Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Density functional theoretical study of the tungsten-doped In_2O_3 catalyst for CO_2 hydrogenation to methanol

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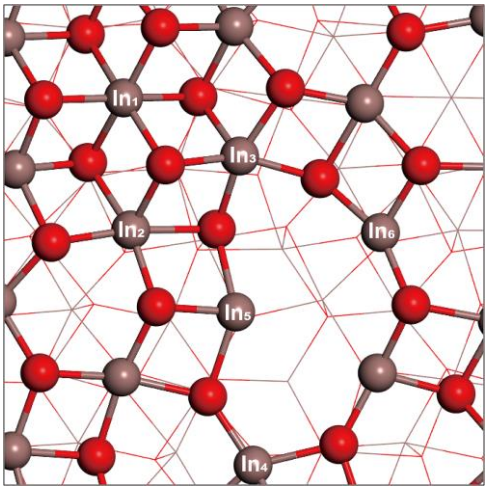


Fig. S1 The doping positions of W on the In_2O_3_D model. Red: O atoms; brown: In atoms.

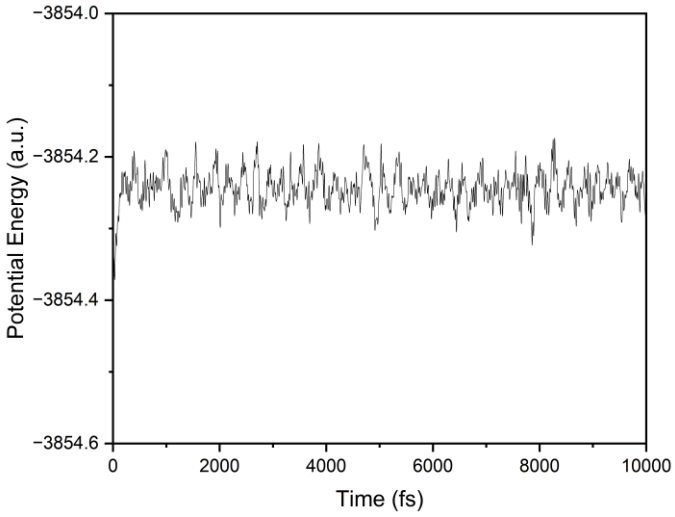


Fig. S2 The potential energy of the W-In_2O_3_D model during the AIMD simulation. The ab initio molecular dynamics (AIMD) simulation was carried out using the CP2K package with a cutoff of 350 Ry. The AIMD simulation was performed in the canonical (NVT) ensemble using Nosé-Hoover thermostats. The temperature was set as 573 K. The time step was set as 1 fs with a time period of 10 ps.

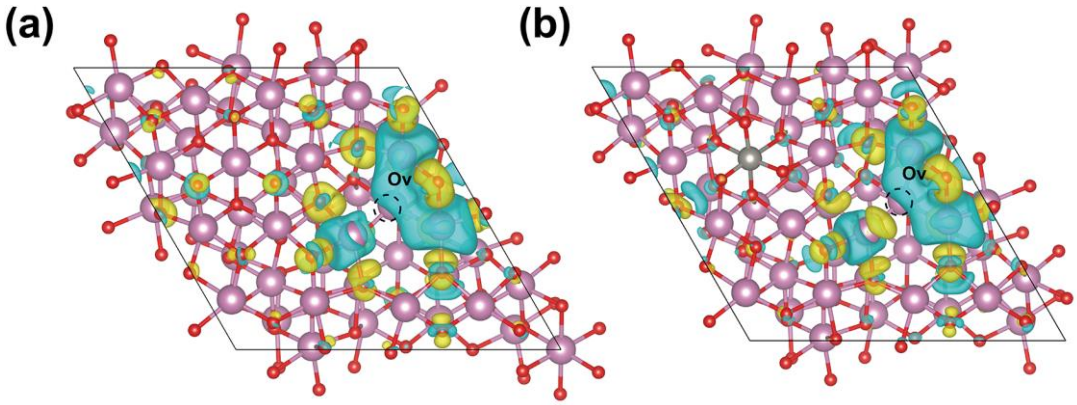


Fig. S3 Deformation charge density for (a) the In_2O_3_D model and (b) the W-In_2O_3_D model. Blue isosurfaces represent depleted electron density region, whereas yellow isosurfaces represent accumulated electron density region. The iso-surface value is 0.0025 |e|/bohr^3.

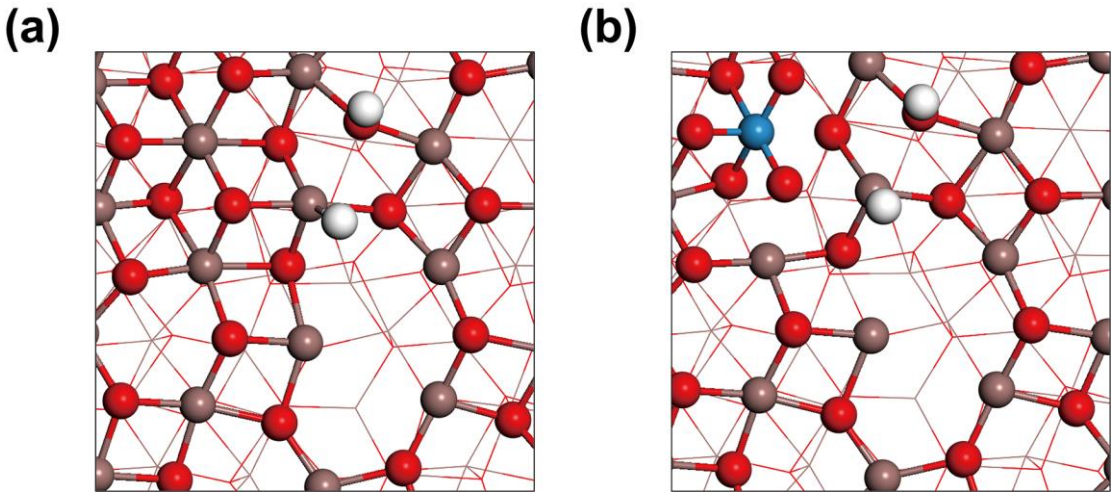


Fig. S4 The configuration of the H_2 dissociative adsorption on (a) the In_2O_3_D model and (b) the W-In_2O_3_D model. Red: O atoms; brown: In atoms; blue: W atom; white: H atoms.

