Supporting information

M Supported on Al-Defective $Al_{2-\delta}O_3$ (M=Fe, Co, Ni, Cu, Ag, Au) as Catalyst for acetylene semi-hydrogenation: A Theoretical Perspective.

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Part S1. Calculation details of $E_{(formation)}$

The formation energy (E_f) of $M_1/Al_{2-\delta}O_3$ is defined as:

$E_f = E(M_1/Al_{2-\delta}O_3) - E(Al_2O_3) + E_{(bulk\text{-}Al)} - E_{(bulk\text{-}M)}$

where $E(M_1/Al_{2-\delta}O_3)$ and $E(Al_2O_3)$ stand for the energy of the $M_1/Al_{2-\delta}O_3$ and Al_2O_3. $E_{(bulk\text{-}Al)}$ and $E_{(bulk\text{-}M)}$ are from the energies of bulk Al and the M in the bulk phase.

For the $M_1(OH)_n/Al_{2-\delta}O_{3-\theta}$, E_f is definded as:

$E_f = E(M_1(OH)_n/Al_{2-\delta}O_{3-\theta}) - E(Al_2O_3) + E_{(bulk\text{-}Al)} - n/2 \times E(H_2) - E_{(bulk\text{-}M)}$

where $E(M_1/Al_{2-\delta}O_3)$ and $E(H_2)$ stand for the energy of the $M_1/Al_{2-\delta}O_3$ and the energy of H_2 in gas phase.

Part S2.

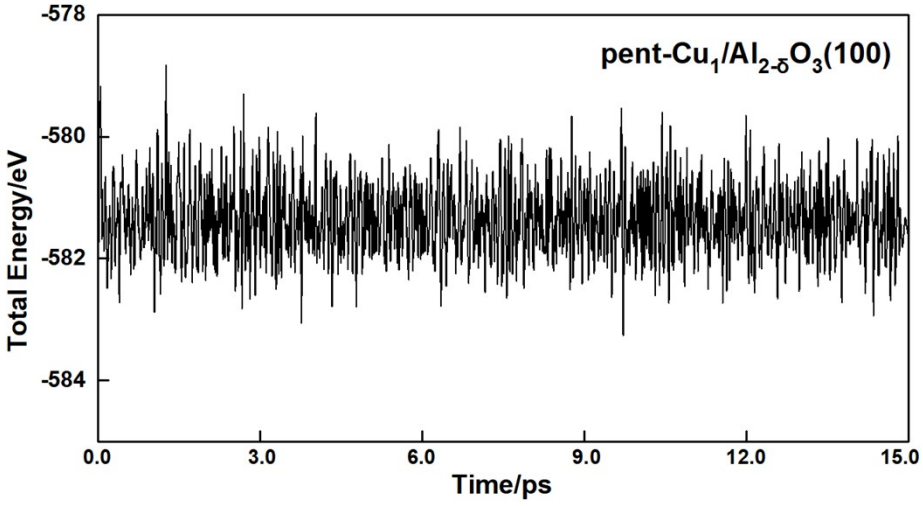

Figure S 1 The variety of total energy with the increase in ion steps at 800K.

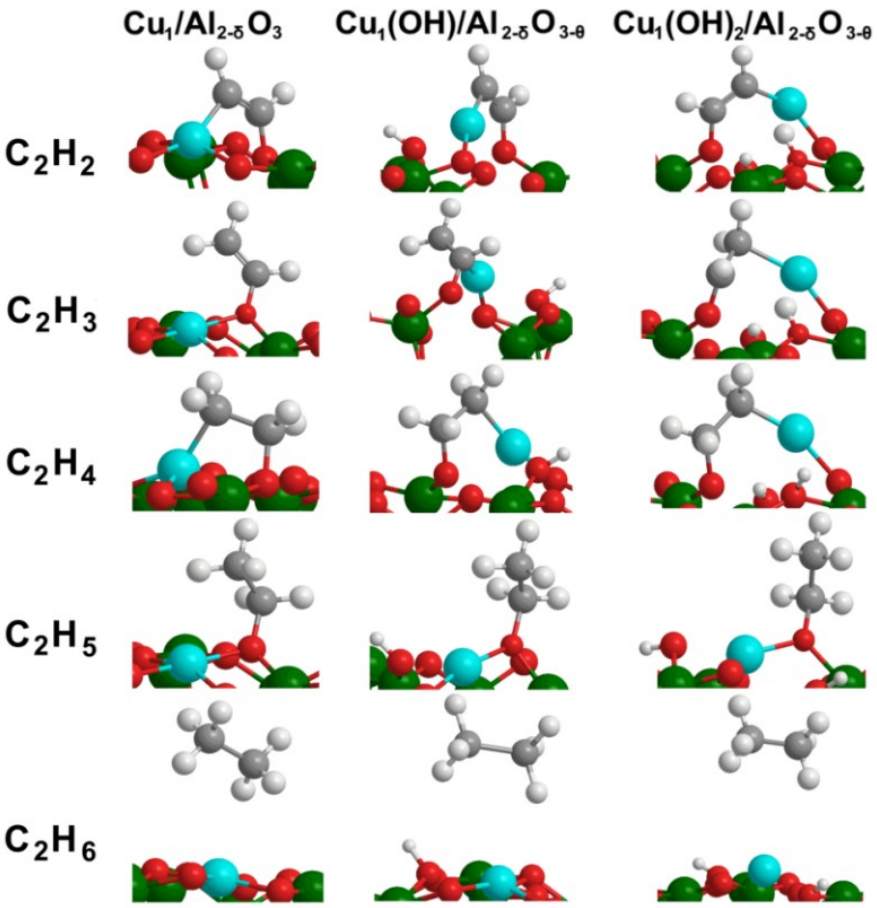

Figure S 2 The configurations of the intermediates on the $Cu_1/Al_{2-\delta}O_3$, $Cu_1(OH)_1/Al_{2-\delta}O_{3-\theta}$, and $Cu_1(OH)_2/Al_{2-\delta}O_{3-\theta}$.

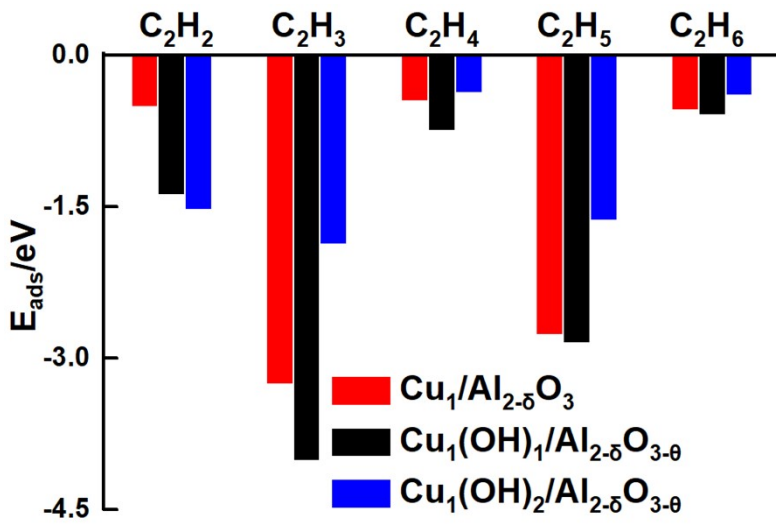

Figure S 3 The adsorption energies of the intermediates on the $Cu_1/Al_{2-\delta}O_3$ and $Cu_1(OH)_n/Al_{2-\delta}O_{3-\theta}$ (n=1, 2).

