

Fig S1. Activation of CO on Co-10 cluster (Co atom: blue, C atom: gray, H atom: white, O atom: red).

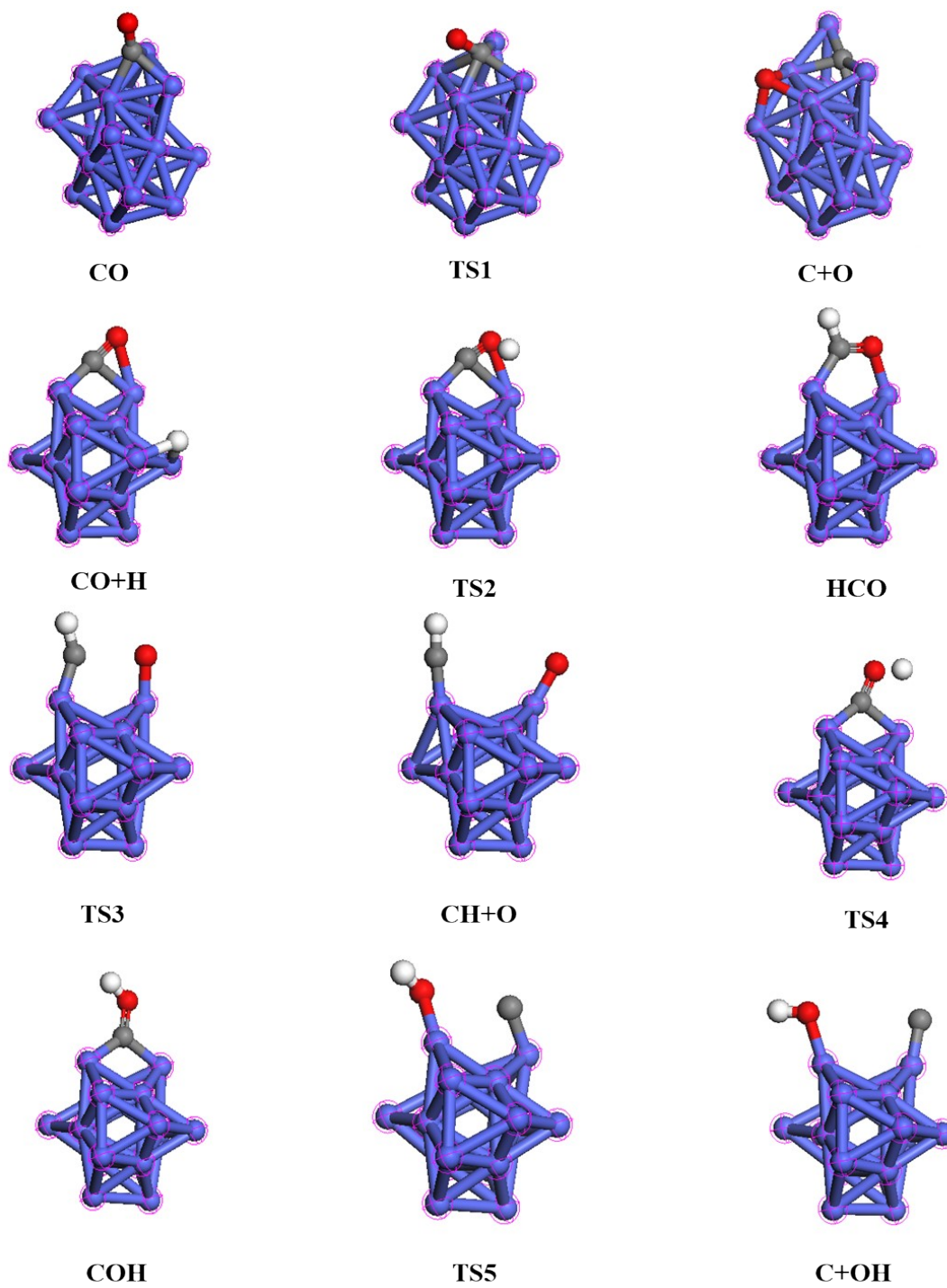


Fig S2. Activation of CO on Co-18 cluster (Co atom: blue, C atom: gray, H atom: white, O atom: red).

