**Supporting Information**

# First-Principles Study of Structure Sensitivity of Chain Growth and Selectivity in Fischer-Tropsch Synthesis on HCP Cobalt Catalysts

*Hai-Yan Su[a], Yong-Hui Zhao[b], Jin-Xun Liu[a], Keju Sun[c,*] and Wei-Xue Li[a,d,*]*

[a]State Key Laboratory of Molecular Reaction Dynamics, State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Science, Dalian 116023, China

[b]CAS Key Laboratory of Low-Carbon Conversion Science and Engineering, Shanghai Advanced Research Institute, Chinese Academy of Science, Shanghai 201210, China

[c]Key Laboratory of Applied Chemistry, College of Environmental and Chemical Engineering, Yanshan University, Qinhuangdao 066004, China

[d]Department of Chemical Physics, College of Chemistry and Materials Science, Hefei National Laboratory for Physical Sciences at the Microscale, iChEM, CAS Center for Excellence in Nanoscience, University of Science and Technology of China, Hefei 230026, China

*E-mail: wxli70@ustc.edu.cn; kjsun@ysu.edu.cn

## S1. Optimized configurations for various intermediates adsorption on Co (0001), stepped Co and Co $(10\bar{1}1)$

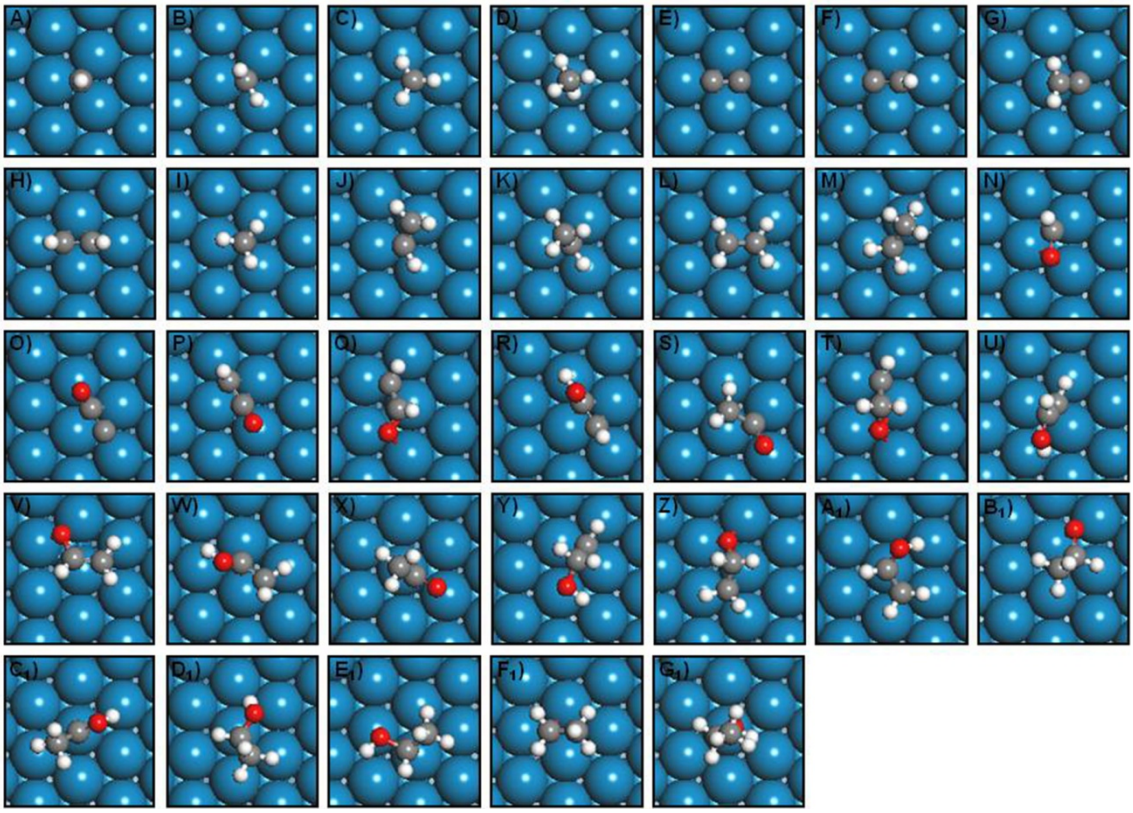
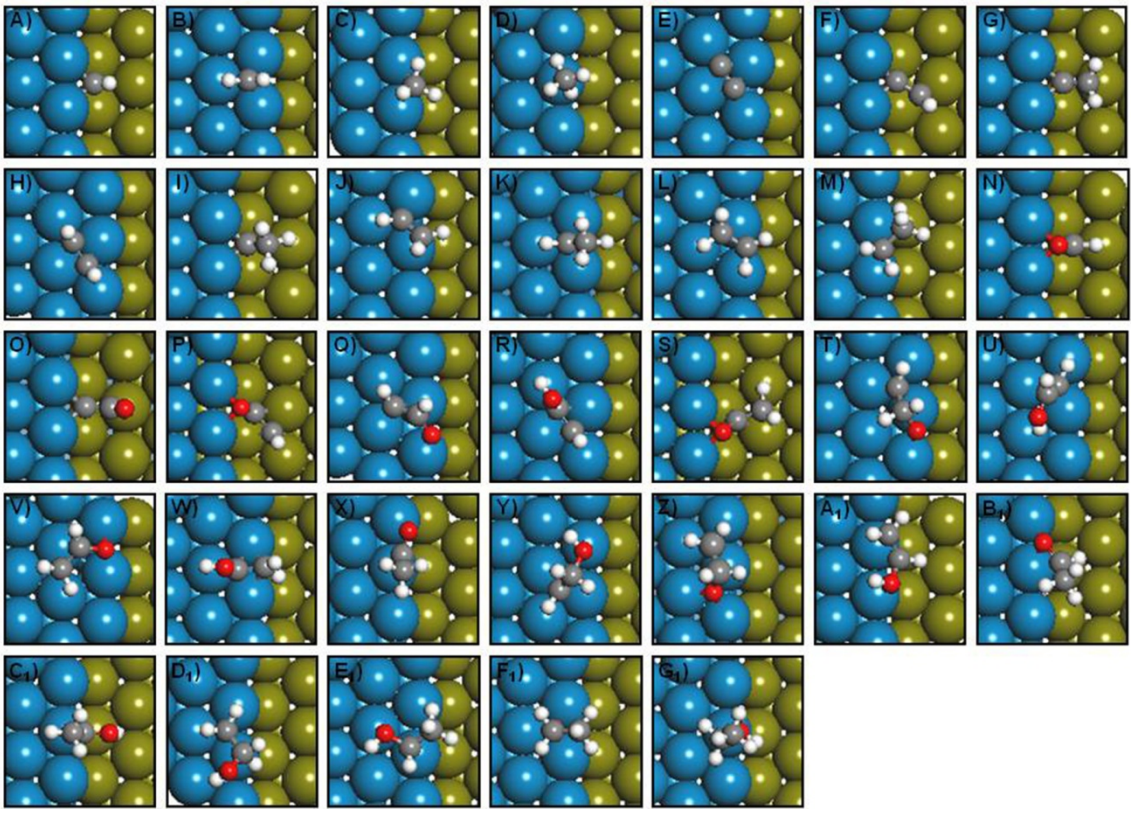



**Figure S1.** Optimized configurations for (A) CH (B) $CH_2$ (C) $CH_3$ (D) $CH_4$ (E) CC (F) CCH (G) $CCH_2$ (H) CHCH (I) $CCH_3$ (J) $CHCH_2$ (K) $CHCH_3$ (L) $CH_2CH_2$ (M) $CH_2CH_3$ (N) HCO (O) CCO (P) CHCO (Q) CHCHO (R) CHCOH (S) $CH_2CO$ (T) $CHCH_2O$ (U) CHCHOH (V) $CH_2CHO$ (W) $CH_2COH$ (X) $CH_3CO$ (Y) $CHCH_2OH$ (Z) $CH_2CH_2O$ ($A_1$) $CH_2CHOH$ ($B_1$) $CH_3CHO$ ($C_1$) $CH_3COH$ ($D_1$) $CH_2CH_2OH$ ($E_1$) $CH_3CHOH$ ($F_1$) $CH_3CH_2O$ ($G_1$) $CH_3CH_2OH$ adsorption on Co (0001). The blue, grey, red and white balls represent Co, C, O and H atom, respectively.