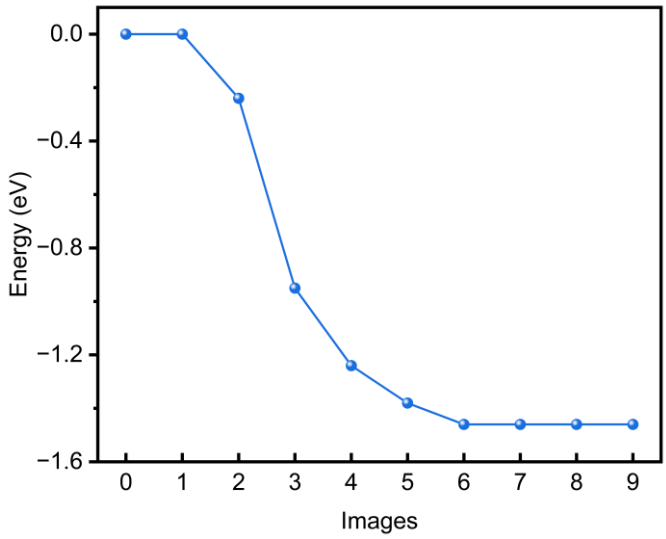
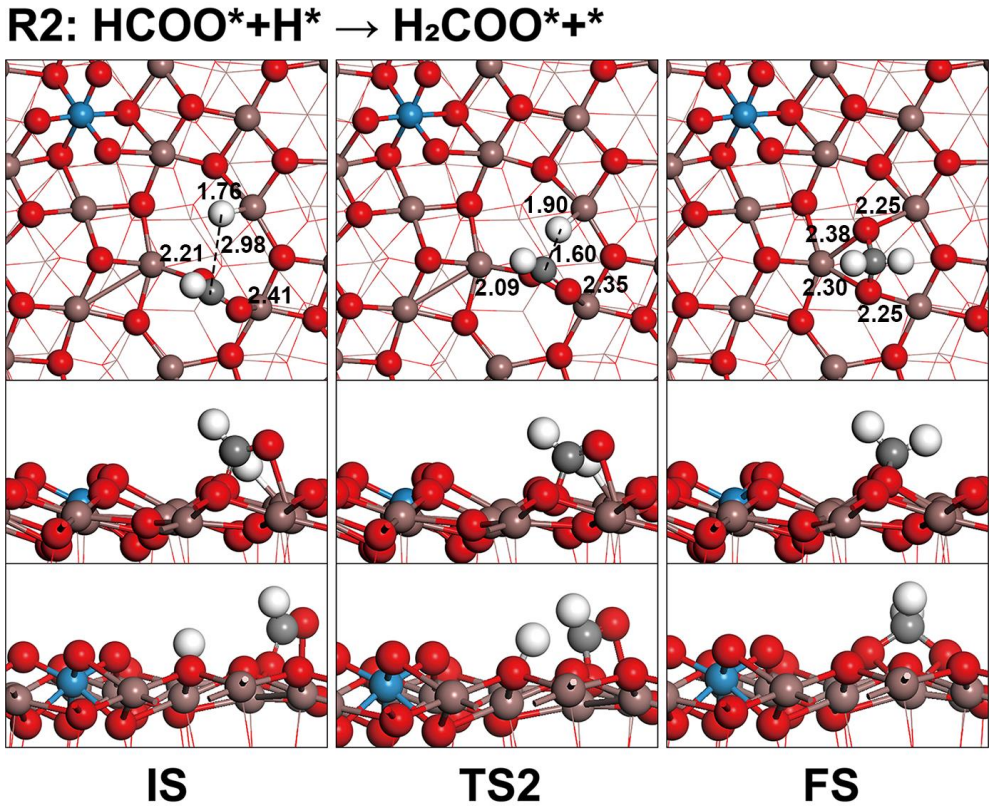
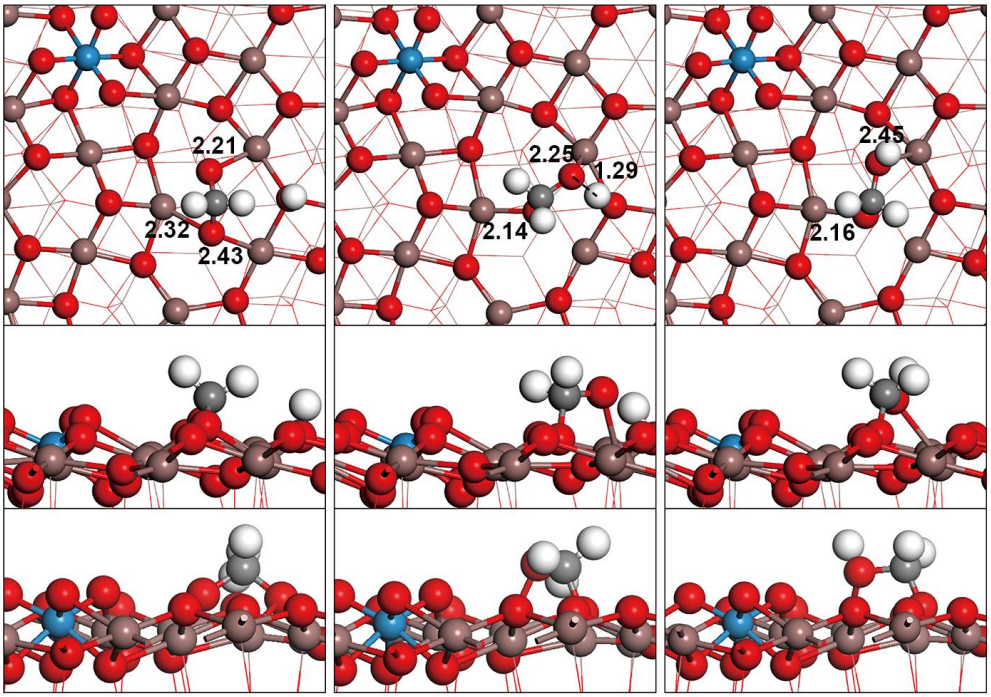


Fig. S5 NEB path for the conversion of CO_2* and H adatom to the HCOO intermediate on the W-In_2O_3_D model.