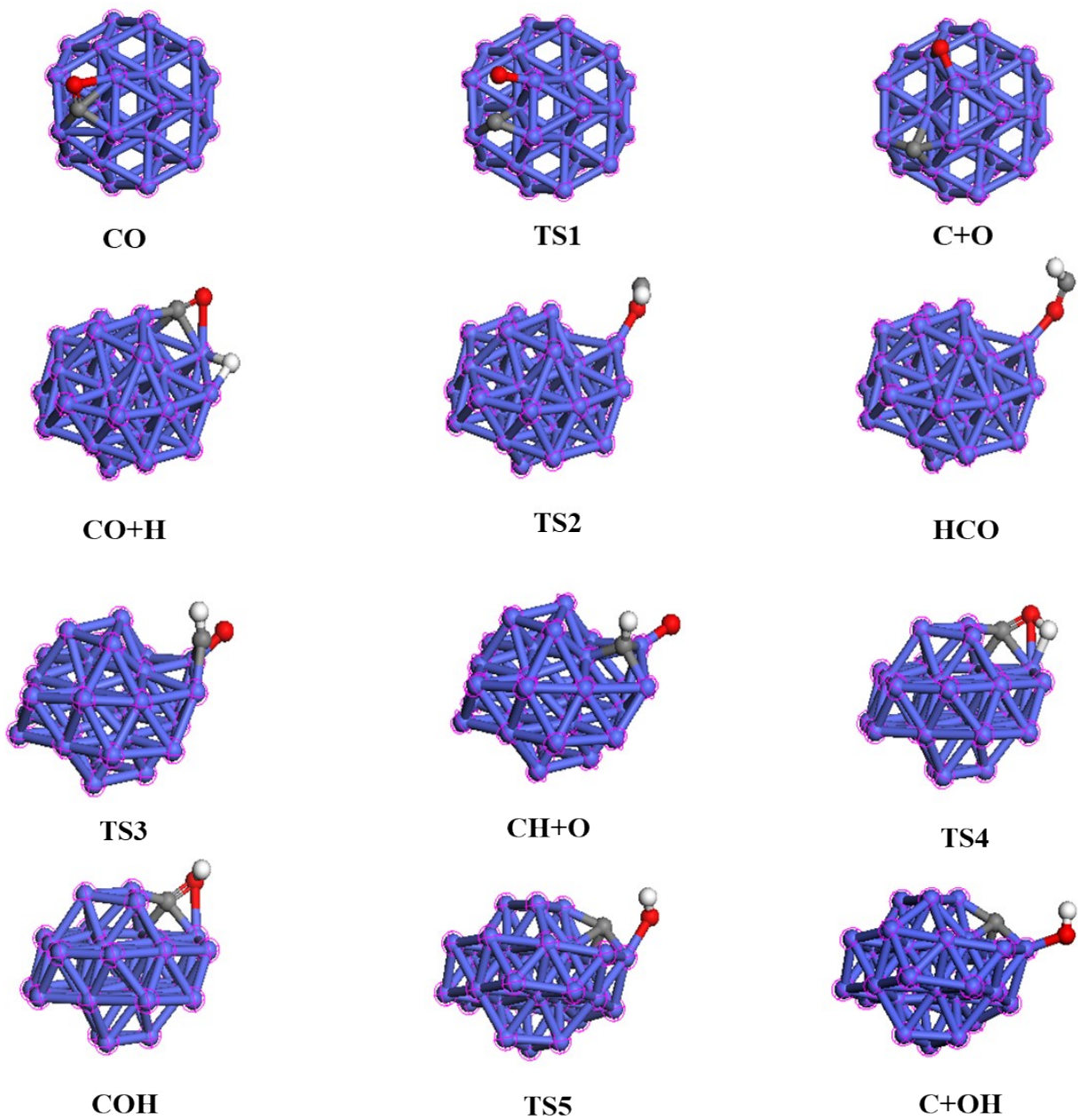


Fig S3. Activation of CO on Co-30 cluster (Co atom: blue, C atom: gray, H atom: white, O atom: red).