Stepped Co




Co $(10\bar{1}1)$

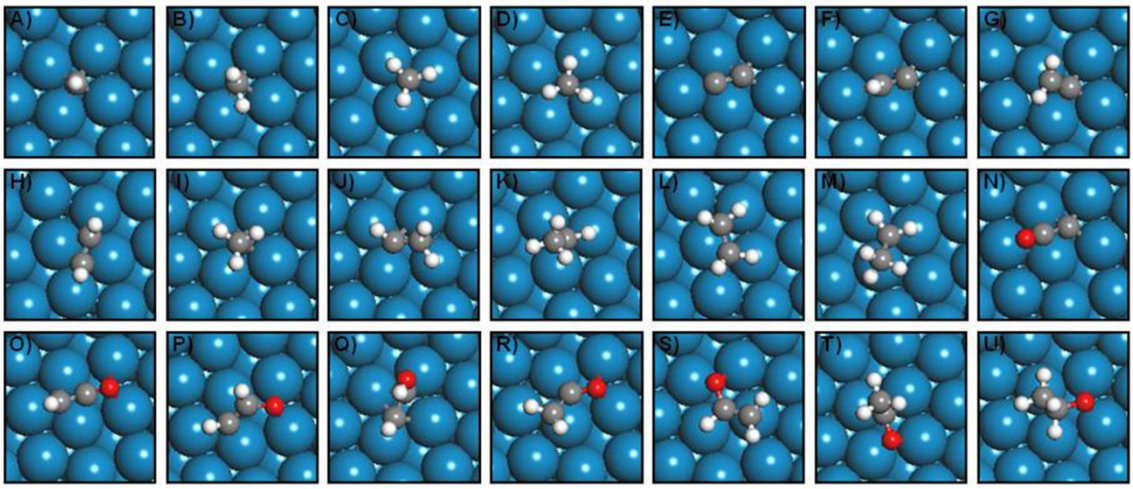
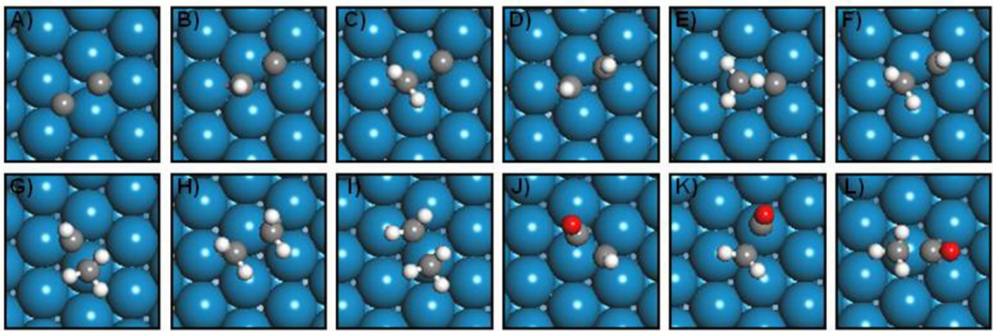