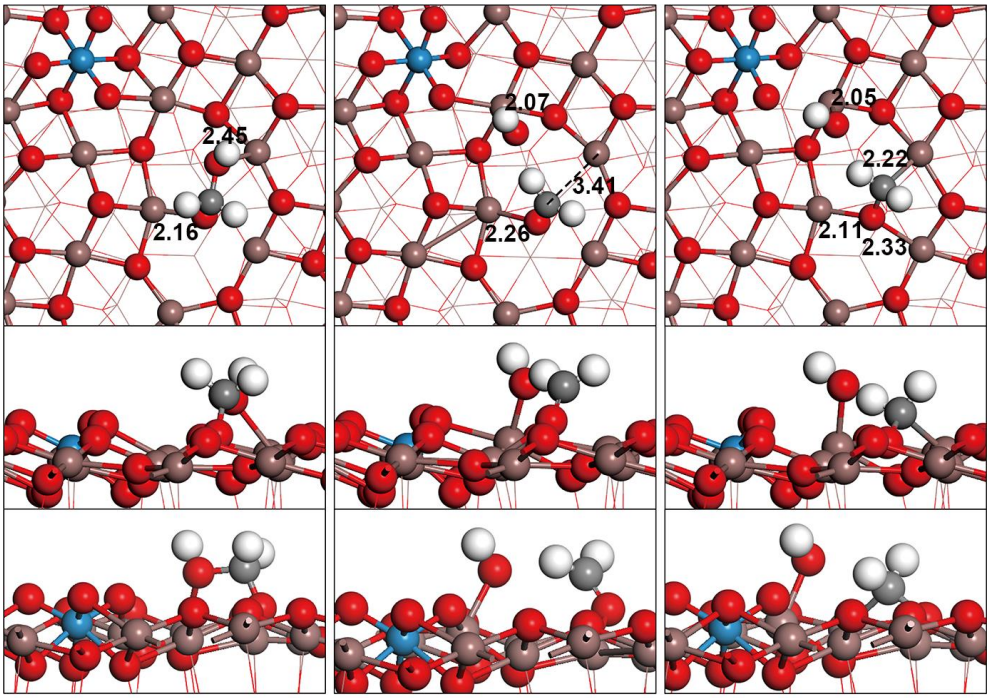


R3: $H_2COO^*+H^* \rightarrow H_2COOH^*+^*$



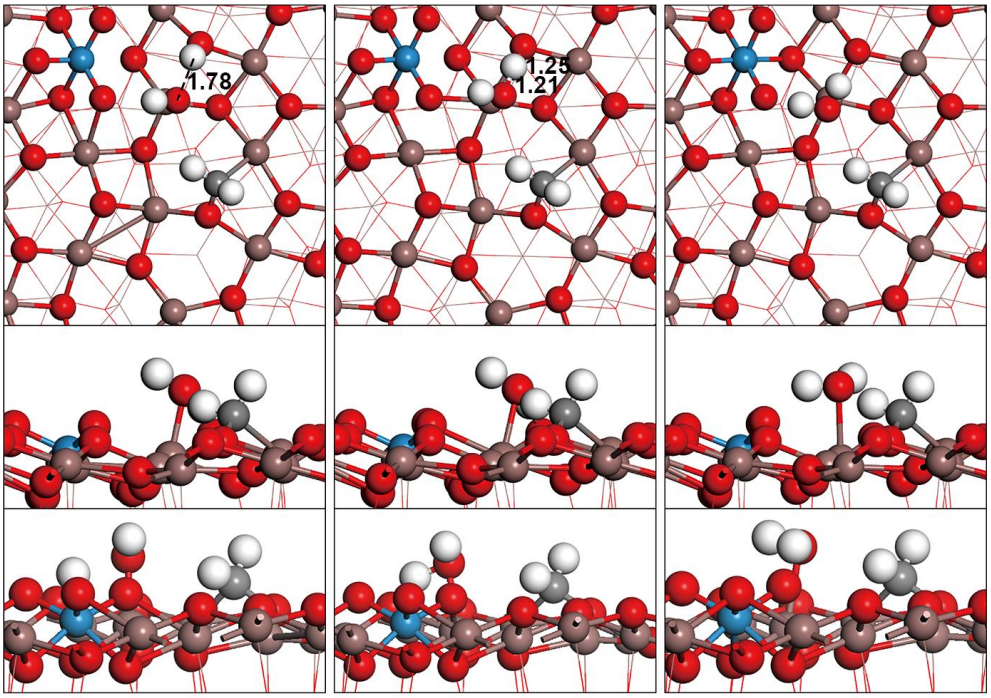
IS TS3 FS

R4: $H_2COOH^*+^* \rightarrow H_2CO^*+OH^*$



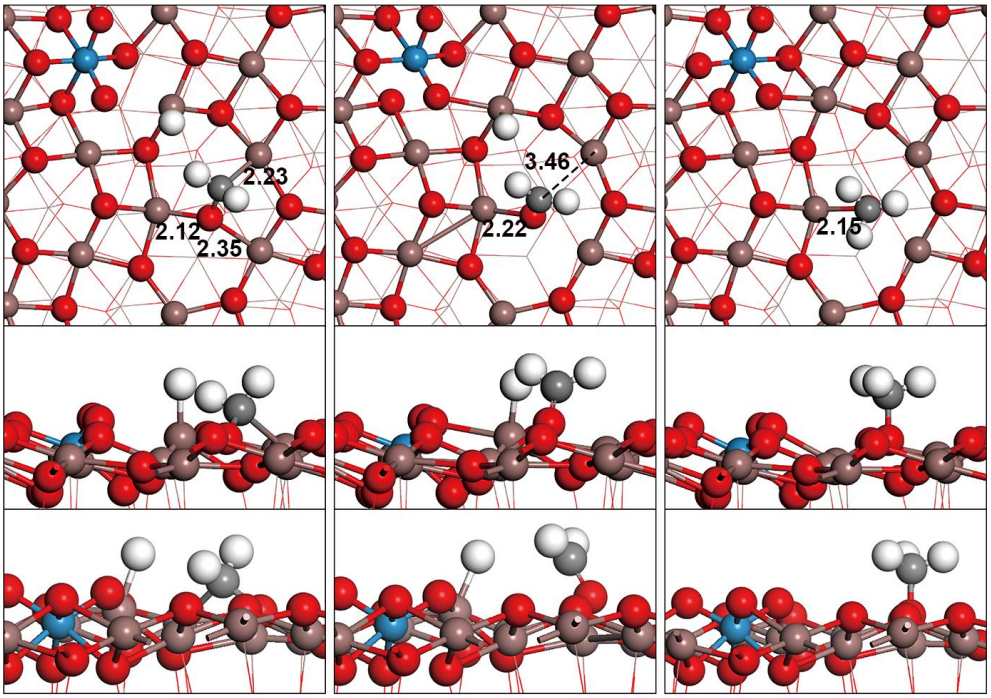
IS TS4 FS

R5: $H_2CO^*+OH^*+H^* \rightarrow H_2CO^*+H_2O^*+^*$