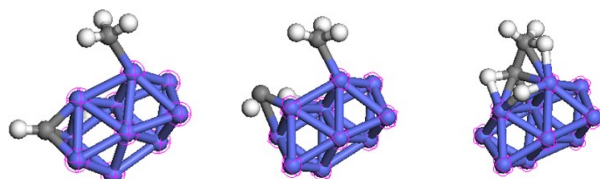
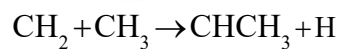
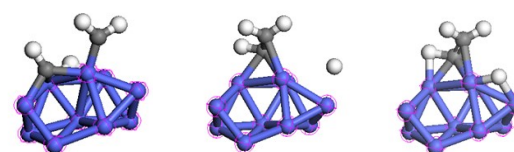
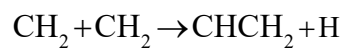
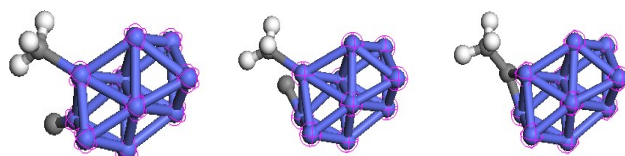
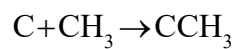
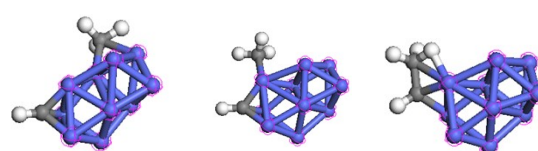
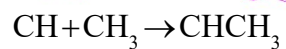
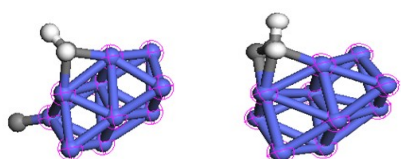
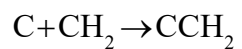
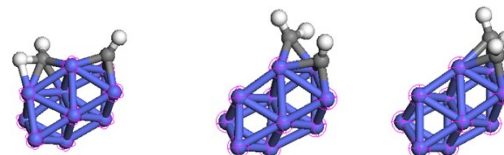
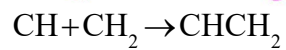
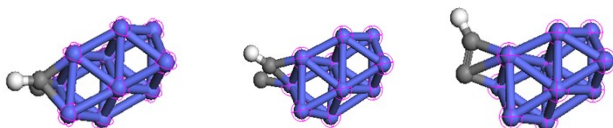
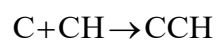
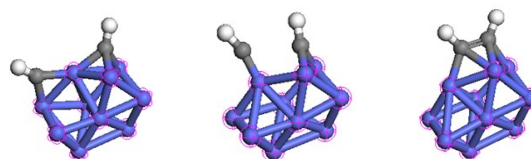
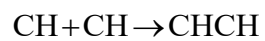
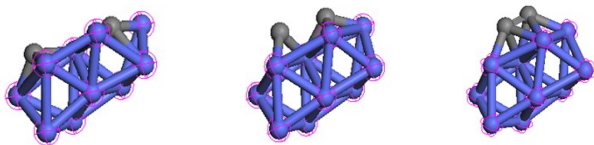
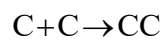


Fig S4. Chain growth of hydrocarbons in C-C reaction on Co-10 cluster (Co atom: blue, C atom: gray, H atom: white).

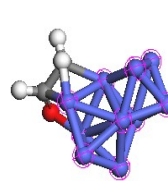
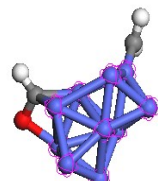
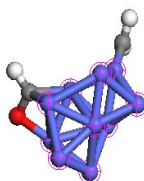
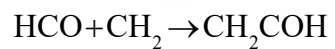
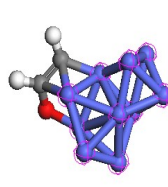
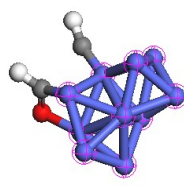
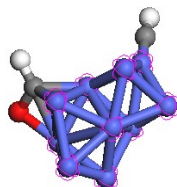
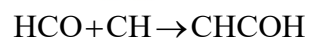
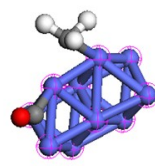
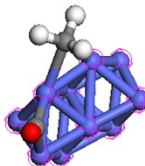
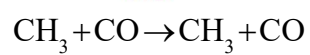
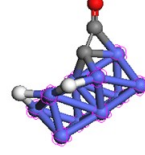
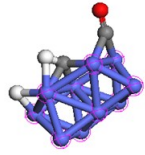
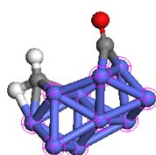
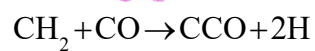
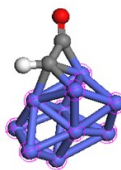
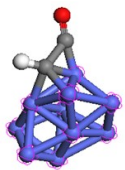
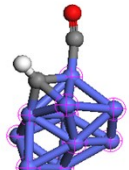
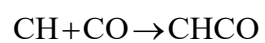
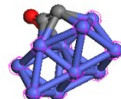
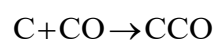