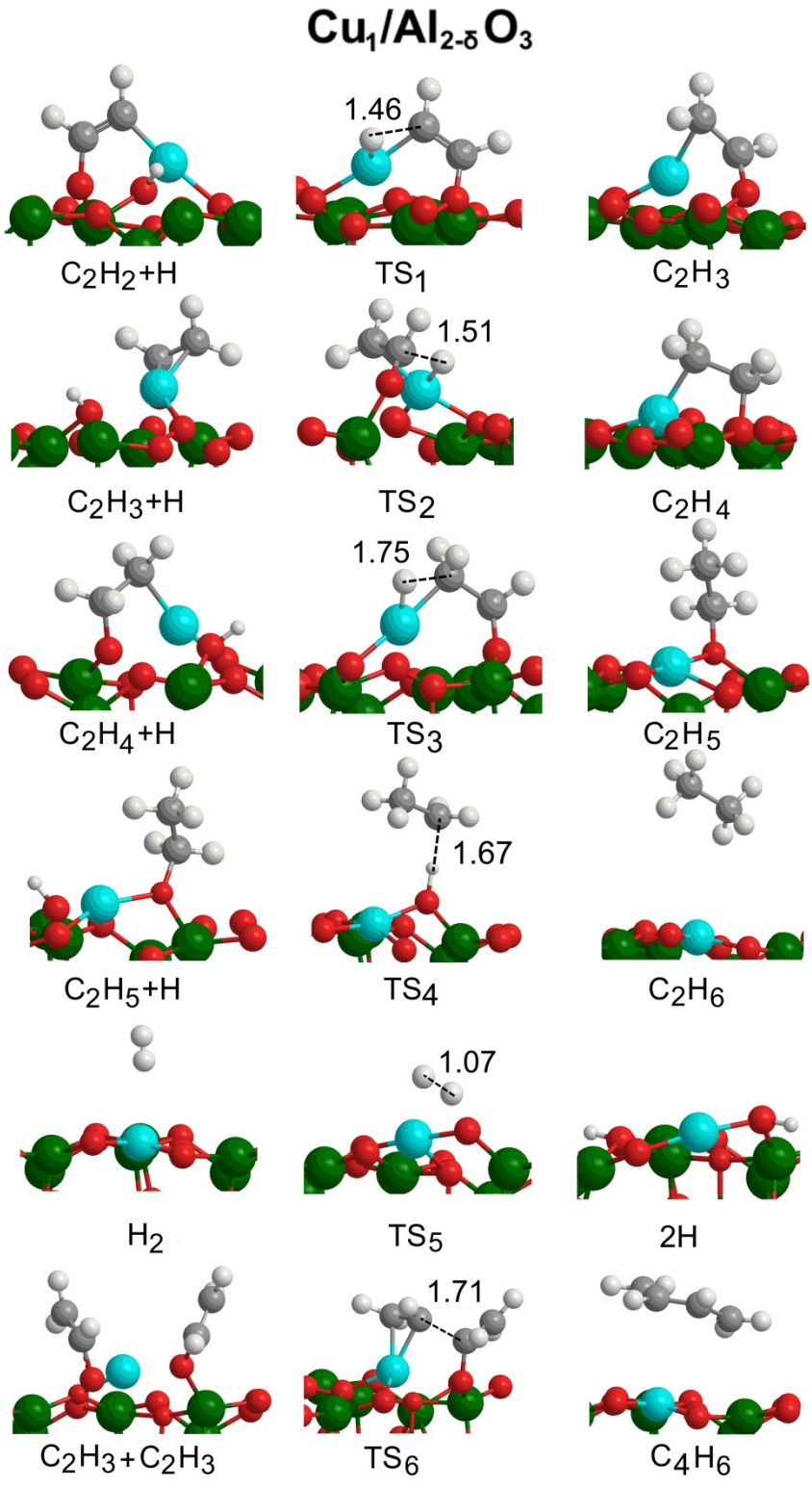

Figure S 4 The structures of possible TSs on the $Cu_1/Al_{2-\delta}O_3$.

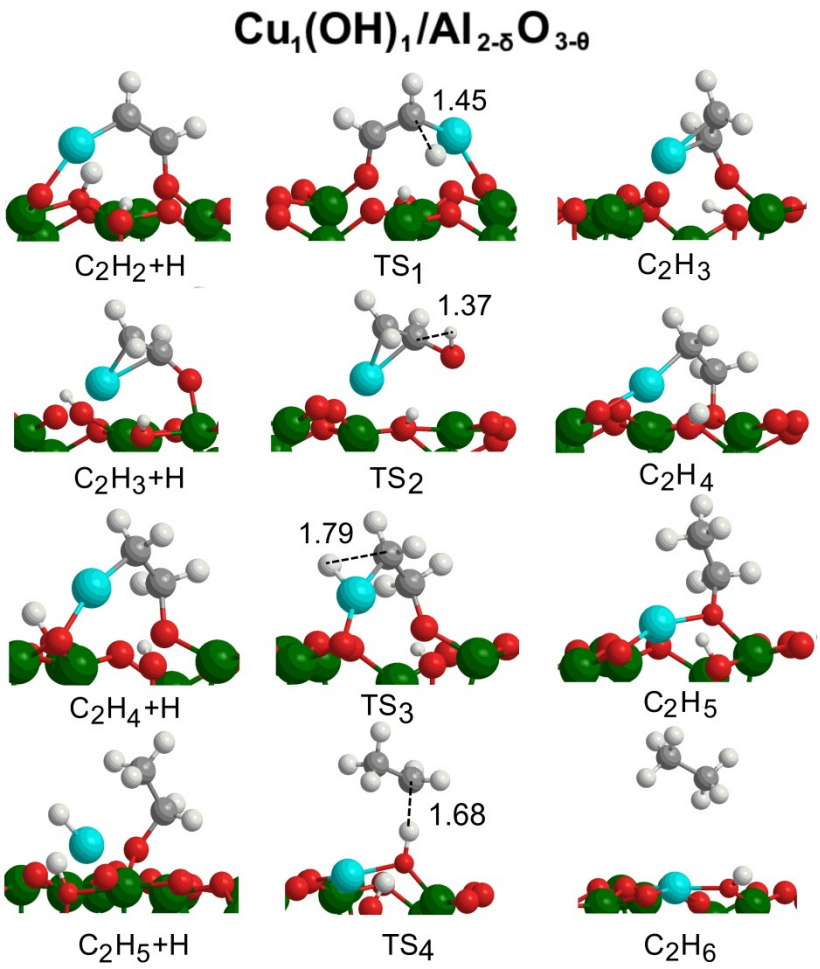

Figure S 5 The structures of possible TSs on the $Cu_1(OH)_1/Al_{2-\delta}O_3$.

