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

Supporting information for

Insights into the Mechanism of Carbon Chain Growth on Zeolite-based Fischer-Tropsch Bifunctional Co/Y Catalyst

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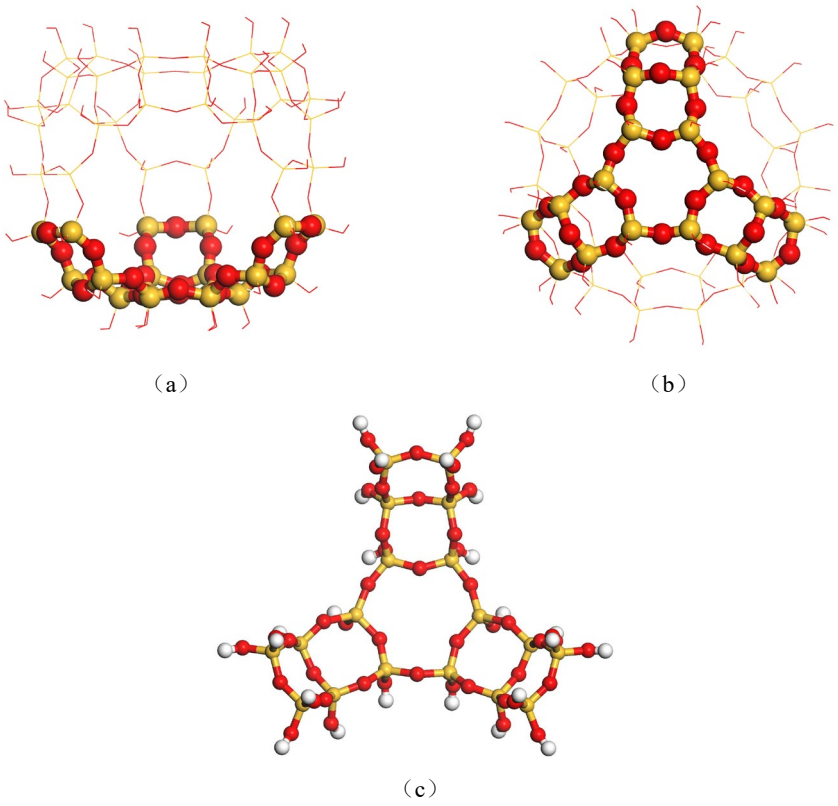


Yellow: Si atom; red: O atom; white: H atom

Figure S1. Structure diagram of Y-zeolite 18T clusters model (a) Super cage left view; (b) Super cage top view; (c) 18T clusters top view

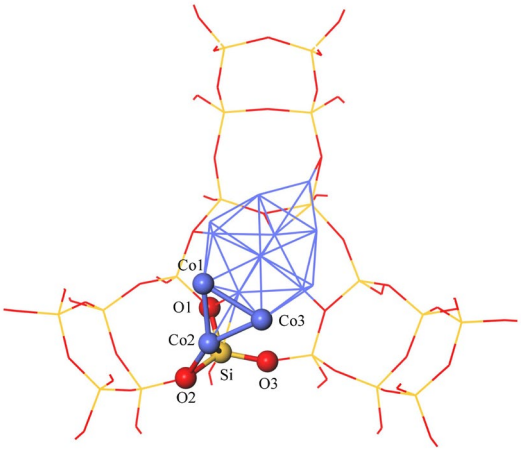


Figure S2. Key parameter related atomic label of Co/Y

Table S1. Bond length of Y-zeolite and clusters before and after Y loaded (based on Figure S2)

Type of the bond	Bond length (Å)	
	Before	After
D(Si-O1)	1.66	1.78
D(Si-O2)	1.68	1.85
D(Si-O3)	1.69	1.75
D(Co1-Co2)	2.26	2.31
D(Co1-Co3)	2.51	2.50
D(Co2-Co3)	2.28	2.27
D(Co2-Si)	-	2.42
D(Co2-O2)	-	2.00

Table S2. Some key angle parameters before and after Y loaded (based on Figure S2)

Type of the bond	Bond Angle (°)	
	Before	After
A(O1-Si-O2)	109.7	113.6
A(O1-Si-O3)	111.9	121.3
A(O2-Si-O3)	111.6	122.2
A(Si-O1-Si)	151.8	150.6
A(Si-O2-Si)	140.2	143.4
A(Si-O3-Si)	152.6	157.9
A(Co1-Co2-Co3)	67.2	66.3
A(Co1-Co3-Co2)	56.1	57.7
A(Co2-Co1-Co3)	56.7	56.0