Fig S5. Chain growth of hydrocarbons in C-CO reaction on Co-10 cluster (Co atom: blue, C atom: gray, H atom: white, O atom: red).

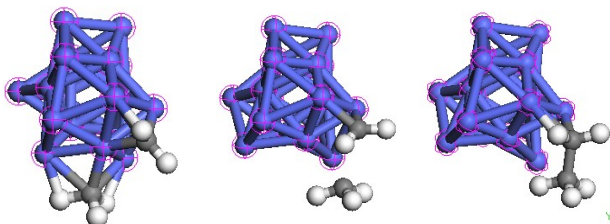
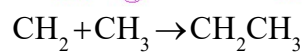
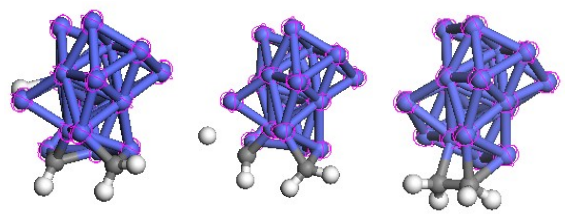
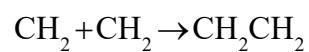
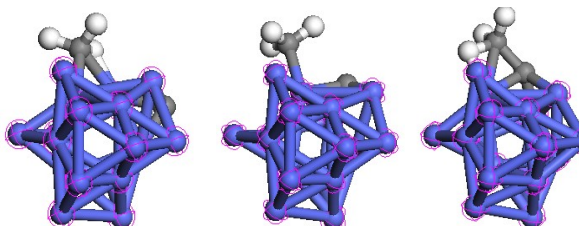
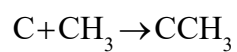
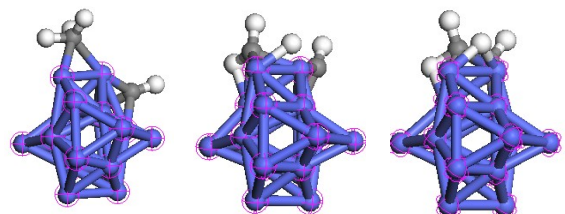
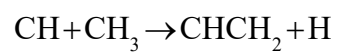
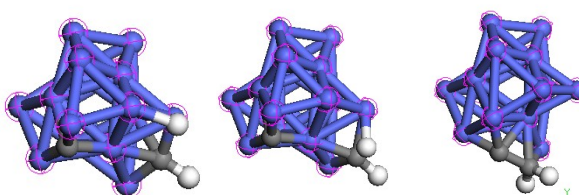
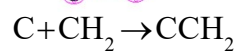
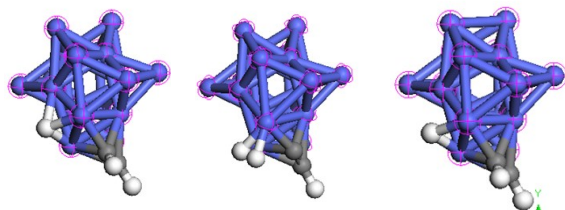
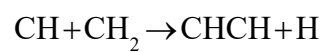
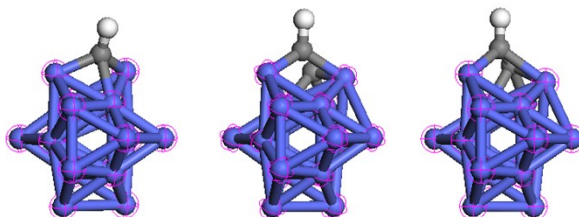
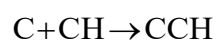
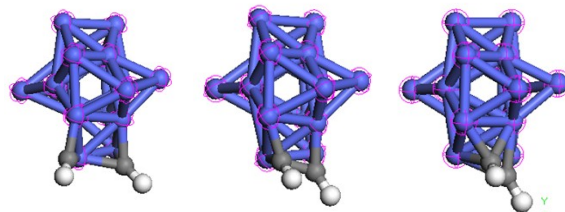
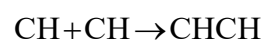
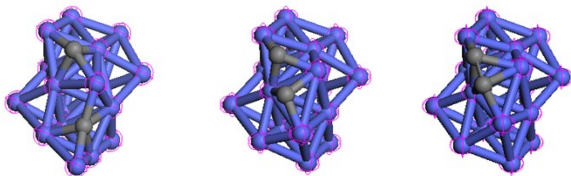
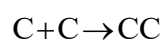