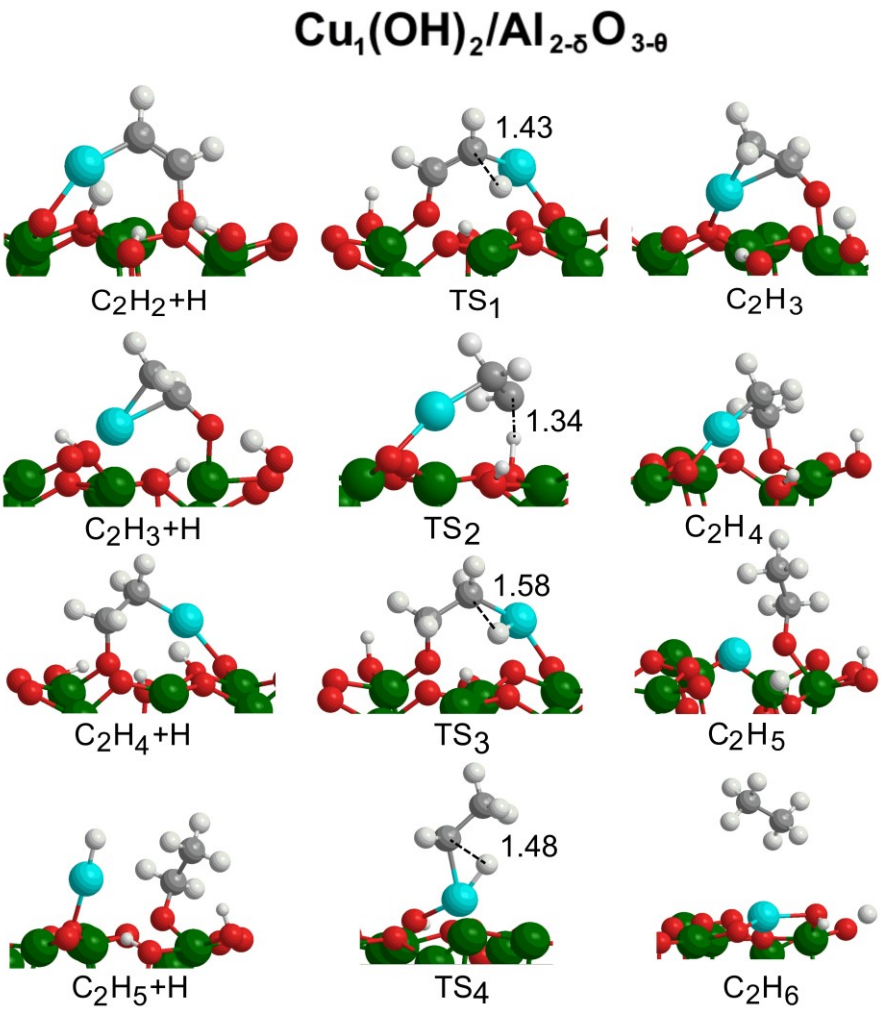

Figure S 6 The structures of possible TSs on the $Cu_1(OH)_2/Al_{2-\delta}O_3$.

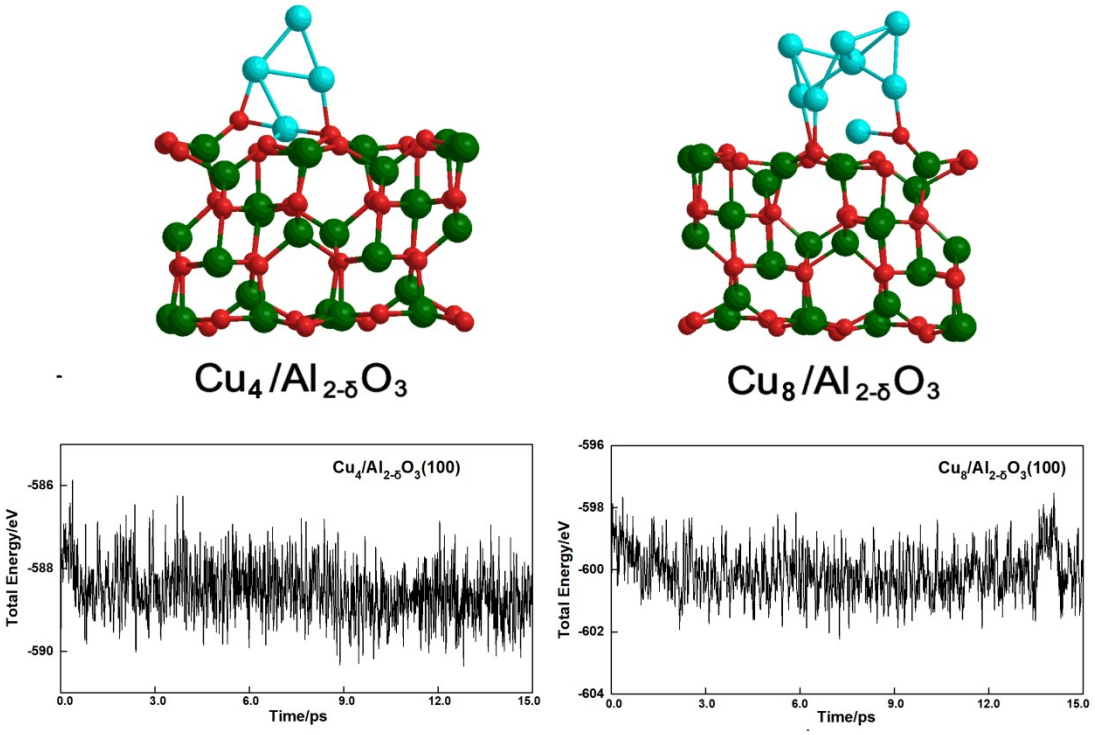

Figure S 7 The structures of $Cu_4/Al_{2-\delta}O_3$ and $Cu_8/Al_{2-\delta}O_3$ and the AIMD simulation at 800K.

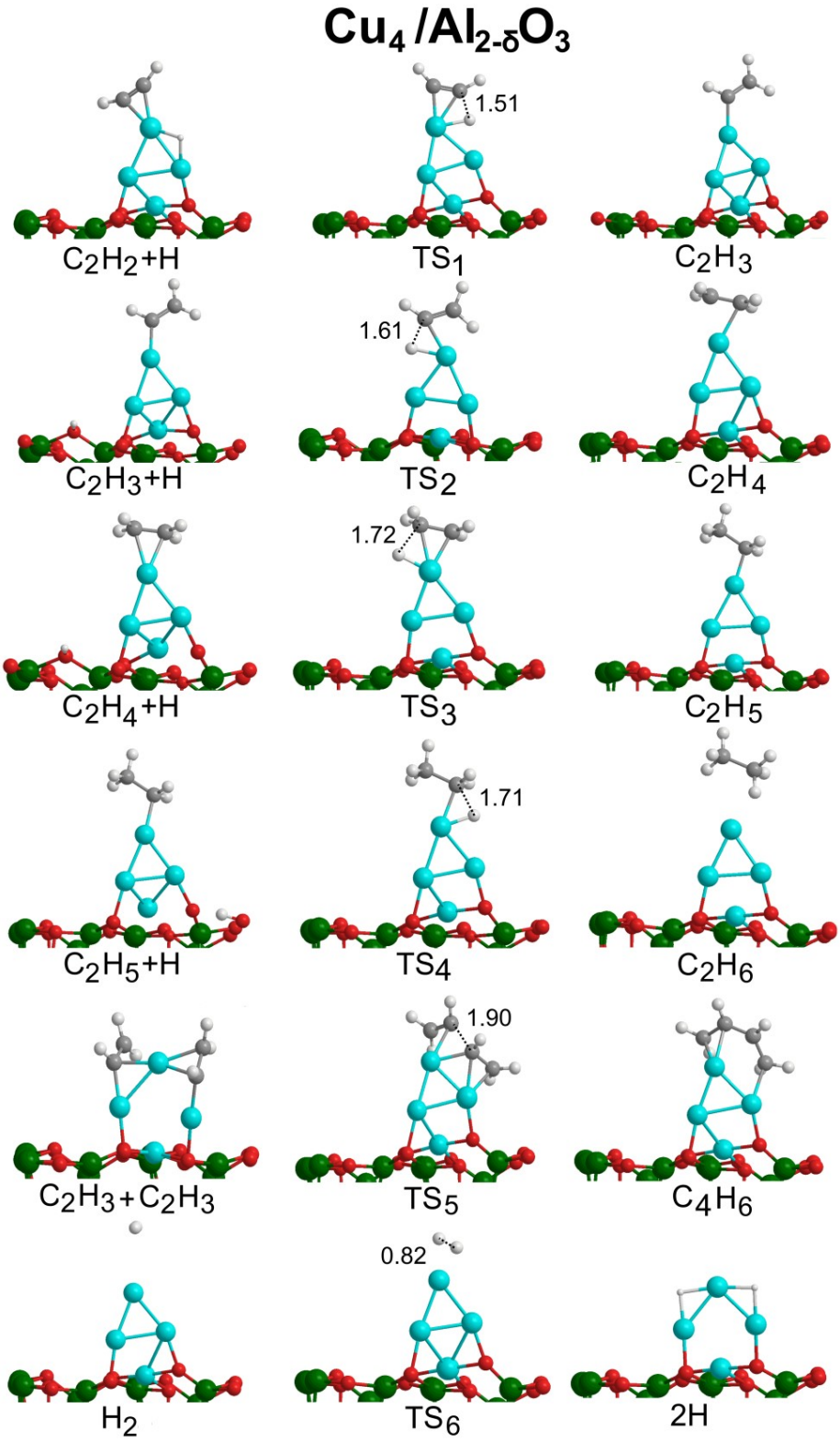

Figure S 8 The structures of possible TSs on the $Cu_4/Al_{2-\delta}O_3$.