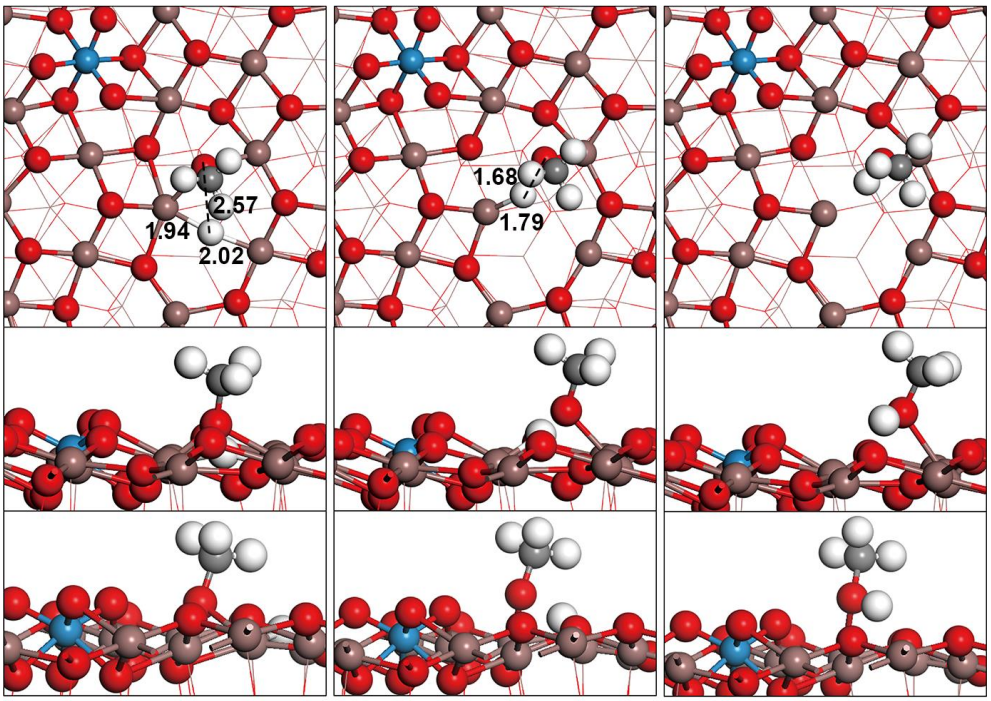
IS TS5 FS

R6: $H_2CO^*+H^* \rightarrow H_3CO^*+^*$



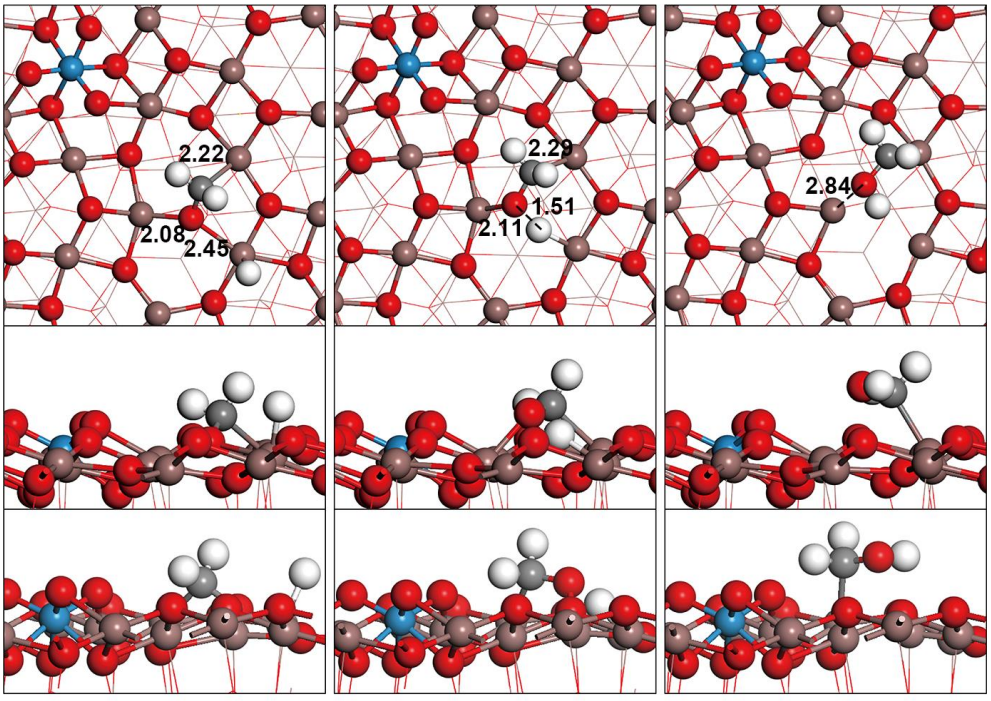
IS TS6 FS

R7: $H_3CO^* + H^* \rightarrow H_3COH^* + *$



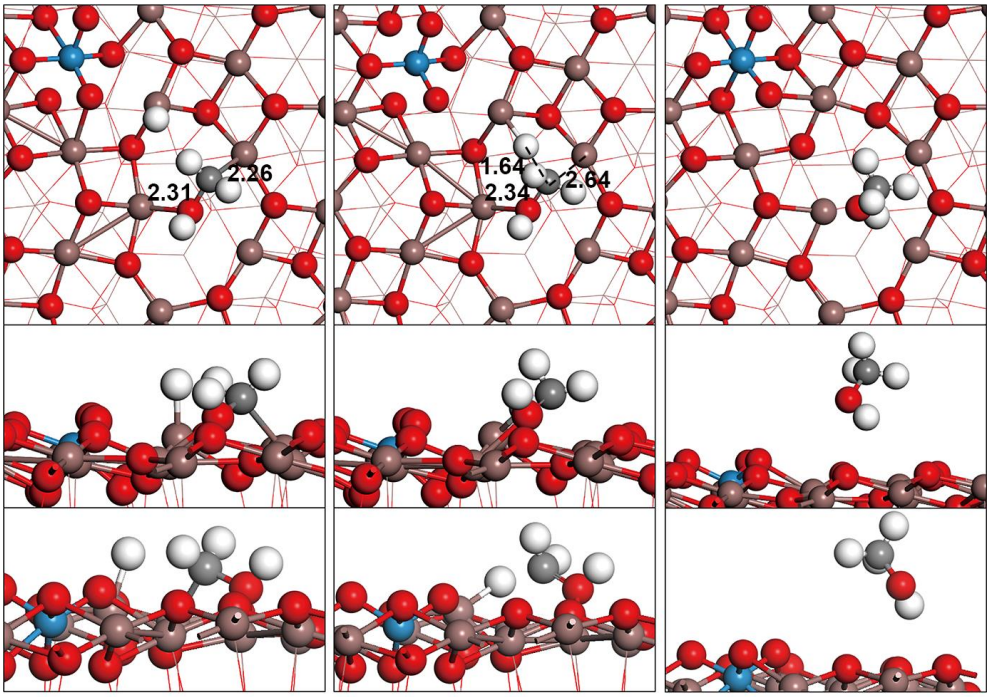
IS TS7 FS

R8: $H_2CO^* + H^* \rightarrow H_2COH^* + *$