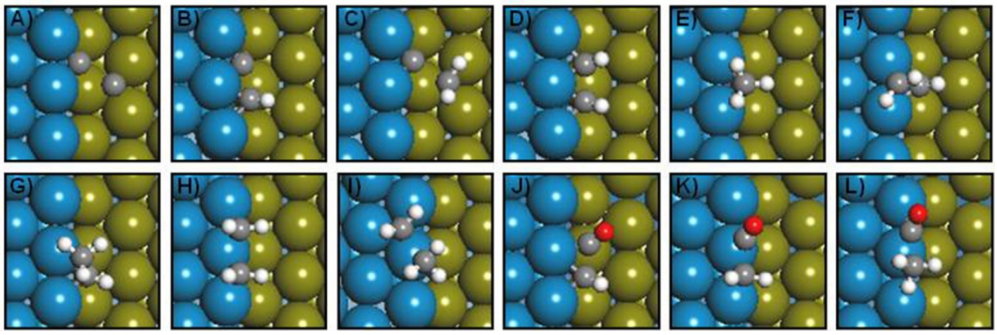

**Figure S2.** Optimized configurations for (A) CH (B) $CH_2$ (C) $CH_3$ (D) $CH_4$ (E) CC (F) CCH (G) $CCH_2$ (H) CHCH (I) $CCH_3$ (J) $CHCH_2$ (K) $CHCH_3$ (L) $CH_2CH_2$ (M) $CH_2CH_3$ (N) HCO/CCO (O) CCO/CHCO (P) CHCO/CHCHO (Q) CHCHO/CHCOH (R) CHCOH/$CH_2$CO (S) $CH_2CO/CH_2CHO$ (T) $CHCH_2O/CH_3CO$ (U) $CHCHOH/CH_3CHO$ (V) $CH_2CHO$ (W) $CH_2COH$ (X) $CH_3CO$ (Y) $CHCH_2OH$ (Z) $CH_2CH_2O$ ($A_1$) $CH_2CHOH$ ($B_1$) $CH_3CHO$ ($C_1$) $CH_3COH$ ($D_1$) $CH_2CH_2OH$ ($E_1$) $CH_3CHOH$ ($F_1$) $CH_3CH_2O$ ($G_1$) $CH_3CH_2OH$ adsorption on the stepped Co and Co $(10\bar{1}1)$. From (N) on, the former/latter structure represents that on stepped Co and Co $(10\bar{1}1)$, respectively. The blue, dark yellow, grey, red and white balls represent upper Co, lower Co, C, O and H atom, respectively.

**S2. Optimized configurations at the transition states of various elementary reactions on Co (0001), stepped Co and Co $(10\bar{1}1)$**

Co (0001)




Stepped Co




Co $(10\bar{1}1)$

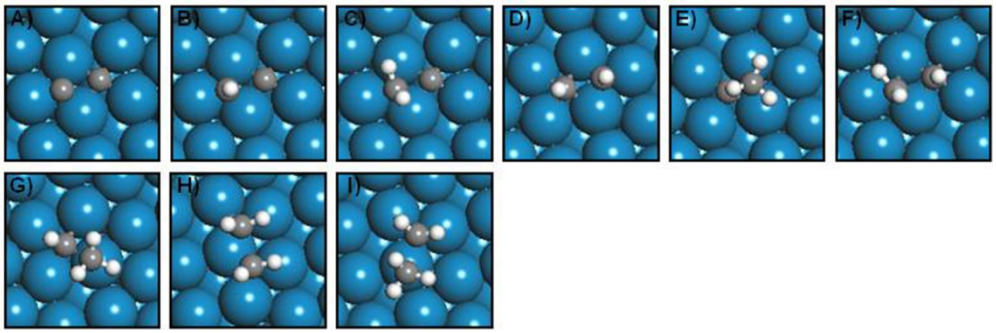
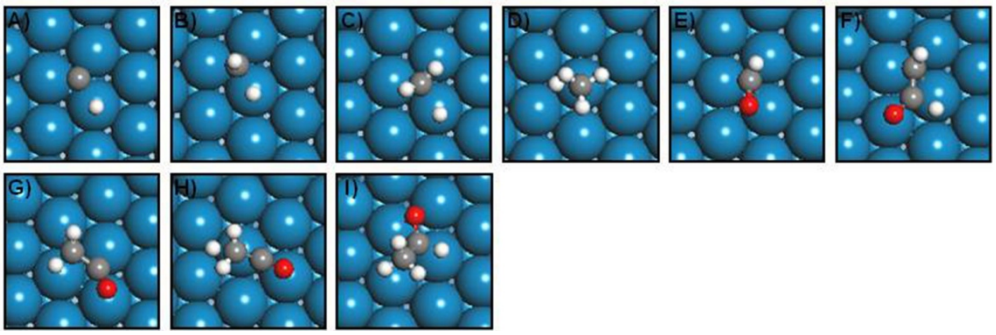
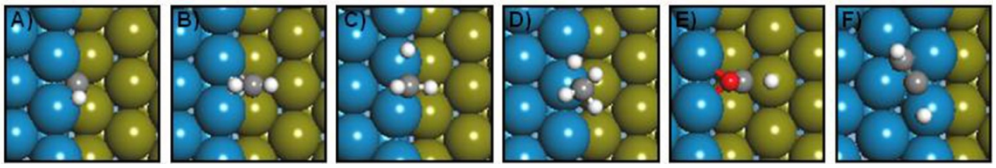