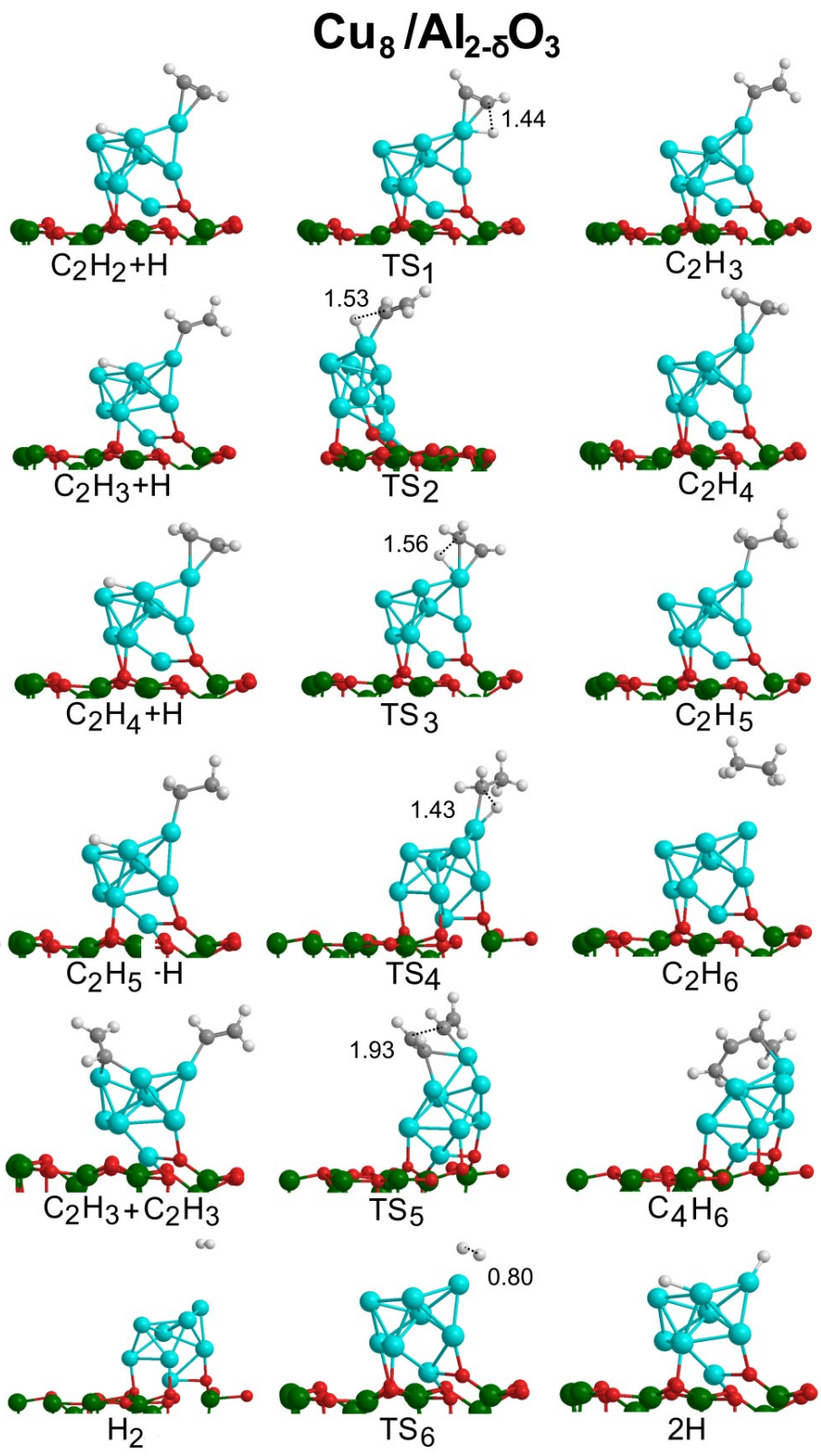

Figure S 9 The structures of possible TSs on the $Cu_8/Al_{2-\delta}O_3$.

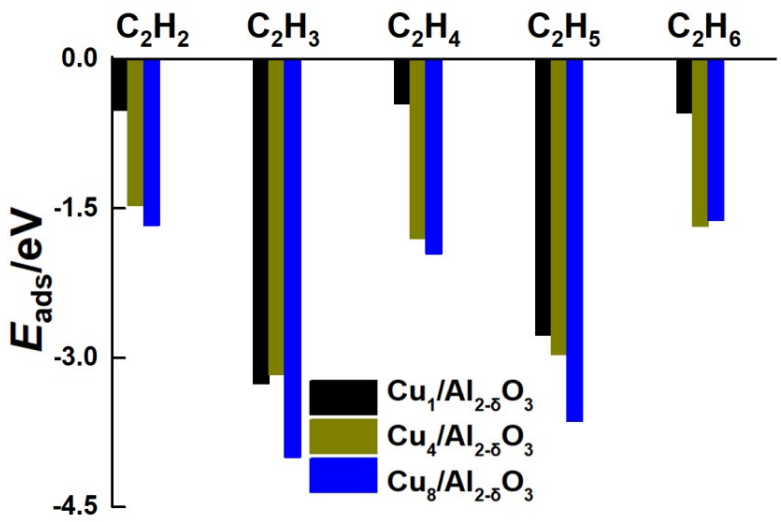

Figure S 10 The adsorption energies of the intermediates on the clean and H pre-covered $Cu_n/Al_{2-\delta}O_3$ (n=1, 4, 8).

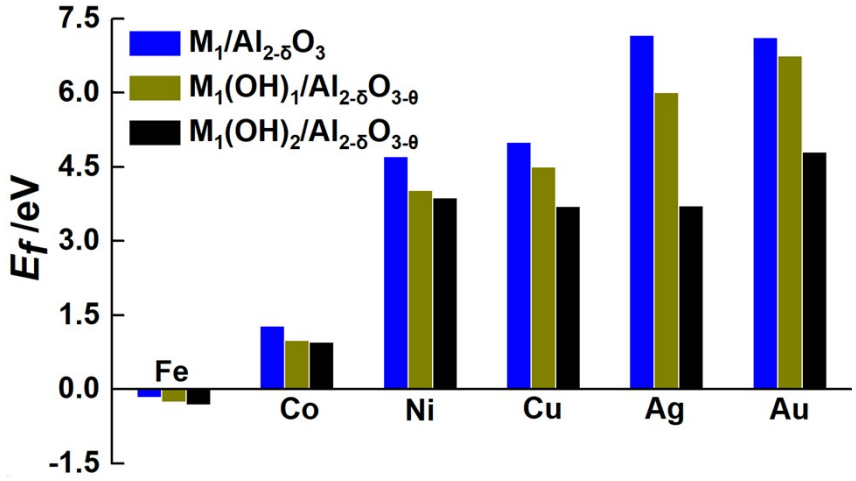

Figure S 11 The formation energy(E_f) of $M_1/Al_{2-\delta}O_3$ and $M_1(OH)_n/Al_{2-\delta}O_{3-\theta}$ (n=1, 2).