Fig S6. Chain growth of hydrocarbons in C-C reaction on Co-18 cluster (Co atom: blue, C atom: gray, H atom: white).

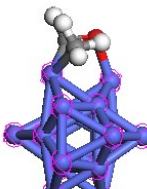
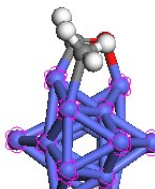
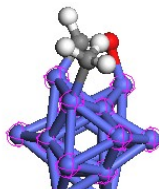
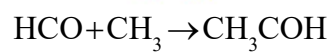
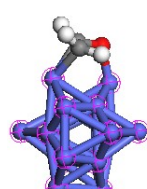
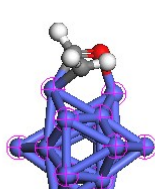
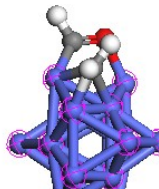
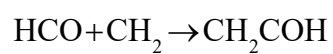
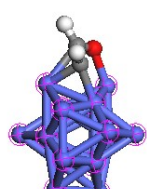
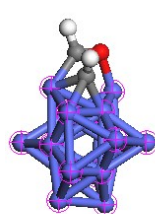
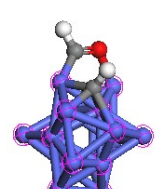
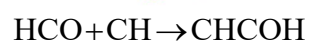
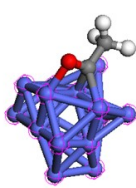
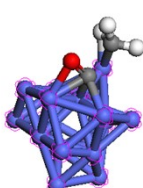
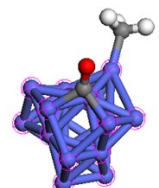
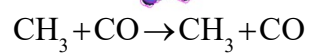
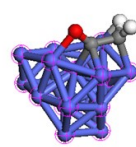
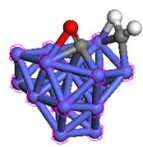
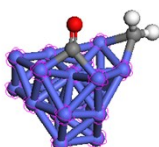
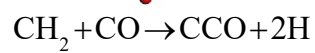
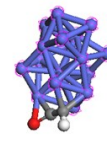
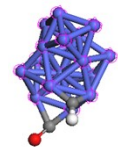
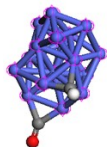
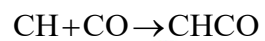
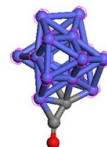
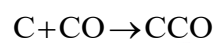


Fig S7. Chain growth of hydrocarbons in C-CO reaction on Co-18 cluster (Co atom: blue, C atom: gray, H atom: white, O atom: red).