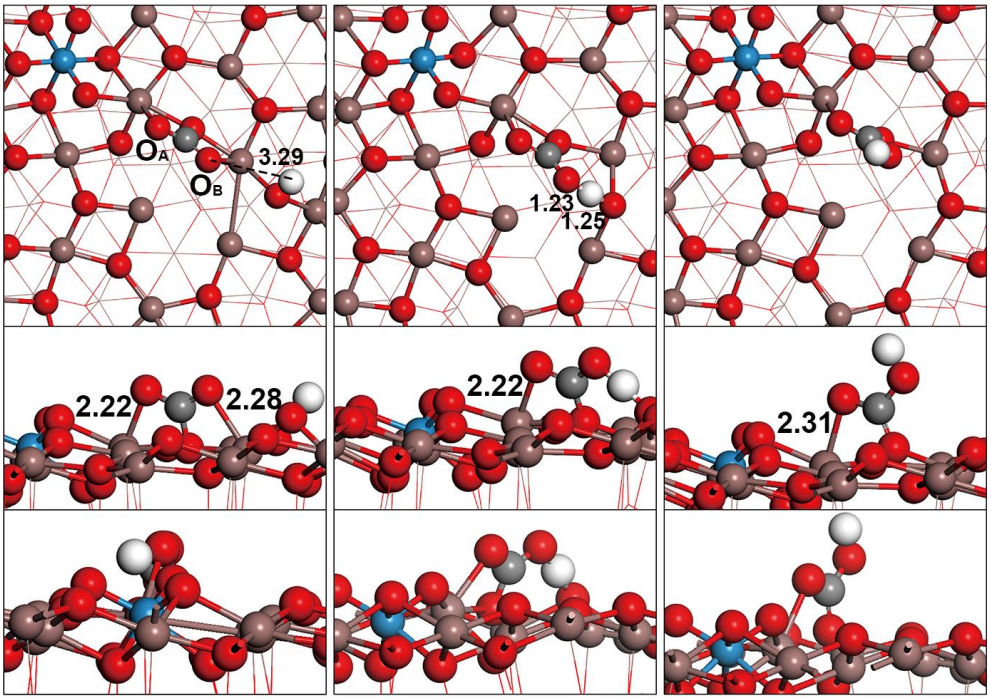
IS TS8 FS

R9: $H_2COH^*+H^* \rightarrow H_3COH(g)+^*+^*$



IS TS9 FS

R10: $CO_2^*+H^* \rightarrow COOH^*+^*$



IS TS10 FS

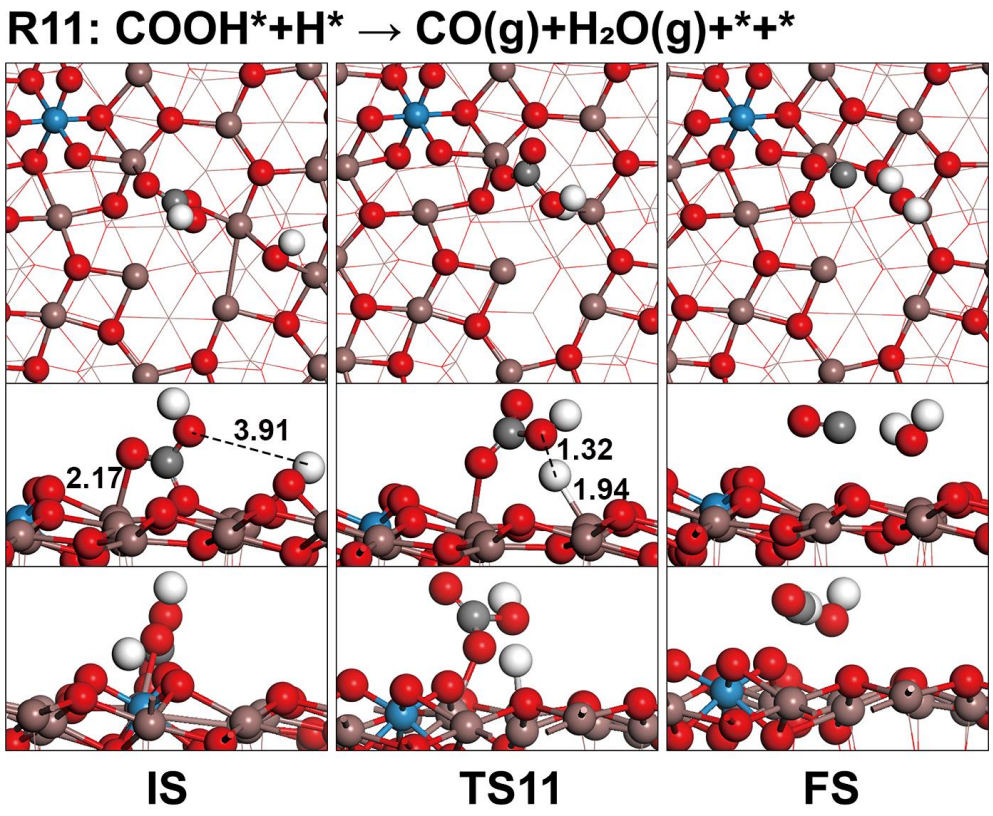
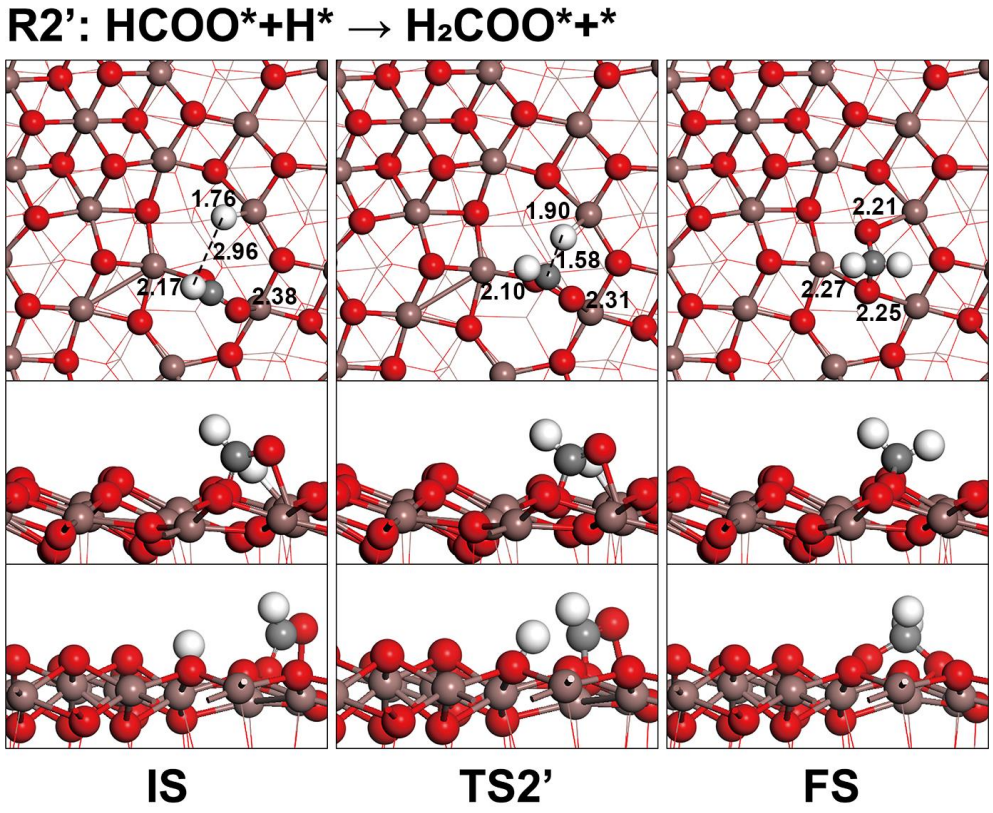