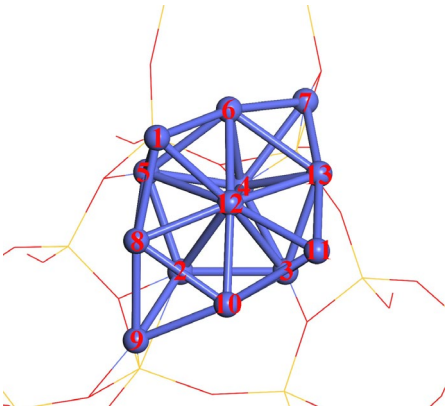


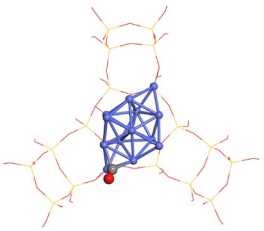
Figure S3. Co atom labeling of Mulliken charge distribution

Table S3. Mulliken charge population of Co atom in Co_{13} and Co/xY (based on Figure S3)

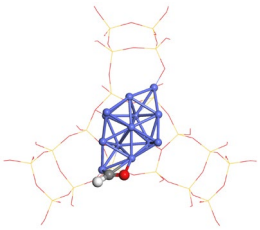
Number	Mulliken charge(|e|)	
	Co_{13}	Co/Y
1	-0.247	-0.382
2	0.100	0.448
3	-0.053	0.176
4	0.110	0.458
5	-0.055	0.094
6	-0.014	-0.107
7	-0.358	-0.372
8	-0.011	-0.116
9	-0.358	-0.348
10	-0.010	-0.086
11	-0.247	-0.389
12	1.153	0.862
13	-0.010	-0.074
Total	0	0.164

Table S4. Charge changes of Co atoms connected with the species during the reaction

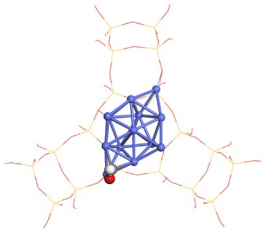
Species	The numbers of Co connected with the species	Sum of Co-charges in Co_{13} (e)	Sum of Co-charges in Co/Y (e)	Charge changes (e)
CO	Co8+Co9+Co10	-0.379	-0.55	-0.171
HCO	Co9+Co10	-0.368	-0.434	-0.066
COH	Co8+Co9+Co10	-0.379	-0.55	-0.171
H_2CO	Co1+Co8	-0.258	-0.498	-0.24
CH	Co8+Co9+Co10	-0.379	-0.55	-0.171
CH_2	Co8+Co9+Co10	-0.379	-0.55	-0.171
CH_3	Co8+Co9+Co10	-0.379	-0.55	-0.171
CH_4	-	-	-	-
CHCH	Co1+Co8	-0.258	-0.498	-0.24
$CHCH_2$	Co1+Co8	-0.258	-0.498	-0.24
$CHCH_3$	Co8+Co9	-0.369	-0.464	-0.095
CH_2CH_2	Co1+Co8	-0.258	-0.498	-0.24
CH_2CH_3	Co8+Co9	-0.369	-0.464	-0.095
CH_3CH_3	-	-	-	-
CHCHCH	Co8+Co9+Co10	-0.379	-0.55	-0.171
$CH_2CH_2CH_2$	Co8+Co9+Co10	-0.379	-0.55	-0.171
CHCHCHCH	Co1+Co8+Co9+Co10	-0.626	-0.932	-0.306
$CH_2CH_2CH_2CH_2$	Co1+Co8+Co9	-0.616	-0.846	-0.23
$CHCH_2CH_3$	Co8+Co9	-0.369	-0.464	-0.095
$CH_2CH_2CH_3$	Co8+Co9	-0.369	-0.464	-0.095
$CHCH_2CH_2CH_3$	Co8+Co9	-0.369	-0.464	-0.095
$CH_2CH_2CH_2CH_3$	Co8+Co9	-0.369	-0.464	-0.095