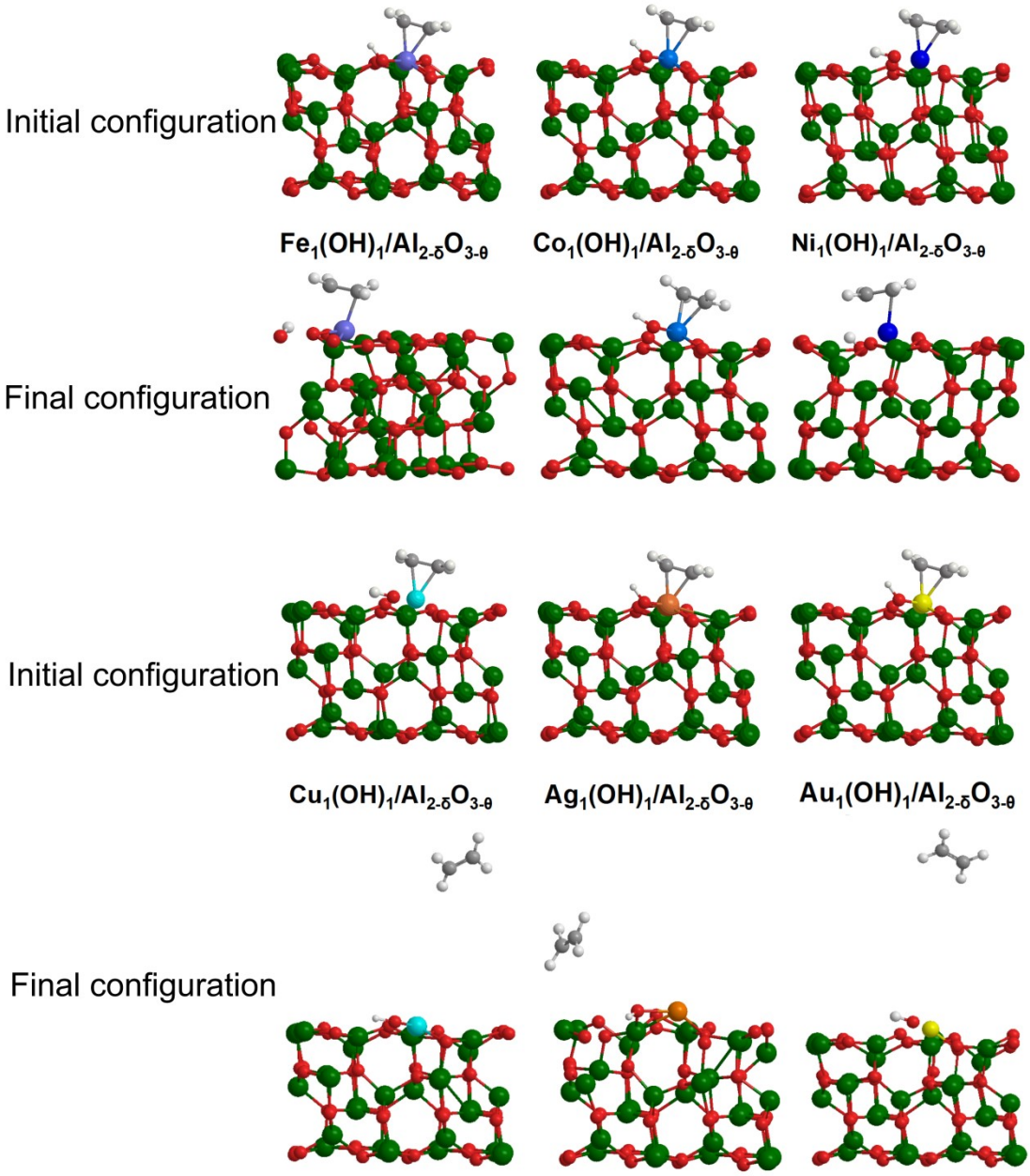

Figure S 12 The configuration of C_2H_4 on the $M_1(OH)_1/Al_{2-\delta}O_3$ (M=Fe, Co, Ni, Cu, Ag, Au) after 15 ps AIMD simulation at 463.15K.

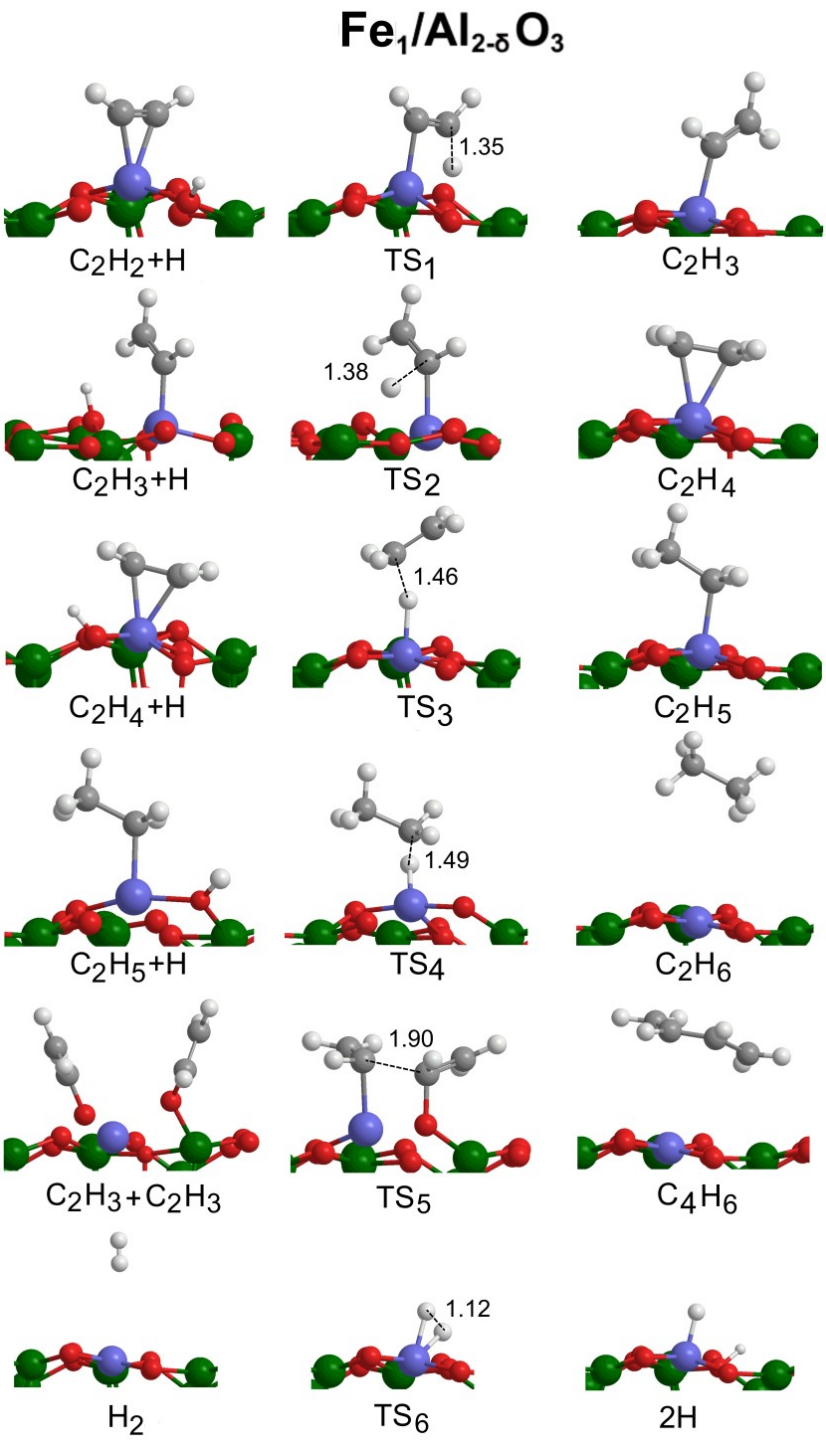

Figure S 13 The structures of possible TSs on the $Fe_1/Al_{2-\delta}O_3$.