**Figure S3.** Optimized configurations at the transition states of (A) C+C (B) C+CH (C) C+$CH_2$ (D) CH+CH (E) C+$CH_3$ (F) CH+$CH_2$ (G) CH+$CH_3$ (H) $CH_2$+$CH_2$ (I) $CH_2$+$CH_3$ (J) CH+CO (K) $CH_2$+CO (L) $CH_3$+CO on Co (0001), stepped Co and Co $(10\bar{1}1)$.

Co (0001)




Stepped Co




Co $(10\bar{1}1)$

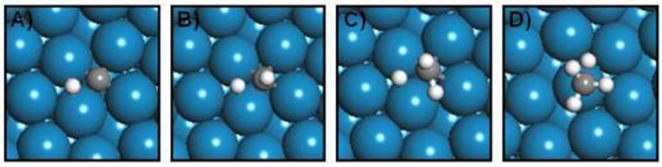



**Figure S4.** Optimized configurations at the transition states of (A) C+H (B) CH+H (C) $CH_2$+H (D) $CH_3$+H (E) CO+H→HCO (F) Co (0001): CHCO+H→CHCHO; stepped Co: CHC+H→CHCH (G) CHCO+H→$CH_2$CO (H) $CH_2$CO+H→$CH_3$CO (I) $CH_3$CO+H→$CH_3$CHO on Co (0001), stepped Co and Co $(10\bar{1}1)$.

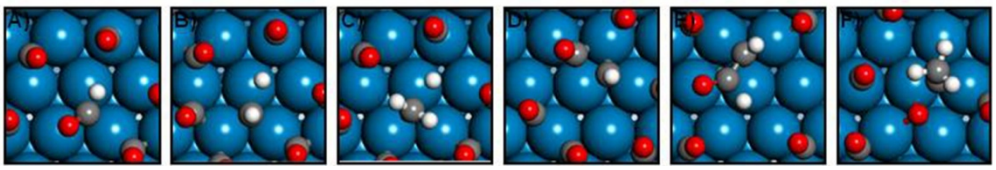



**Figure S5.** Optimized configurations at the transition states of (A) CO+H→HCO (B) CH+H (C) $CH_2$+H (D) CH+CO (E) CHCO+H→CHCHO (F) $CH_3$CO→$CH_3$C+O at a constant C coverage of 7/12 ML on Co (0001).

## S3. Adsorption energies and sites of various intermediates and activation energies, reaction heat and geometric information at the transition states of various elementary reactions on Co (0001), stepped Co and Co $(10\bar{1}1)$

**Table S1.** Calculated adsorption energies ($E_{ADS}$, in eV) and favorable adsorption sites of various intermediates on Co (0001), stepped Co and Co $(10\bar{1}1)$. The order of C atom in "Site" corresponds to that in "Species" unless $\alpha$ or $\beta$-C is indicated.