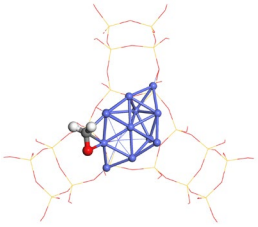
CO



HCO

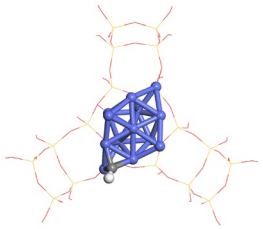


COH

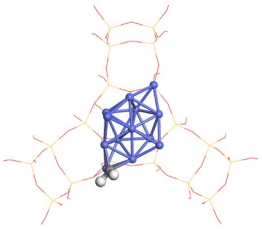


H_2CO

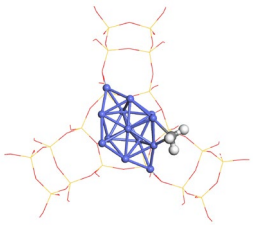
（a）H-assisted in CO dissociation



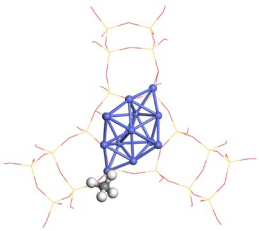
CH



CH_2

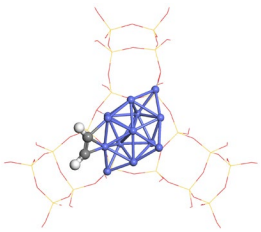


CH_3

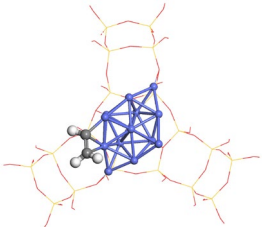


CH_4

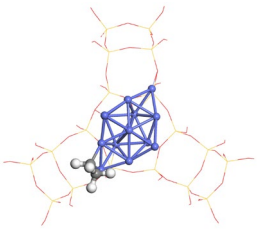
（b）C_1 hydrogenation



CHCH



$CHCH_2$



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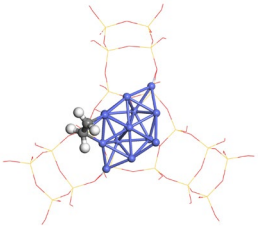
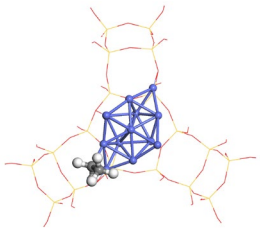
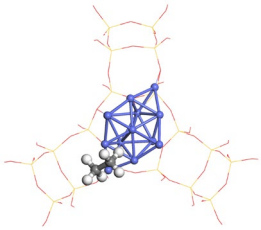