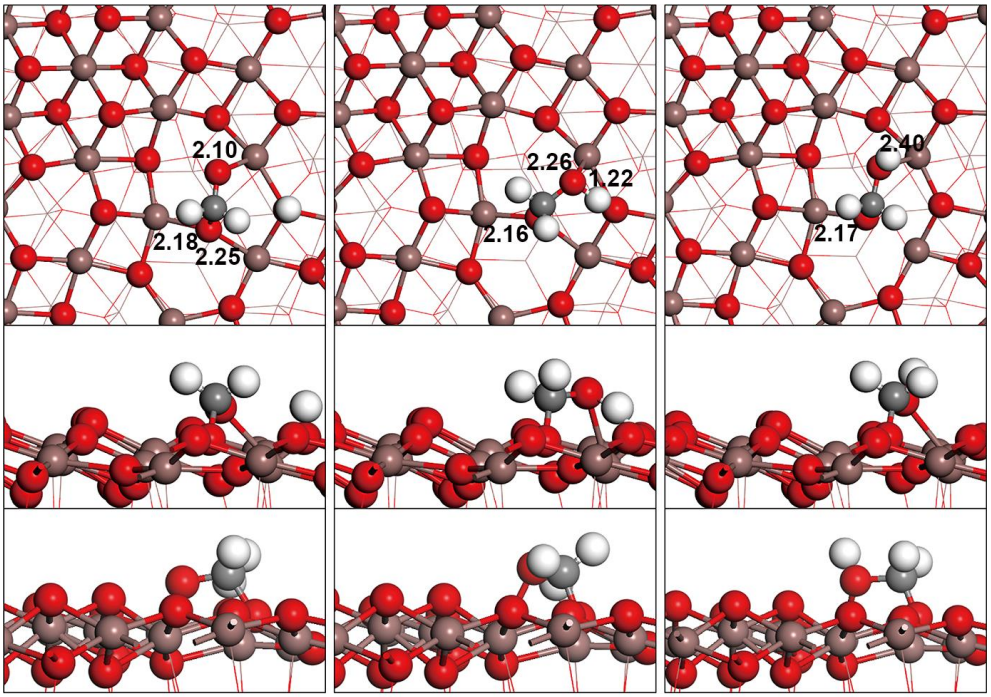


Fig. S6 The top and side views of all initial, transition, and final states for the methanol synthesis and RWGS reaction on the W-In_2O_3_D model. Red: O atoms; brown: In atoms; blue: W atom; gray: C atom; white: H atoms. The bond length is in angstroms.