| Species | (0001) | | Step | | $(10\bar{1}1)$ | |
|---|---|---|---|---|---|---|
| | $E_{ADS}$ | Site | $E_{ADS}$ | Site | $E_{ADS}$ | Site |
| H | -0.53 | fcc | -0.52 | hcp | -0.59 | fcc |
| O | -2.62 | hcp | -2.86 | hcp | -3.02 | four-fold |
| C | -6.88 | hcp | -7.64 | four-fold | -8.15 | four-fold |
| CO | -1.67 | hcp | -1.83 | hcp | -1.85 | four-fold |
| HCO | -2.22 | $C_{bri}$-$O_{bri}$ | -2.83 | $C_{hcp}$-$O_{bri}$ | | |
| CH | -6.30 | hcp | -6.62 | four-fold | -7.02 | four-fold |
| $CH_2$ | -3.98 | hcp | -4.11 | hcp | -4.37 | four-fold |
| $CH_3$ | -1.97 | fcc | -2.18 | bri | -2.10 | fcc |
| $CH_4$ | -0.02 | top | -0.01 | top | -0.02 | four-fold |
| CCO | -4.79 | $C_{hcp}$-$C_{bri}$ | -5.32 | $C_{four\text{-}fold}$-$C_{top}$ | -5.63 | $C_{four\text{-}fold}$-$C_{bri}$ |
| CHCO | -3.42 | $C_{fcc}$-$C_{hcp}$ | -3.74 | $C_{fcc}$-$C_{bri}$-$O_{bri}$ | -3.81 | $C_{hcp}$-$C_{bri}$-$O_{bri}$ |
| $CH_2CO$ | -1.07 | $C_{top}$-$C_{bri}$-$O_{top}$ | -1.55 | $C_{top}$-$C_{bri}$-$O_{bri}$ | -1.74 | $C_{top}$-$C_{bri}$-$O_{bri}$ |
| CHCHO | -4.31 | $C_{bri}$-$C_{top}$-$O_{bri}$ | -4.69 | $C_{fcc}$-$O_{top}$ | -4.89 | $\beta C_{hcp}$-$O_{bri}$ |
| CHCOH | -2.92 | $C_{hcp}$-$C_{fcc}$ | -2.94 | $C_{hcp}$-$C_{fcc}$ | -2.97 | $C_{bri}$-$C_{bri}$ |
| CHCHOH | -2.91 | $\beta C_{hcp}$ | -3.03 | $\beta C_{hcp}$ | | |
| $CH_3CO$ | -1.99 | $\alpha C_{top}$-$O_{top}$ | -2.33 | $\alpha C_{top}$-$O_{top}$ | -2.60 | $\alpha C_{bri}$-$O_{bri}$ |
| $CH_2CHO$ | -2.31 | $C_{top}$-$C_{top}$-$O_{bri}$ | -2.68 | $C_{top}$-$C_{top}$-$O_{bri}$ | -2.63 | $C_{top}$-$C_{bri}$-$O_{bri}$ |
| $CH_2COH$ | -2.62 | $C_{bri}$-$C_{bri}$ | -2.82 | $C_{top}$-$C_{hcp}$ | | |
| $CHCH_2OH$ | -3.88 | $\beta C_{hcp}$ | -3.92 | $\beta C_{fcc}$ | | |