CH_2CH_2

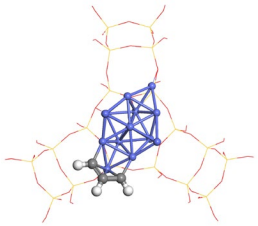


CH_2CH_3

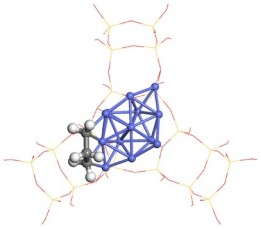


CH_3CH_3

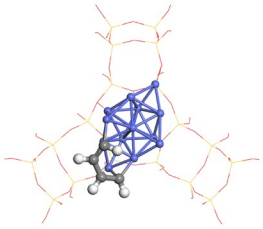
（c）CH_x-CH_x coupling



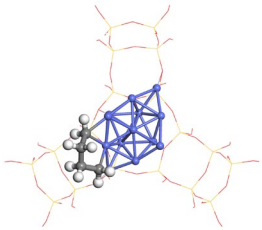
CHCHCH



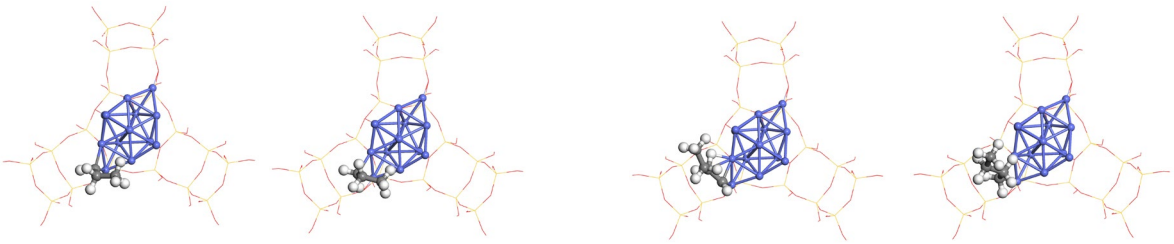
$CH_2CH_2CH_2$



CHCHCHCH



$CH_2CH_2CH_2CH_2$



$CHCH_2CH_3$ $CH_2CH_2CH_3$ $CHCH_2CH_2CH_3$ $CH_2CH_2CH_2CH_3$

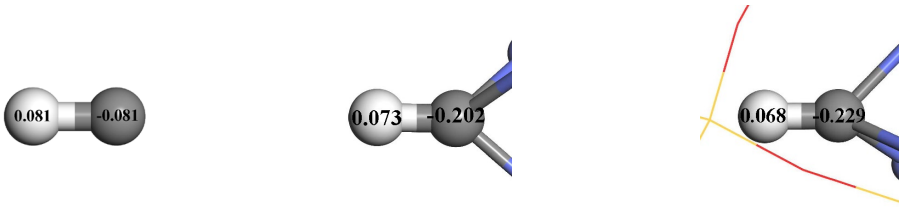
（d）C_2~C_4 growth

Gray: C atom; white: H atom; blue: Co atom

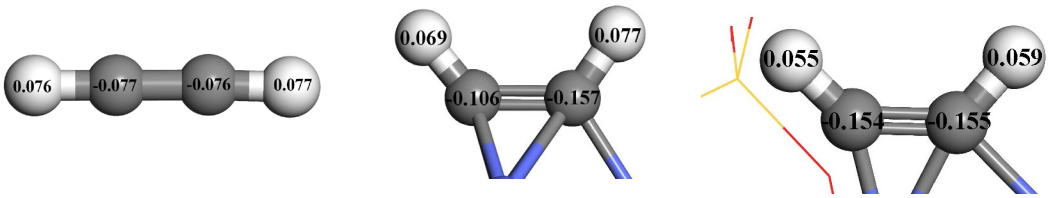
Figure S4. Single adsorption stable adsorption configuration of related species on Co/Y

Table S5. Stable adsorption configuration and Co-C bond length of related species on Co/Y

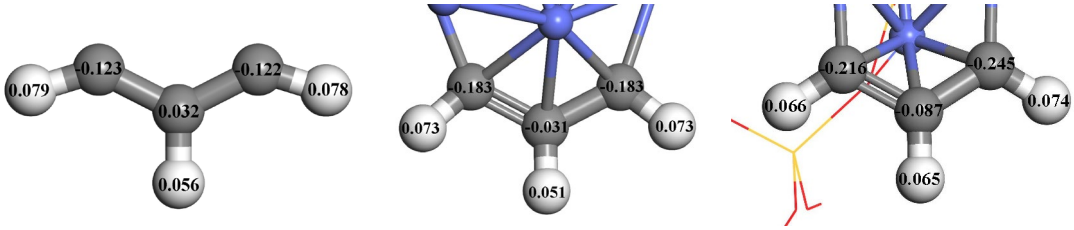
Reaction	Species	Stable adsorption configuration	Bond length (Å)
H-assisted in CO dissociation	CO	hollow	2.033、1.943、1.879
	HCO	bridge	2.257、1.787
	COH	hollow	1.861、1.909、1.826
	H_2CO	bridge	2.100、2.070
C_1 hydrogenation	CH	hollow	1.894、1.855、1.835
	CH_2	hollow	1.959、1.999、1.934
	CH_3	hollow	2.178、2.191、2.043
	CH_4	-	-
CH_x-CH_x coupling	CHCH	bridge (Horizontal)	2.058、1.955、1.847
	$CHCH_2$	bridge (Horizontal)	1.928、2.022、2.090
	$CHCH_3$	bridge (Vertical)	1.887、1.925
	CH_2CH_2	bridge (Horizontal)	1.977、2.083、2.088
	CH_2CH_3	bridge (Vertical)	1.989、2.189
	CH_3CH_3	-	-
C_2~C_4 growth	CHCHCH	bridge (Horizontal)	1.898、1.970、2.156、2.048、1.905
	$CH_2CH_2CH_2$	bridge (Horizontal)	2.035、2.097、2.263、2.168、2.039
	CHCHCHCH	bridge (Horizontal)	1.953、1.996、2.057、1.968、1.925
	$CH_2CH_2CH_2CH_2$	bridge (Horizontal)	2.103、2.058、1.998、2.250
Steric hindrance	$CHCH_2CH_3$	bridge (Vertical)	2.144、2.173
	$CH_2CH_2CH_3$	bridge (Vertical)	1.990、2.197
	$CHCH_2CH_2CH_3$	bridge (Vertical)	1.932、1.884
	$CH_2CH_2CH_2CH_3$	bridge (Vertical)	2.005、2.152