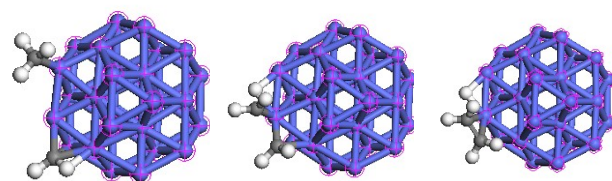
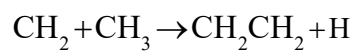
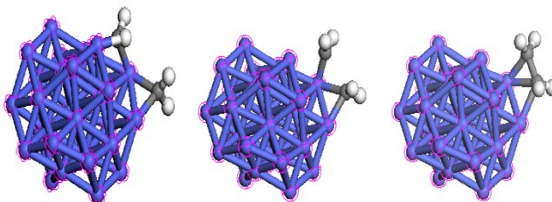
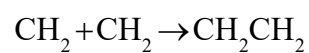
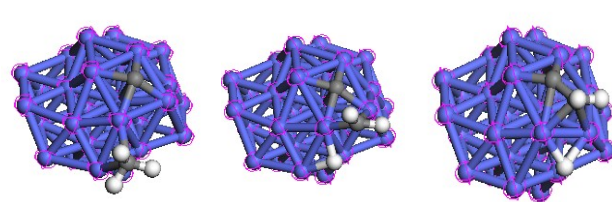
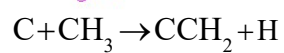
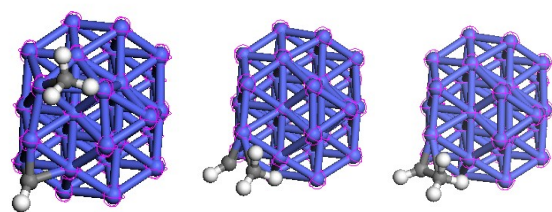
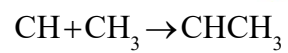
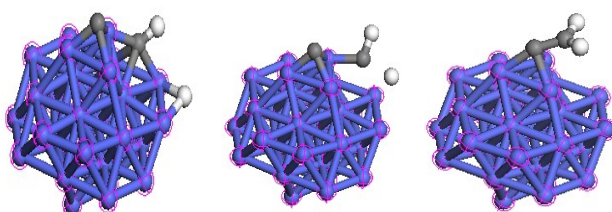
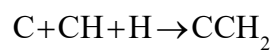
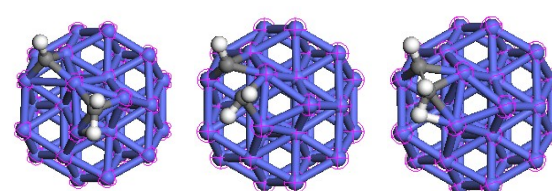
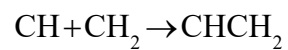
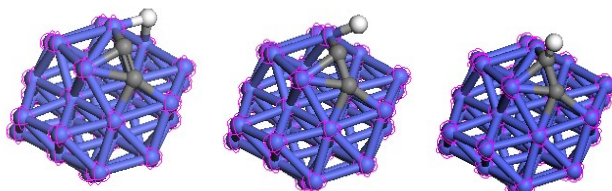
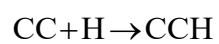
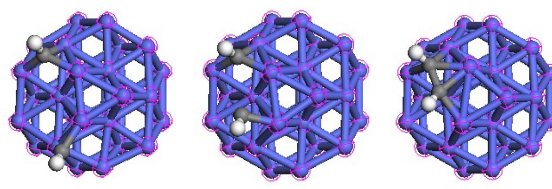
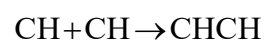
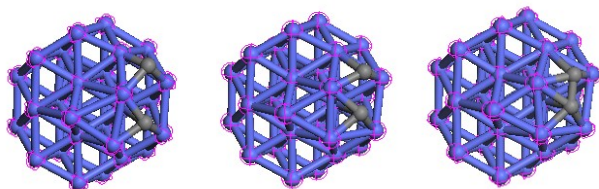
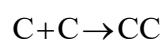


Fig S8. Chain growth of hydrocarbons in C-C reaction on Co-30 cluster (Co atom: blue, C atom: gray, H atom: white).