| | | | | | | |
|---|---|---|---|---|---|---|
| $CH_2CHOH$ | -0.63 | $C_{fcc}$-$C_{top}$ | -1.10 | $C_{top}$-$C_{top}$ | | |
| $CH_3COH$ | -2.34 | $\alpha C_{top}$ | -2.78 | $\alpha C_{top}$ | | |
| $CH_3CHO$ | -0.53 | $\alpha C_{bri}$-$O_{bri}$ | -1.07 | $\alpha C_{top}$-$O_{bri}$ | -0.95 | $\alpha C_{bri}$-$O_{bri}$ |
| $CH_2CH_2OH$ | -1.64 | $\beta C_{fcc}$ | -1.85 | $\beta C_{bri}$ | | |
| $CH_3CH_2O$ | -2.80 | $O_{hcp}$ | -3.02 | $O_{hcp}$ | | |
| $CH_3CHOH$ | -1.23 | $\alpha C_{top}$ | -1.41 | $\alpha C_{top}$ | | |
| $CH_3CH_2OH$ | -0.27 | $O_{top}$ | -0.52 | $O_{top}$ | | |
| CC | -7.27 | $C_{fcc}$-$C_{hcp}$ | -8.10 | $C_{fcc}$-$C_{hcp}$ | -7.94 | $C_{four\text{-}fold}$-$C_{hcp}$ |
| CHC | -5.47 | $C_{fcc}$-$C_{hcp}$ | -5.73 | $C_{bri}$-$C_{four\text{-}fold}$ | -6.16 | $C_{bri}$-$C_{four\text{-}fold}$ |
| $CH_2C$ | -4.13 | $C_{hcp}$ | -4.40 | $C_{top}$-$C_{four\text{-}fold}$ | -4.63 | $C_{bri}$-$C_{four\text{-}fold}$ |
| CHCH | -2.63 | $C_{fcc}$-$C_{hcp}$ | -2.60 | $C_{fcc}$-$C_{hcp}$ | -2.74 | $C_{fcc}$-$C_{hcp}$ |
| $CH_3C$ | -5.48 | $C_{hcp}$ | -5.54 | $C_{four\text{-}fold}$ | -5.95 | $C_{four\text{-}fold}$ |
| $CH_2CH$ | -2.78 | $C_{top}$-$C_{hcp}$ | -3.08 | $C_{top}$-$C_{hcp}$ | -2.93 | $C_{bri}$-$C_{bri}$ |
| $CH_3CH$ | -3.64 | $C_{hcp}$ | -3.76 | $C_{hcp}$ | -3.83 | $C_{fcc}$ |
| $CH_2CH_2$ | -0.77 | $C_{top}$-$C_{hcp}$ | -0.98 | $C_{bri}$-$C_{bri}$ | -0.89 | $C_{bri}$-$C_{bri}$ |
| $CH_3CH_2$ | -1.50 | $C_{hcp}$ | -1.86 | $C_{bri}$ | -1.67 | $C_{fcc}$ |
| $CH_3CH_3$ | -0.01 | $C_{top}$-$C_{hcp}$ | -0.02 | $C_{top}$ | -0.04 | $C_{top}$-$C_{hcp}$ |

**Table S2.** Calculated activation energies ($E_{ACT}$ in eV), reaction heat ($\Delta H$ in eV) and geometric information ($d$ in Å) at the TSs for various elementary reactions on Co (0001), stepped Co and Co $(10\bar{1}1)$. $\Delta H$ is calculated with respected to separate adsorbed states. $E_{ACT}$ in parentheses is with respected to adsorbed CH+CH, C+C and C+C on the three surfaces, respectively.