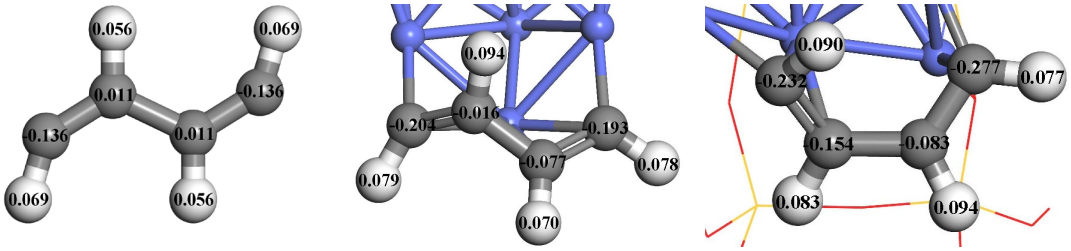
(a) CH



(b) CHCH

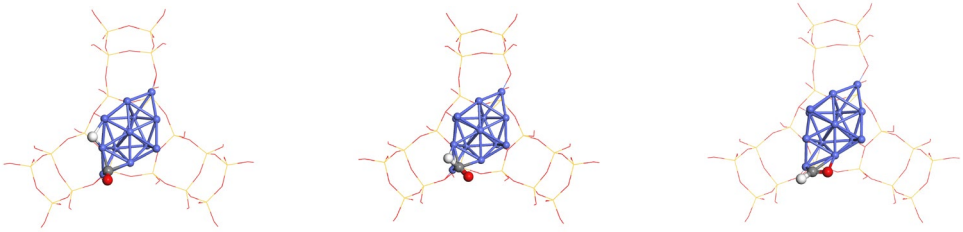


(c) CHCHCH

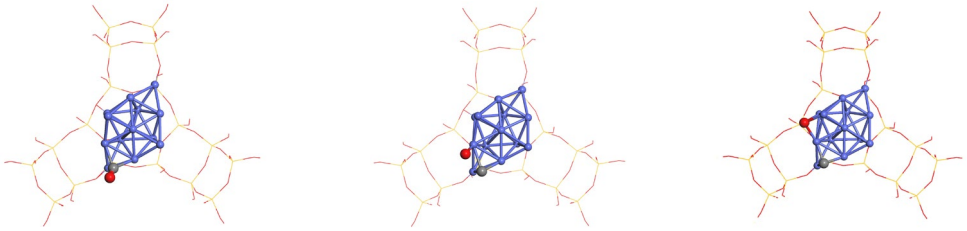


(d) CHCHCHCH

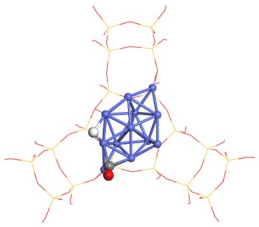
Figure S5. Mulliken population maps of key species on vacuum, Co_{13} and Co / Y (from left to right)



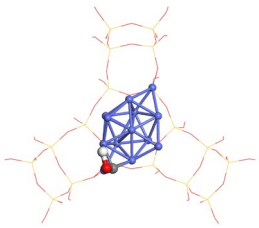
CO+H TS-1 HCO



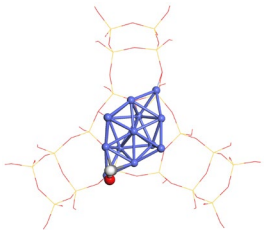
CO TS-2 C+O



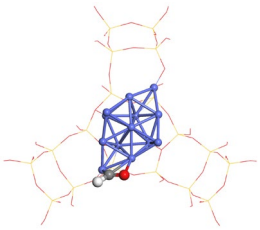
CO+H



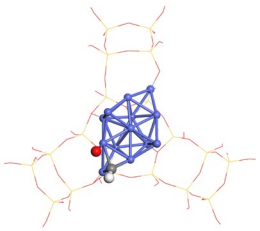
TS-3



COH



HCO



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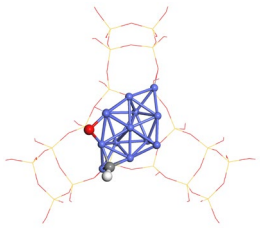
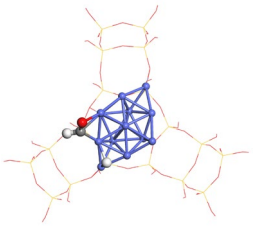
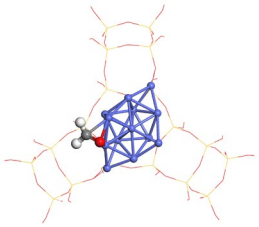


CH+O



HCO+H



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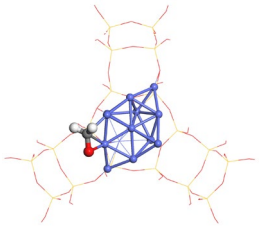
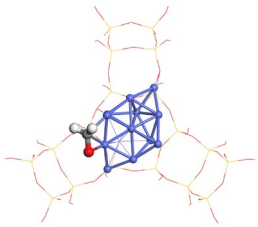


H_2CO



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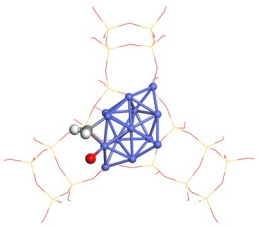

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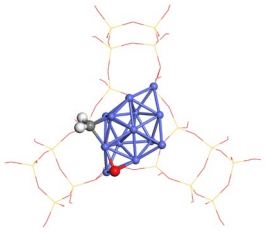
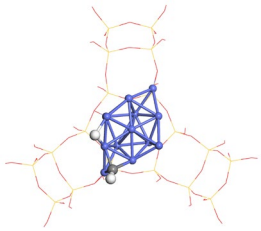
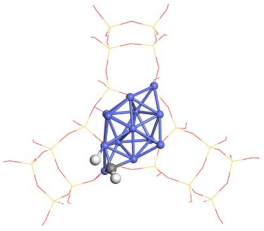


