Mo_2C (101) surface