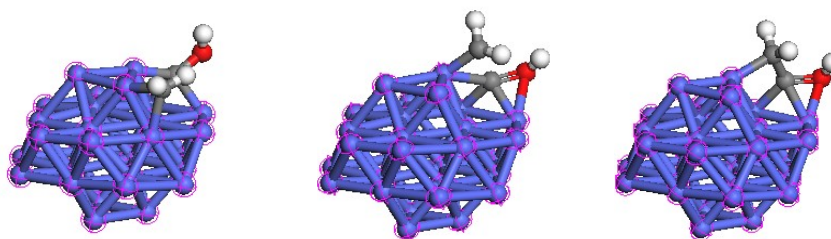
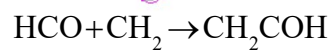
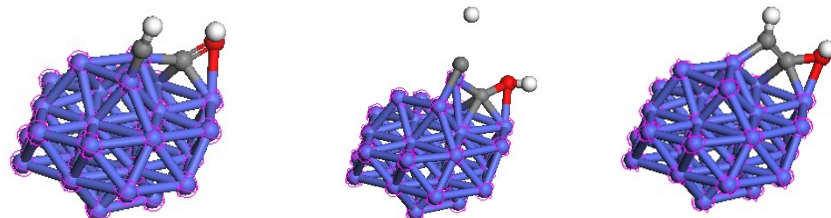
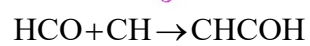
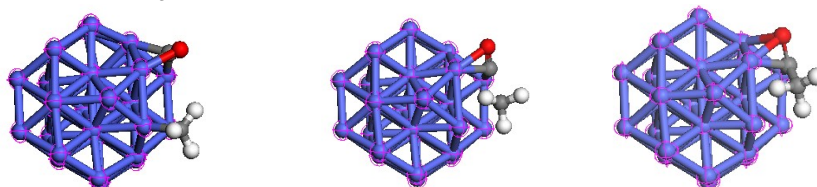
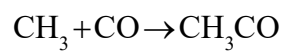
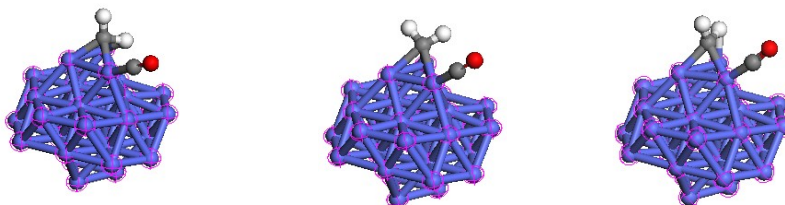
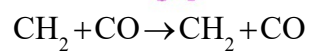
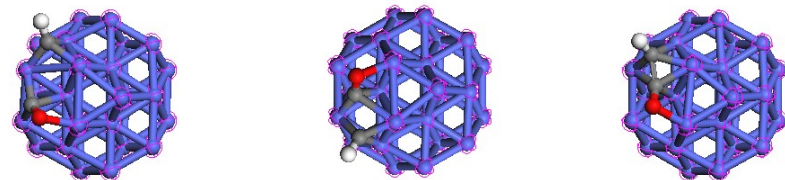
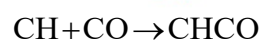
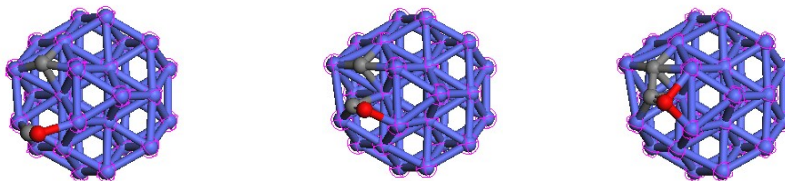
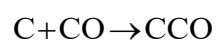


Fig S9. Chain growth of hydrocarbons in C-CO reaction on Co-30 cluster (Co atom: blue, C atom: gray, H atom: white, O atom: red).

Table S1. The adsorption energy ( $E_a$ , eV) of  $C_1$  species on Co-10, Co-18 and Co-30 clusters.

	Co-10	Co-18	Co-30
CH	-6.34	-8.37	-18.89
CH <sub>2</sub>	-5.24	-6.01	-17.13
CH <sub>3</sub>	-2.63	-3.60	-8.22
CH <sub>4</sub>	0.049	-0.88	-5.11

Table S2. C-C bond length ( $d_{C-C}$ , Å), C-O bond length ( $d_{C-O}$ , Å), Barrier energy ( $E_b$ , eV), Reaction energy ( $\Delta E_r$ , eV) Effective barrier energy ( $E_{eff}$ , eV) of formation hydrocarbon species on Co-10clusters.