CH_2+O



CH+H



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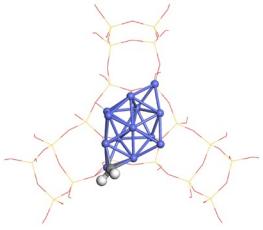
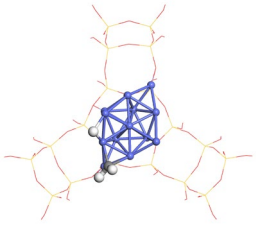
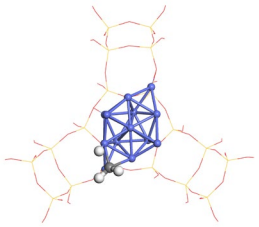


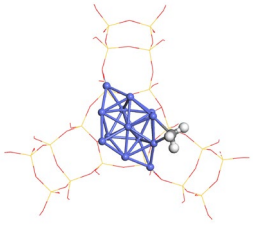
CH_2



CH_2+H



TS-8



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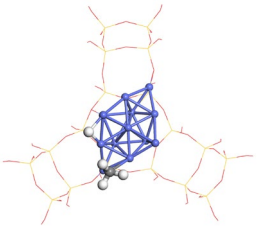
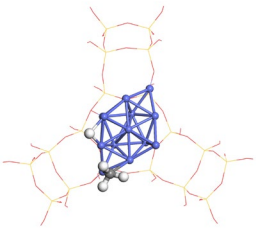
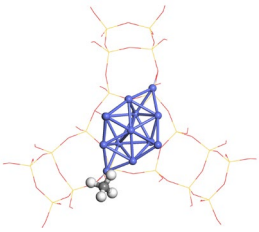


CH_3+H



TS-9



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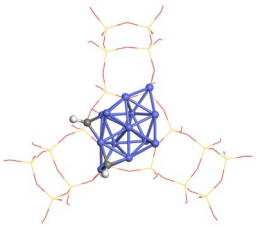
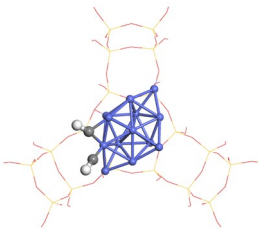
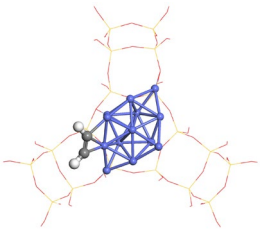