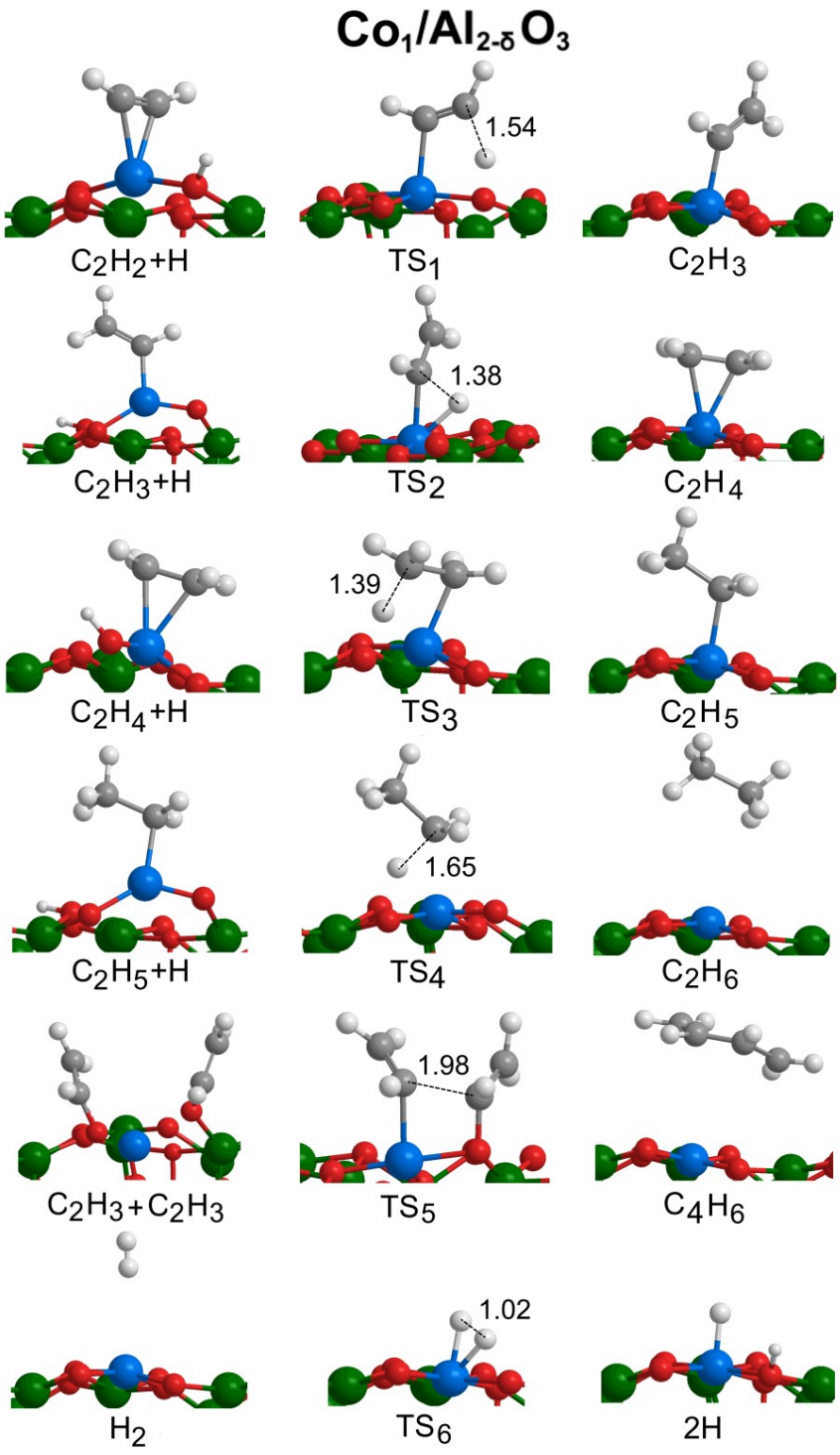

Figure S 14 The structures of possible TSs on the $Co_1/Al_{2-\delta}O_3$.

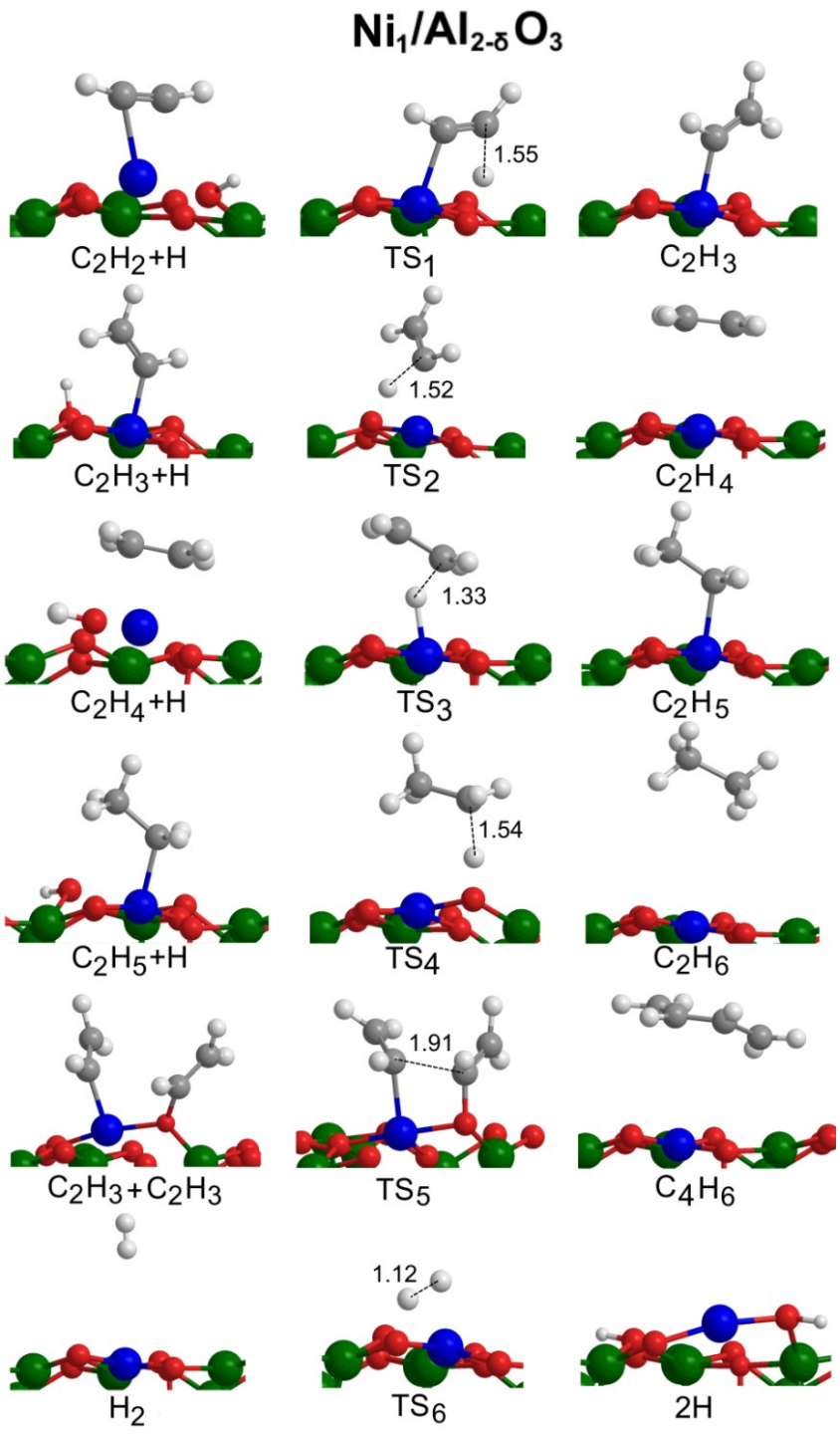

Figure S 15 The structures of possible TSs on the $Ni_1/Al_{2-\delta}O_3$.