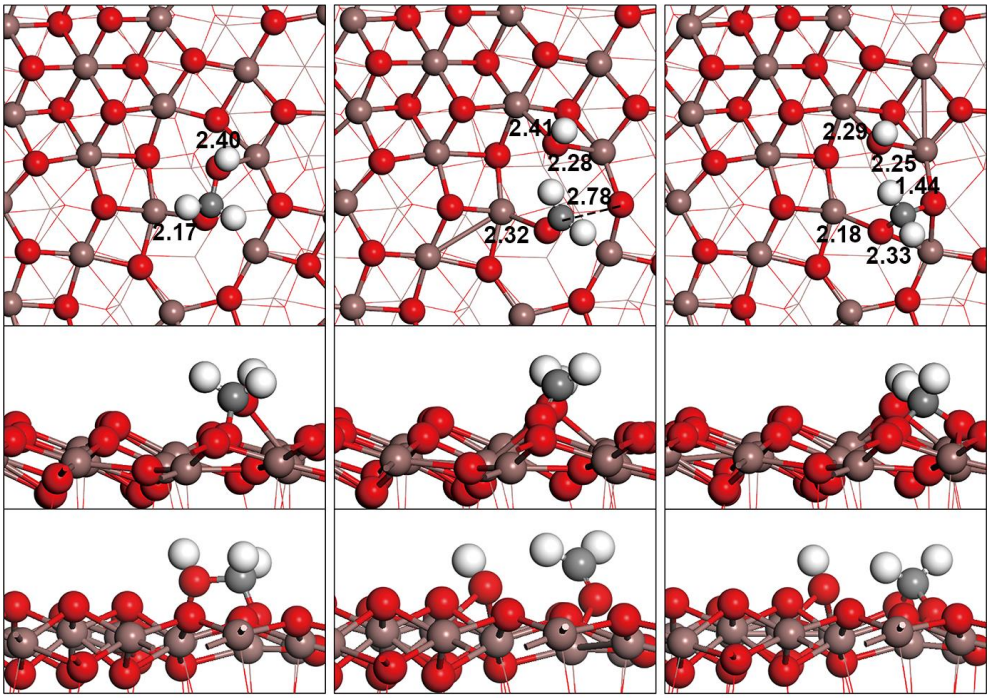


R3': $H_2COO^*+H^* \rightarrow H_2COOH^*+^*$



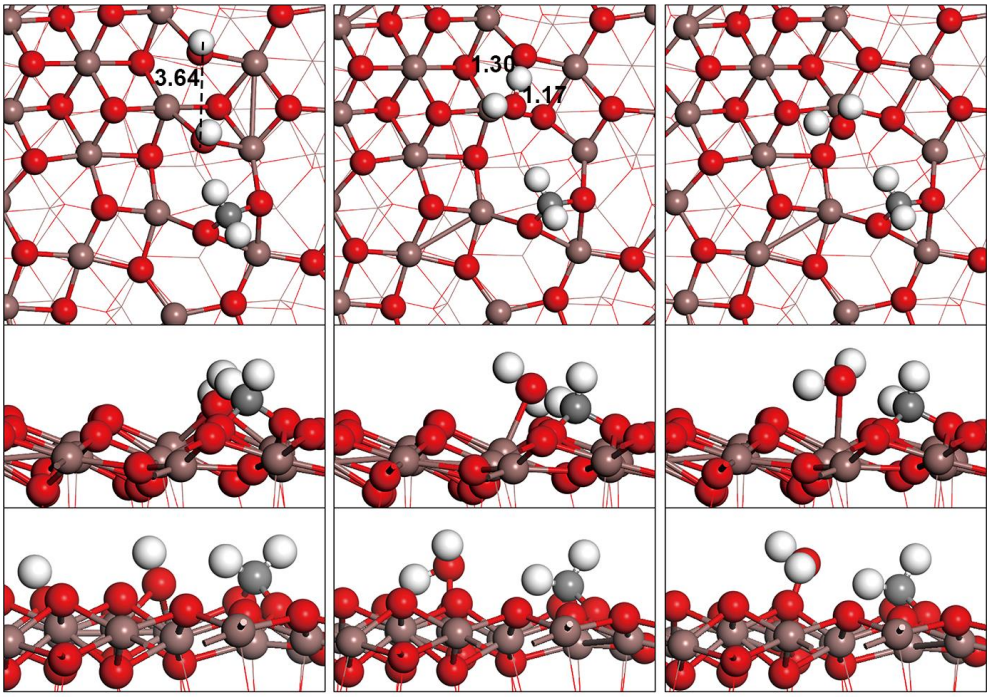
IS TS3' FS

R4': $H_2COOH^*+^* \rightarrow H_2CO^*+OH^*$



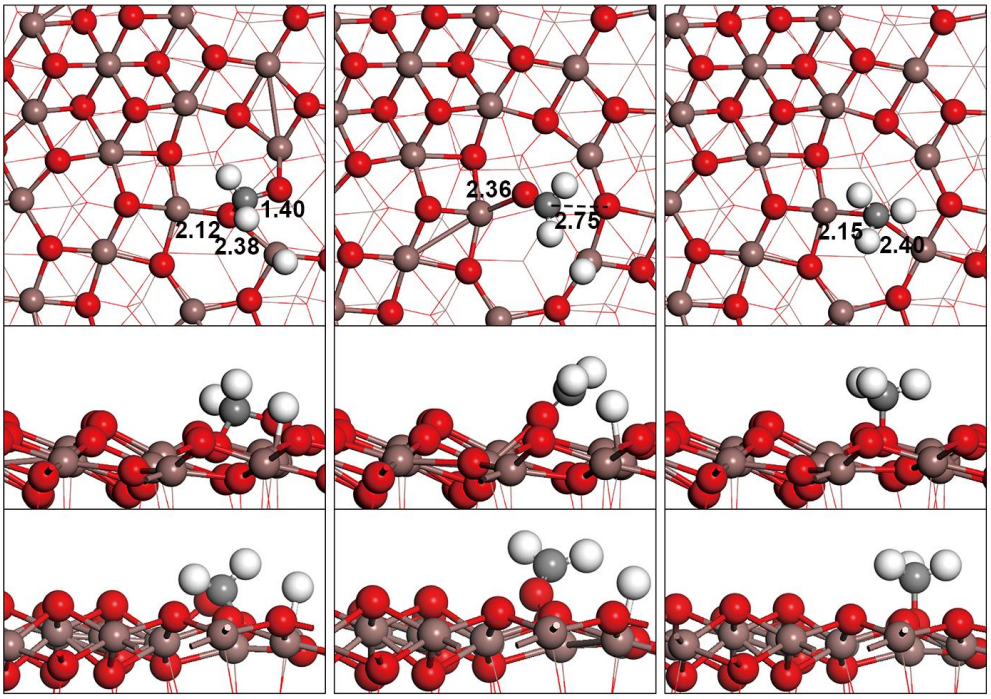
IS TS4' FS

R5': $H_2CO^*+OH^*+H^* \rightarrow H_2CO^*+H_2O^*+^*$



IS TS5' FS

R6': $H_2CO^*+H^* \rightarrow H_3CO^*+^*$



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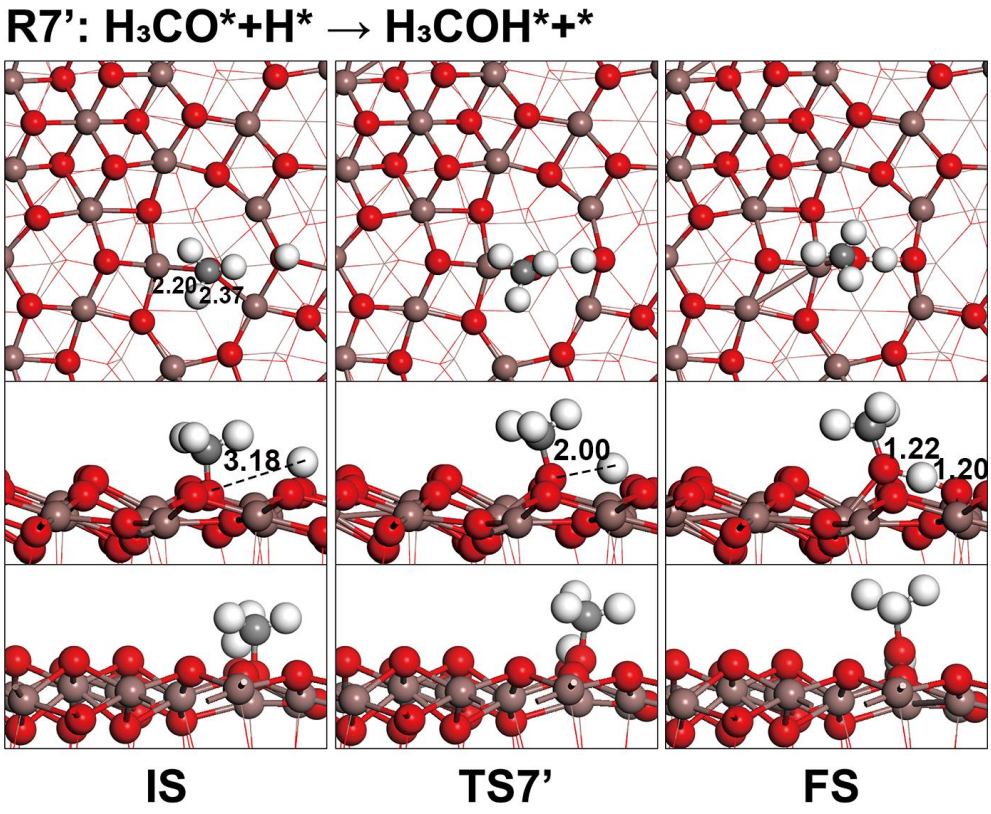

Fig. S7 The top and side views of all initial, transition, and final states for the methanol synthesis on the In_2O_3_D model. Red: O atoms; brown: In atoms; blue: W atom; gray: C atom; white: H atoms. The bond length is in angstroms.

Table S1 The formation energy of W doping obtained by different doping positions

doping position	formation energy (eV)
In_1	-11.12
In_2	-10.93
In_3	-11.07
In_4	-10.03
In_5	-8.29
In_6	-9.72