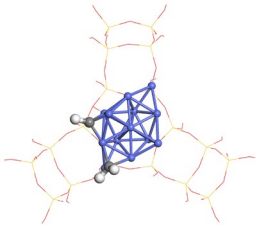
CH+CH



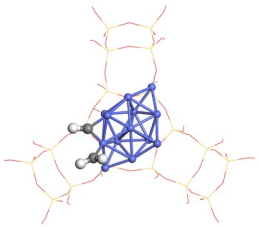
TS-10



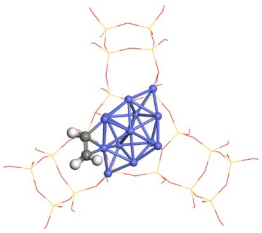
CHCH



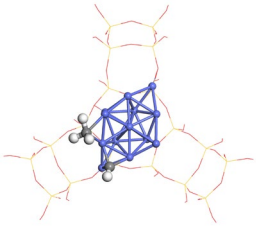
CH+CH_2



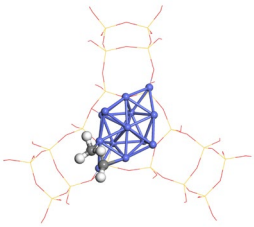
TS-11



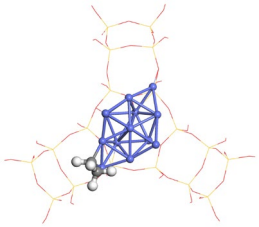
$CHCH_2$



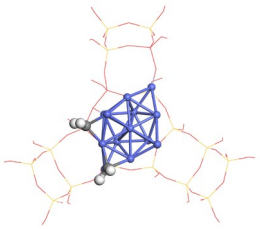
CH+CH_3



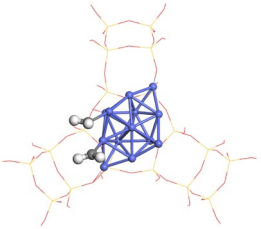
TS-12



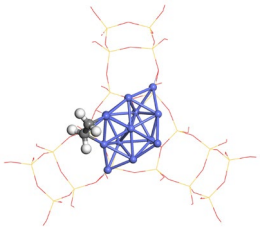
$CHCH_3$



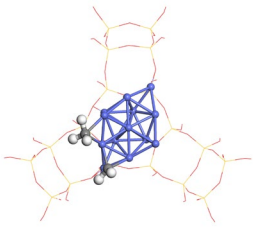
CH_2+CH_2



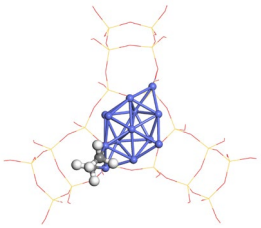
TS-13



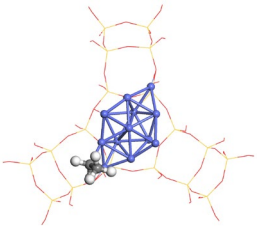
CH_2CH_2



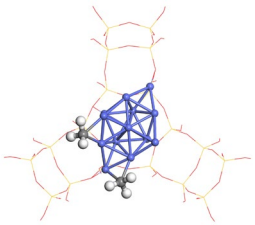
CH_2+CH_3



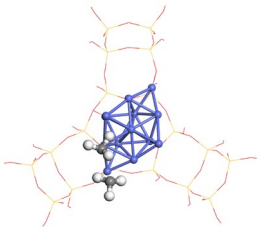
TS-14



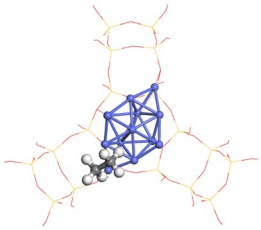
CH_2CH_3



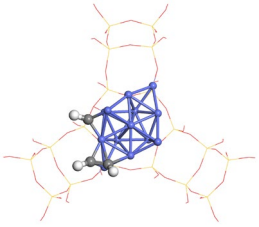
CH_3+CH_3



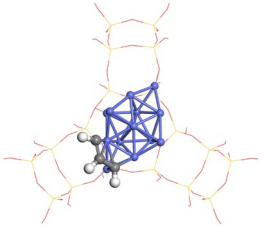
TS-15



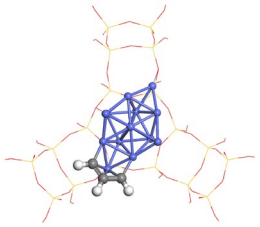
CH_3CH_3



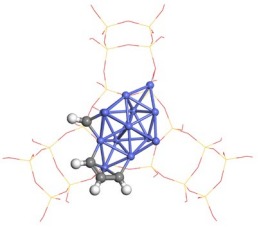
CHCH+CH



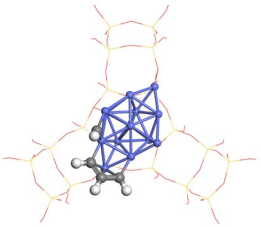
TS-16



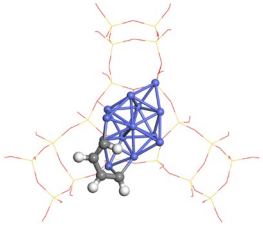
CHCHCH



CHCHCH+CH



TS-17



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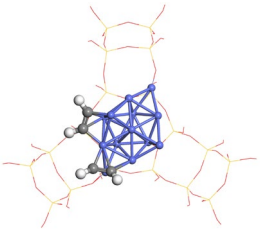
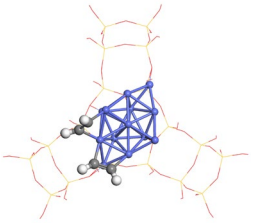
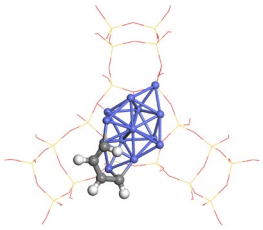