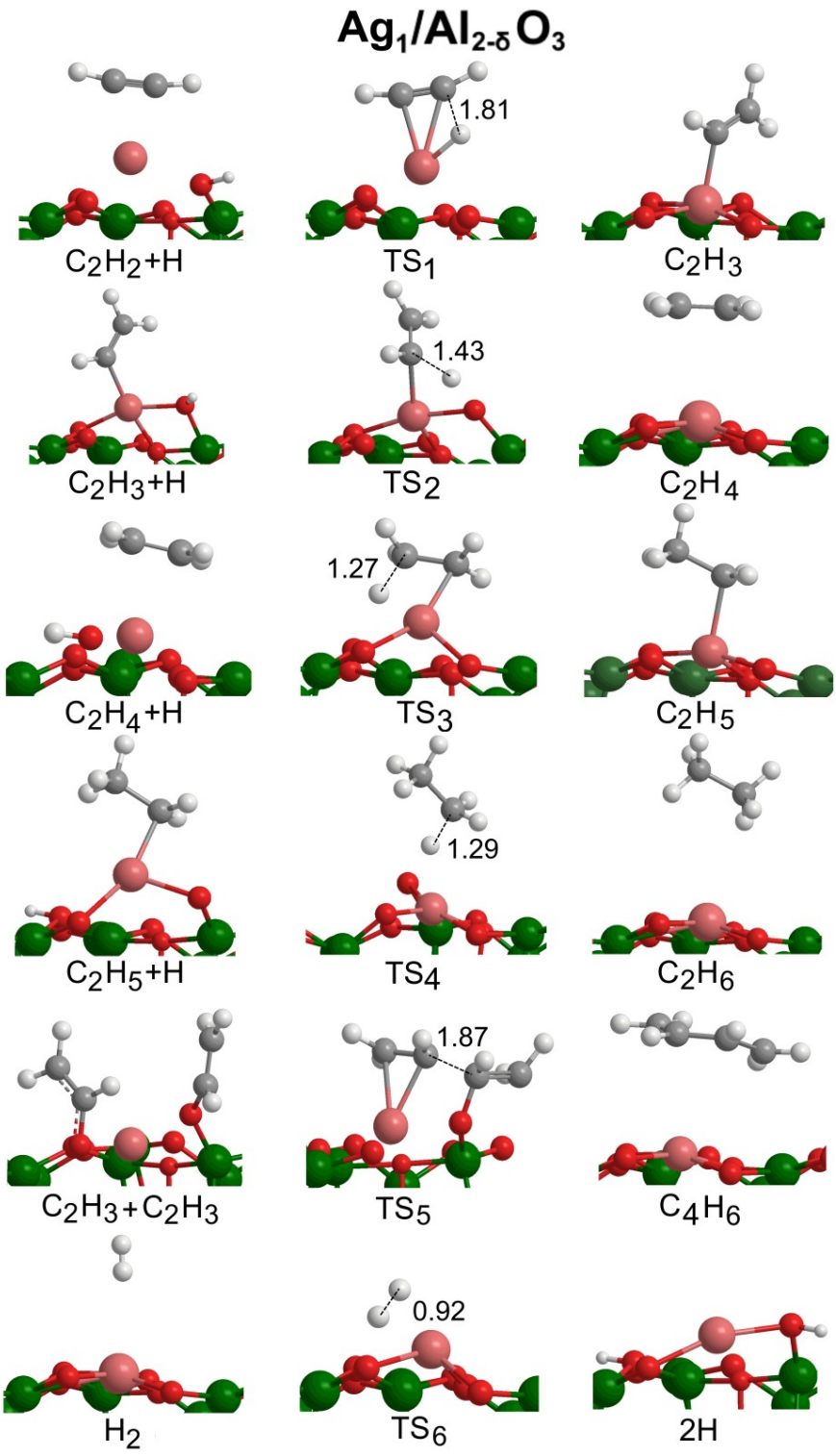

Figure S 16 The structures of possible TSs on the $Ag_1/Al_{2-\delta}O_3$.

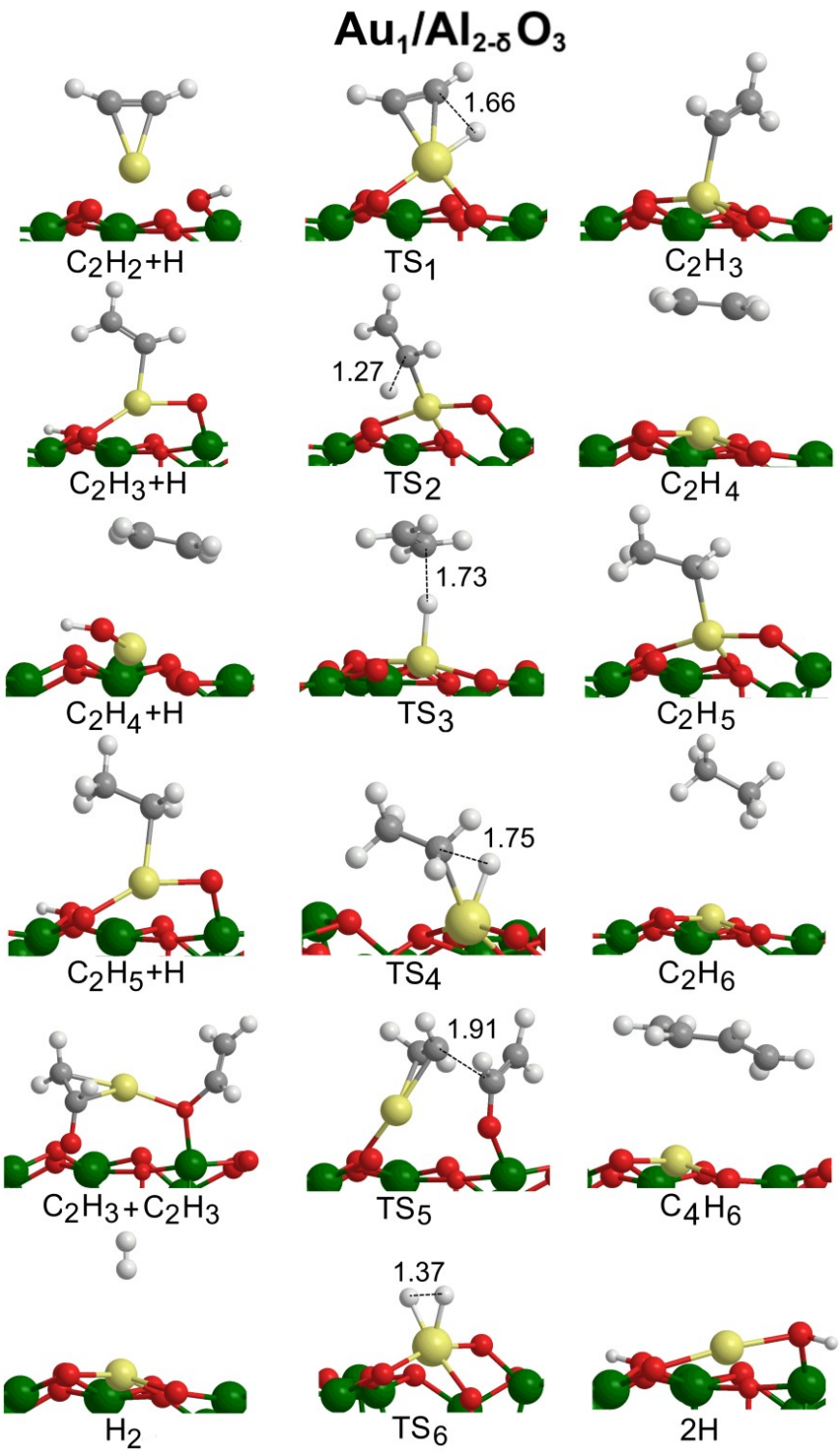

Figure S 17 The structures of possible TSs on the $Au_1/Al_{2-\delta}O_3$.