Table S2 The degree of TOF control (X_{TOF}) for each intermediate or transition state for the methanol synthesis on the W-In_2O_3_D model and the In_2O_3_D model

X(TOF)	H_3CO^* (W-In_2O_3)	H_2COH^* (W-In_2O_3)	H_3CO^* (In_2O_3)
X(TOF, T1)	0.00	0.00	0.00
X(TOF, T2)	0.00	0.00	0.00
X(TOF, T3)	0.00	0.00	0.00
X(TOF, T4)	0.00	0.00	0.00
X(TOF, T5)	0.00	0.00	0.00
X(TOF, T6)	0.00	0.00	0.00
X(TOF, T7)	0.04	0.00	0.05
X(TOF, T8)	0.00	0.00	0.00
X(TOF, T9)	0.00	0.00	0.00
X(TOF, T10)	0.00	0.00	0.00
X(TOF, T11)	0.00	0.00	0.00
X(TOF, T12)	0.96	0.00	0.95
X(TOF, T13)	0.00	0.00	0.00
X(TOF, T14)	0.00	1.00	0.00
X(TOF, T15)	0.00		0.00
X(TOF, I1)	0.66	0.72	0.00
X(TOF, I2)	0.00	0.00	0.00
X(TOF, I3)	0.09	0.10	0.08
X(TOF, I4)	0.00	0.00	0.00
X(TOF, I5)	0.16	0.18	0.00
X(TOF, I6)	0.00	0.00	0.00
X(TOF, I7)	0.00	0.00	0.00
X(TOF, I8)	0.00	0.00	0.00
X(TOF, I9)	0.00	0.00	0.00
X(TOF, I10)	0.00	0.00	0.00
X(TOF, I11)	0.00	0.00	0.00
X(TOF, I12)	0.00	0.00	0.00
X(TOF, I13)	0.06	0.00	0.90
X(TOF, I14)	0.00	0.00	0.02
X(TOF, I15)	0.03		0.00