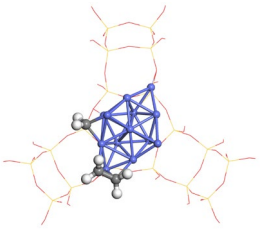
CHCH+CHCH



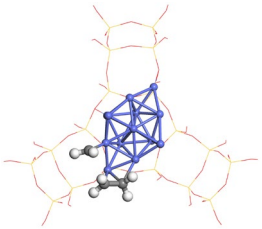
TS-18



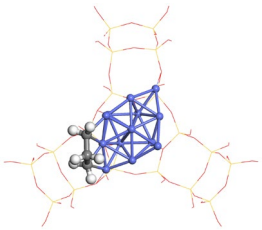
CHCHCHCH



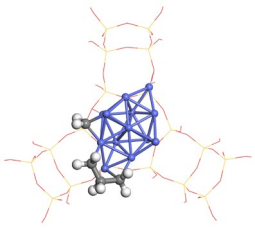
$CH_2CH_2+CH_2$



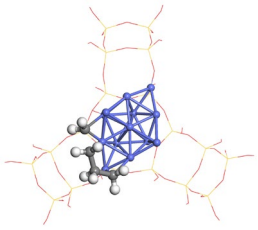
TS-19



$CH_2CH_2CH_2$



$CH_2CH_2CH_2+CH_2$



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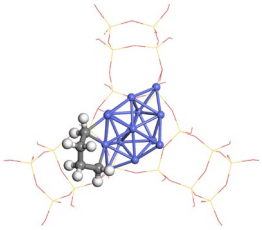
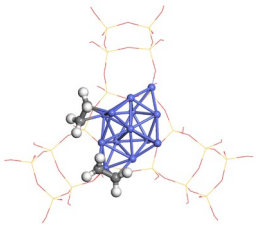
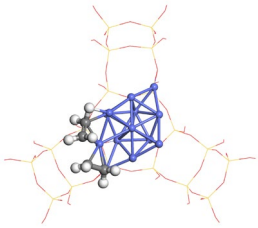


$CH_2CH_2CH_2CH_2$



$CH_2CH_2+CH_2CH_2$



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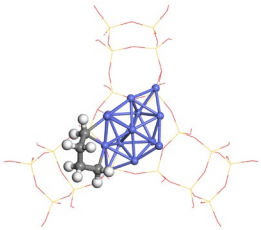
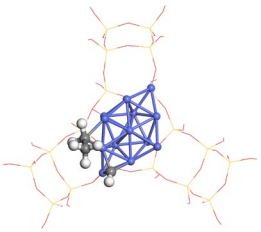
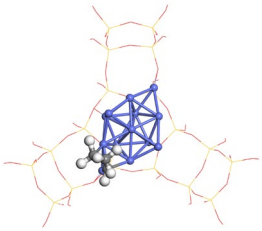


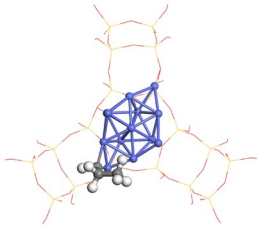
$CH_2CH_2CH_2CH_2$



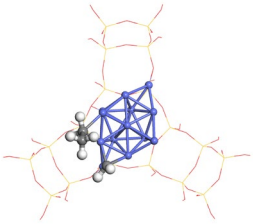
CH_2CH_3+CH



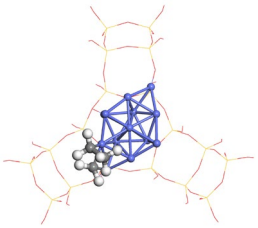
TS-22



$CHCH_2CH_3$



$CH_2CH_3+CH_2$



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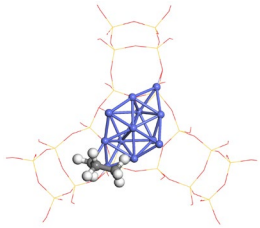
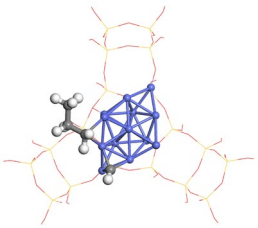
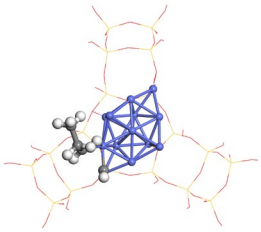


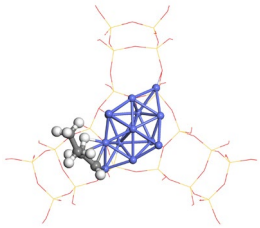
$CH_2CH_2CH_3$



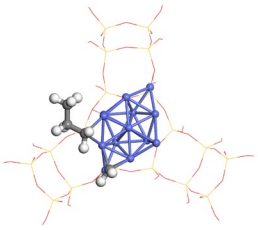
$CH_2CH_2CH_3+CH$



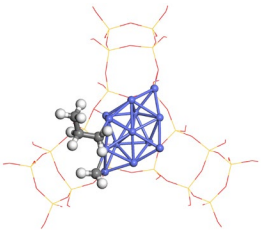
TS-24



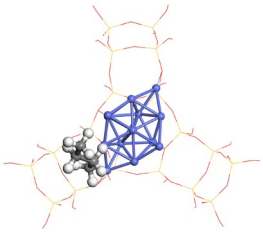
$CHCH_2CH_2CH_3$



$CH_2CH_2CH_3+CH_2$



TS-25



$CH_2CH_2CH_2CH_3$

Figure S6. Stable configuration of the initial state, transition state and end state of the reaction on Co/Y