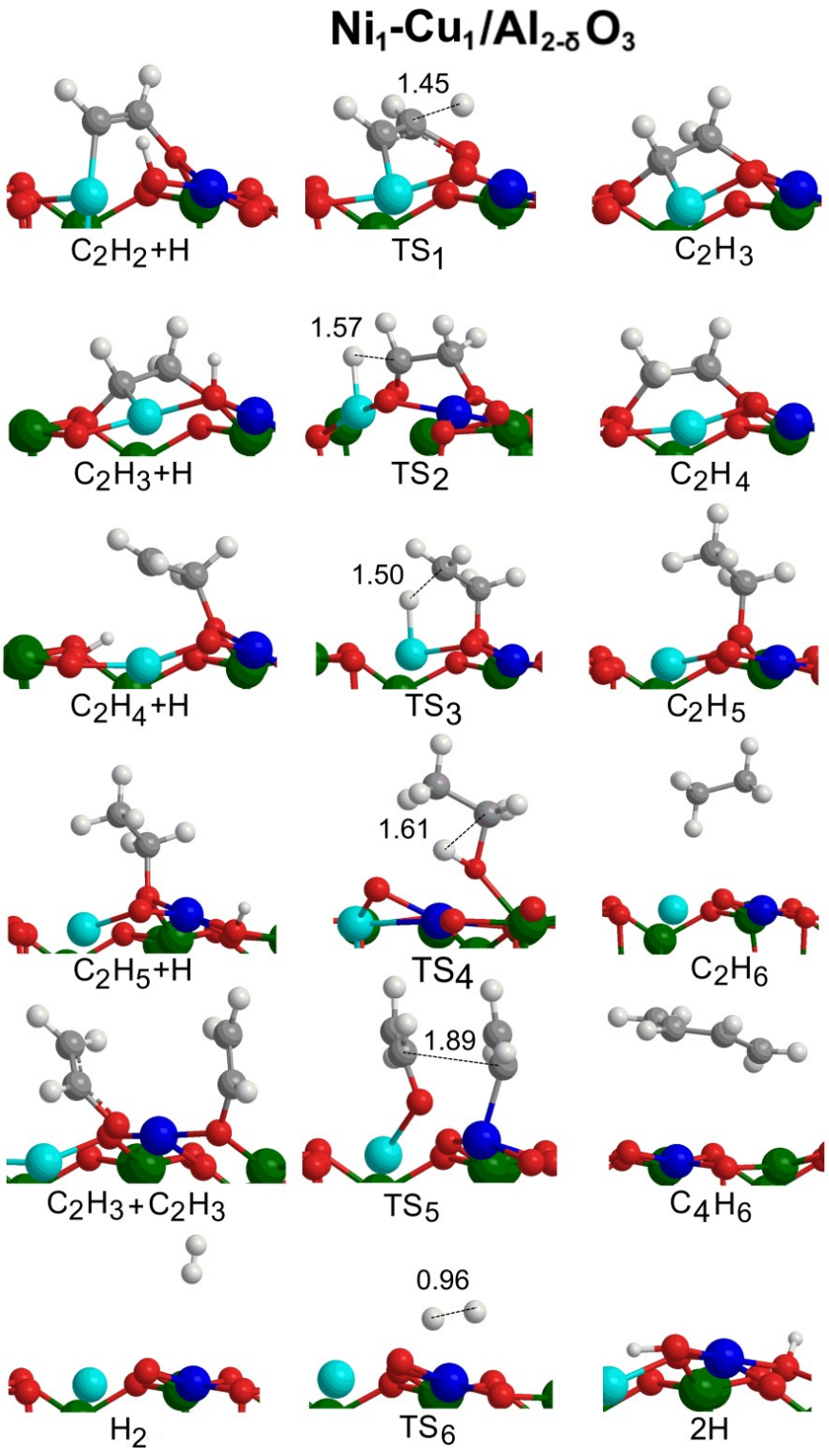

Figure S 18 The structures of possible TSs on the Ni_1-$Cu_1/Al_{2-\delta}O_3$.

Table S 1 The adsorption energies (eV) of the intermdiates on the $M_1/Al_{2-\delta}O_3$ (M=Fe, Co, Ni, Cu, Ag, Au).

		C_2H_2	C_2H_3	C_2H_4	C_2H_5	C_2H_6	1,3-C_4H_6
$Fe_1/Al_2O_3(100)$	PBE	-0.13	-2.39	-0.39	-2.00	-0.01	-0.39
	rPBE-vdW	-0.60	-2.60	-1.03	-2.14	-0.37	-1.05
$Co_1/Al_2O_3(100)$	PBE	-0.08	-2.36	-0.30	-1.99	0.04	-0.37
	rPBE-vdW	-0.63	-2.65	-0.97	-2.18	-0.60	-1.00
$Ni_1/Al_2O_3(100)$	PBE	-0.10	-2.47	-0.31	-2.15	-0.03	-0.31
	rPBE-vdW	-0.58	-2.77	-0.94	-2.36	-0.63	-0.98
$Cu_1/Al_2O_3(100)$	PBE	-0.07	-2.39	-0.03	-1.95	-0.02	-0.22
	rPBE-vdW	-0.51	-2.67	-0.45	-2.01	-0.54	-0.94
$Ag_1/Al_2O_3(100)$	PBE	-0.11	-0.87	-0.07	-0.74	-0.01	-0.29
	rPBE-vdW	-0.48	-1.10	-0.46	-0.91	-0.53	-0.82
$Au_1/Al_2O_3(100)$	PBE	-0.04	-1.03	-0.01	-0.89	-0.02	-0.26
	rPBE-vdW	-0.47	-1.31	-0.32	-1.00	-0.38	-0.84

Table S 2 The parameter of the pathways on the $Cu_1/Al_{2-\delta}O_3$ in the microkinetic modeling.

Elementray step	/eV		/s^{-1}	
$H_{2(g)}+2^*=2H^*$	$E_{a,+}$	0.80	A_+	4.2×10^{11}
	$E_{a,-}$	3.00	A_-	2.1×10^{13}
$C_2H_{2(g)}+^*=C_2H_2^*$	$E_{a,+}$	0.00	A_+	6.7×10^{7}
	$E_{a,-}$	0.51	A_-	4.9×10^{17}
$C_2H_2^*+H^*=C_2H_3^*+^*$	$E_{a,+}$	0.76	A_+	1.4×10^{13}
	$E_{a,-}$	1.24	A_-	1.6×10^{13}
$C_2H_3^*+H^*=C_2H_4^*+^*$	$E_{a,+}$	1.43	A_+	1.4×10^{13}
	$E_{a,-}$	0.62	A_-	1.5×10^{13}
$C_2H_4^*+H^*=C_2H_5^*+^*$	$E_{a,+}$	1.57	A_+	1.5×10^{13}
	$E_{a,-}$	2.93	A_-	1.8×10^{13}
$C_2H_5^*+H^*=C_2H_{6(g)}+2^*$	$E_{a,+}$	1.59	A_+	1.4×10^{13}
	$E_{a,-}$	1.75	A_-	1.7×10^{13}
$2C_2H_3^*=C_4H_6^*+^*$	$E_{a,+}$	1.70	A_+	1.6×10^{13}
	$E_{a,-}$	2.30	A_-	1.6×10^{13}
$C_4H_6^*=C_4H_{6(g)}+^*$	$E_{a,+}$	0.89	A_+	1.0×10^{18}
	$E_{a,-}$	0.00	A_-	4.7×10^{7}
$C_2H_4^*=C_2H_{4(g)}+^*$	$E_{a,+}$	0.45	A_+	5.4×10^{17}
	$E_{a,-}$	0.00	A_-	6.5×10^{7}

Table S 3 The adsorption energies of possible intermediates (eV).

Surface	C_2H_2	C_2H_3	C_2H_4	C_2H_5	C_2H_6	1,3-C_4H_6	Surface	C_2H_2	C_2H_4
$Fe_1/Al_{2-\delta}O_3$	-0.60	-2.92	-0.70	-2.56	-0.92	-0.90	$Fe_1(OH)_1/Al_{2-\delta}O_{3-\theta}$	-1.55	-1.23
$Co_1/Al_{2-\delta}O_3$	-0.64	-2.93	-0.66	-2.54	-0.44	-1.00	$Co_1(OH)_1/Al_{2-\delta}O_{3-\theta}$	-1.16	-1.19
$Ni_1/Al_{2-\delta}O_3$	-0.58	-3.03	-0.65	-2.70	-0.59	-1.02	$Ni_1(OH)_1/Al_{2-\delta}O_{3-\theta}$	-0.71	-0.90
$Ag_1/Al_{2-\delta}O_3$	-0.47	-1.27	-0.46	-1.21	-0.57	-0.92	$Ag_1(OH)_1/Al_{2-\delta}O_{3-\theta}$	-1.79	-0.59
$Au_1/Al_{2-\delta}O_3$	-0.10	-1.40	-0.32	-1.44	-0.46	-0.83	$Au_1(OH)_1/Al_{2-\delta}O_{3-\theta}$	-0.98	-0.79