| Reactions | (0001) | | | Step | | | $(10\bar{1}1)$ | | |
|---|---|---|---|---|---|---|---|---|---|
| | $E_{ACT}$ | $\Delta H$ | $d$ | $E_{ACT}$ | $\Delta H$ | $d$ | $E_{ACT}$ | $\Delta H$ | $d$ |
| **C-O bond scission steps** | | | | | | | | | |
| CO→C+O | 2.35 | 0.67 | 1.83 | 1.37 | -0.18 | 2.10 | 1.20 | -0.83 | 1.75 |
| HCO→CH+O | 0.68 | -0.73 | 1.78 | 0.74 | -0.68 | 1.91 | | | |
| CCO→CC+O | 1.60 | -0.19 | 1.77 | 1.16 | -0.74 | 2.08 | 1.58 | -0.42 | 1.81 |
| CHCO→CHC+O | 1.53 | -0.32 | 1.76 | 0.81 | -0.51 | 2.01 | 1.23 | -1.01 | 1.77 |
| CHCOH→CHC+OH | 1.25 | -0.32 | 2.07 | | | | | | |
| CHCHO→CHCH+O | 0.71 | -0.97 | 1.77 | 0.81 | -0.81 | 1.83 | 0.99 | -0.90 | 1.91 |
| $CH_2CO→CH_2C+O$ | 0.76 | -0.64 | 2.28 | 0.69 | -0.67 | 1.85 | 1.05 | -0.87 | 2.05 |
| $CH_2CHO→CH_2CH+O$ | 1.22 | -0.18 | 1.89 | 1.36 | -0.34 | 1.87 | | | |
| $CH_3CO→CH_3C + O$ | 0.64 | -0.72 | 1.79 | 0.68 | -0.68 | 1.91 | 0.78 | -0.99 | 1.97 |
| $CH_3CHO→CH_3CH+O$ | 0.72 | -0.50 | 1.84 | 0.98 | -0.32 | 1.97 | | | |
| **C-C coupling steps** | | | | | | | | | |
| CH+CO→CHCO | 0.83 | 0.34 | 1.77 | 1.29 | 0.50 | 1.66 | | | |
| $CH_2+CO→CH_2CO$ | 0.60 | 0.54 | 1.77 | 0.62 | 0.34 | 1.80 | | | |
| $CH_3+CO→CH_3CO$ | 1.37 | 0.57 | 1.88 | 1.32 | 0.60 | 1.86 | | | |
| C+C→CC | 1.30(1.94) | -0.46 | 2.01 | 1.78(1.78) | 0.23 | 2.02 | 2.24(2.24) | 1.41 | 1.97 |
| C+CH→CCH | 0.83(1.15) | -0.64 | 1.92 | 1.35(1.46) | 0.18 | 1.81 | 1.37(1.65) | 0.66 | 1.99 |
| $C+CH_2→CCH_2$ | 0.76(1.40) | -0.77 | 2.00 | 0.79(1.39) | -0.15 | 2.02 | 1.34(2.31) | 0.38 | 1.95 |
| $C+CH_3→CCH_3$ | 0.96(1.44) | -0.82 | 2.12 | 0.99(1.34) | 0.10 | 1.99 | 1.13(2.25) | 0.11 | 2.06 |
| CH+CH→CHCH | 0.68(0.68) | -0.59 | 1.91 | 1.12(1.35) | 0.06 | 1.81 | 1.33(1.88) | 0.73 | 1.90 |
| $CH+CH_2→CHCH_2$ | 0.66(0.97) | -0.17 | 1.95 | 1.26(1.97) | -0.02 | 2.04 | 1.35(2.60) | 0.79 | 1.96 |
| $CH+CH_3→CHCH_3$ | 1.06(1.22) | 0.04 | 1.98 | 1.38(1.84) | 0.46 | 1.96 | 1.51(2.90) | 0.71 | 1.99 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $CH_2+CH_2 \rightarrow CH_2CH_2$ | 0.41(1.04) | -0.56 | 2.05 | 0.37(1.58) | -0.52 | 2.18 | 0.92(2.87) | 0.09 | 1.98 |
| $CH_2+CH_3 \rightarrow CH_2CH_3$ | 0.95(1.42) | -0.13 | 2.07 | 0.89(1.85) | -0.15 | 2.07 | 1.26(3.35) | 0.22 | 2.10 |
| **Hydrogenation steps** | | | | | | | | | |
| $CO+H \rightarrow HCO$ | 1.23 | 1.08 | 1.30 | 0.65 | 0.61 | 1.50 | | | |
| $CHCO+H \rightarrow CHCHO$ | 1.22 | 0.37 | 1.28 | | | | | | |
| $CHCO+H \rightarrow CH_2CO$ | 0.78 | 0.51 | 1.12 | | | | | | |
| $CH_2CO+H \rightarrow CH_3CO$ | 0.84 | -0.12 | 1.62 | | | | | | |
| $CH_3CO+H \rightarrow CH_3CHO$ | 0.42 | 0.32 | 1.18 | | | | | | |
| $C+H \rightarrow CH$ | 0.72 | -0.32 | 1.69 | 0.87 | 0.11 | 1.65 | 0.80 | 0.28 | 1.43 |
| $CH+H \rightarrow CH_2$ | 0.55 | 0.31 | 1.61 | 0.76 | 0.49 | 1.45 | 0.73 | 0.70 | 1.31 |
| $CH_2+H \rightarrow CH_3$ | 0.54 | -0.16 | 1.74 | 0.45 | -0.26 | 1.76 | 0.75 | 0.15 | 1.47 |
| $CH_3+H \rightarrow CH_4$ | 1.04 | 0.03 | 1.60 | 0.92 | 0.25 | 1.63 | 1.04 | 0.21 | 1.59 |
| $CHC+H \rightarrow CHCH$ | | | | 0.89 | 0.00 | 1.67 | | | |