Reaction	$d_{C-C}$ (Å)	$d_{C-O}$ (Å)	$E_b$ (eV)	$\Delta E_r$ (eV)	$E_{eff}$ (eV)
C+C	1.35		2.16	0.2	4.02
C+CH	1.34		1.23	-0.69	2.75
C+CH <sub>2</sub>	1.39		1.58	-1.86	1.92
C+CH <sub>3</sub>	1.48		1.09	-1.1	1.43
CH+CH	1.40		2.24	-0.22	3.43
CH+CH <sub>2</sub>	1.43		1.82	0.05	2.47
CH+CH <sub>3</sub>	1.50		0.99	0.48	0.99
CH <sub>2</sub> +CH <sub>2</sub>	--		1.33	-0.78	1.43
CH <sub>2</sub> +CH <sub>3</sub>	--		4.21	1.66	3.67
C+CO	1.28	1.40	1.74	1.13	2.07
CH+CO	1.43	1.22	1.34	1.01	1.34
CH <sub>2</sub> +CO	--	--	0.87	-0.05	0.32
CH <sub>3</sub> +CO	--	--	0.5	0.17	-0.14
CH+CHO	1.42	1.35	1.07	-1.76	1.07

Table S3. C-C bond length ( $d_{C-C}$ , Å), C-O bond length ( $d_{C-O}$ , Å), Barrier energy ( $E_b$ , eV), Reaction energy ( $\Delta E_r$ , eV) Effective barrier energy ( $E_{eff}$ , eV) of formation hydrocarbon species on Co-18 clusters.

Reaction	$d_{C-C}$ (Å)	$d_{C-O}$ (Å)	$E_b$ (eV)	$\Delta E_r$ (eV)	$E_{eff}$ (eV)
C+C	1.37		2.99	1.88	1.82
C+CH	1.39		1.71	0.51	0.41
C+CH <sub>2</sub>	1.44		1.44	1.23	0.98
C+CH <sub>3</sub>	1.48		0.42	-0.42	0.42
CH+CH	1.43		0.63	-0.44	-0.8
CH+CH <sub>2</sub>	--		1.78	0.14	1.19
CH+CH <sub>3</sub>	--		1.33	0.37	1.2
CH <sub>2</sub> +CH <sub>2</sub>	1.48		2.67	0.57	2.91
CH <sub>2</sub> +CH <sub>3</sub>	1.53		2.00	-0.09	2.71
C+CO	1.41	1.23	0.66	-1.93	0.66
CH+CO	1.44	1.29	1.72	1.26	1.59
CH <sub>2</sub> +CO	1.49	1.33	1.49	0.64	2.19
CH <sub>3</sub> +CO	1.52	1.33	2.26	1.17	3.43
CH+CHO	1.43	1.30	0.67	0.08	0.67
CH <sub>2</sub> +CHO	1.43	1.30	0.93	-0.12	1.77
CH <sub>3</sub> +CHO	--	--	0.83	0.55	2.13

Table S4. C-C bond length ( $d_{C-C}$ , Å), C-O bond length ( $d_{C-O}$ , Å), Barrier energy ( $E_b$ , eV), Reaction energy ( $\Delta E_r$ , eV) Effective barrier energy ( $E_{eff}$ , eV) of formation hydrocarbon species on Co-30clusters.

Reaction	$d_{C-C}$ (Å)	$d_{C-O}$ (Å)	$E_b$ (eV)	$\Delta E_r$ (eV)	$E_{eff}$ (eV)
C+C	1.46		0.48	0.02	0.48
C+CH	1.42		0.67	-0.34	0.53
C+CH <sub>2</sub>	1.39		3.50	0.91	3.90
C+CH <sub>3</sub>	--	s	1.28	0.11	0.94
CH+CH	1.45		1.65	-0.22	1.38
CH+CH <sub>2</sub>	1.47		1.52	0.42	1.79
CH+CH <sub>3</sub>	1.51		2.09	0.61	1.61
CH <sub>2</sub> +CH <sub>2</sub>	1.47		1.57	-0.12	2.38
CH <sub>2</sub> +CH <sub>3</sub>	--		2.27	-0.3	2.33
C+CO	1.45	1.37	1.78	0.85	1.91
CH+CO	1.47	1.33	0.97	0.41	0.97
CH <sub>2</sub> +CO	--	--	0.7	0.06	1.23
CH <sub>3</sub> +CO	1.52	1.35	2.92	1.59	2.71
CH+HCO	1.37		6.05	-0.57	5.91
CH <sub>2</sub> +HCO	1.47		1.8	0.34	2.2