Electronic Supplementary Information for:

# CO Activation and Methanation Mechanism on Hexagonal Close-packed Co Catalysts: Effect of Functionals, Carbon Deposition and Surface Structure

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**Table S1.** The activation energies ($\Delta E_{act}$ in eV) and reaction energies ($\Delta H$ in eV) of selected surface reactions with or without ZPE corrections.

| Reactions | $\Delta E_{act}$ | | $\Delta H$ | |
|---|---|---|---|---|
| | No ZPE | ZPE | No ZPE | ZPE |
| $CO*+H*\rightarrow CHO*+*$ | 1.23 | 1.28 | 1.08 | 1.19 |
| $CO*+H*\rightarrow COH*+*$ | 1.85 | 1.77 | 0.85 | 0.96 |
| $CHO*+*\rightarrow CH*+O*$ | 0.63 | 0.58 | -0.73 | -0.77 |
| $CHO*+H*\rightarrow CH_2O*+*$ | 0.45 | 0.43 | 0.23 | 0.33 |
| $CHO*+H*\rightarrow CHOH*+*$ | 1.17 | 1.05 | 0.43 | 0.51 |
| $CH_2O*+*\rightarrow CH_2*+O*$ | 0.70 | 0.63 | -0.65 | -0.74 |

**Table S2.** Adsorption energies ($\Delta E_{ads}$ in eV) and the most stable adsorption sites of various intermediates in CO methanation on Co (0001). The $\Delta E_{ads}$ of H and O are calculated with respected to $1/2H_2$ and $1/2O_2$ in gas phase. The calculated coverages ($\theta$ in ML) of various intermediates in the microkinetic study at 503 K, 1atm and $H_2$/CO ratio of 2 are also listed. The coverages of CO and the vacant site are $8.71 \times 10^{-1}$ and $1.08 \times 10^{-3}$, respectively.

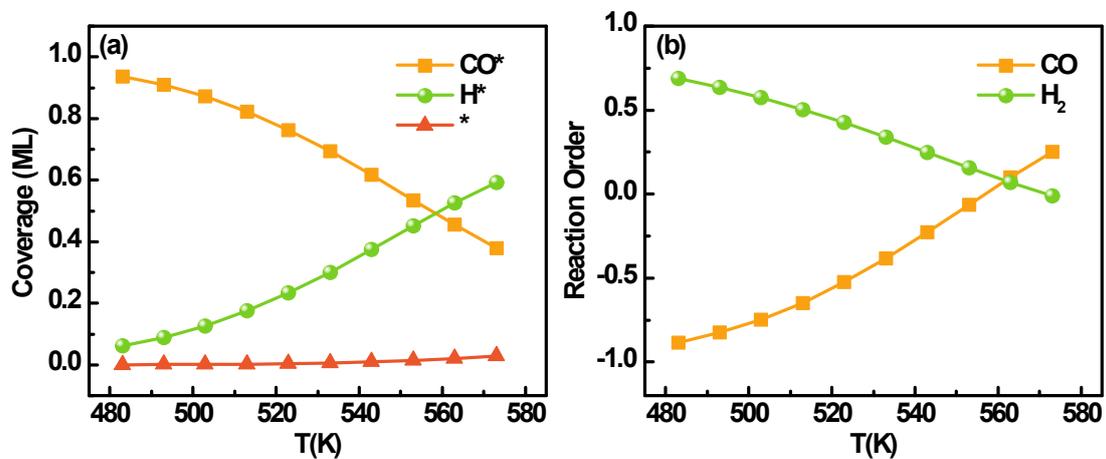| Intermediates | $\Delta E_{Ads}$ | Site | $\theta$ |
|---|---|---|---|
| H | -0.53 | fcc | $1.27 \times 10^{-1}$ |
| O | -2.62 | hcp | $1.02 \times 10^{-5}$ |
| C | -6.99 | hcp | $1.32 \times 10^{-15}$ |
| OH | -3.65 | $O_{hcp}$ | $3.96 \times 10^{-7}$ |
| CH | -6.42 | $C_{hcp}$ | $2.56 \times 10^{-10}$ |
| $CH_2$ | -3.98 | $C_{hcp}$ | $2.30 \times 10^{-11}$ |
| $CH_3$ | -1.97 | $C_{fcc}$ | $9.27 \times 10^{-8}$ |
| CHO | -2.21 | $C_{bri}$-hcp-$O_{bri}$ | $2.06 \times 10^{-9}$ |
| COH | -4.27 | $C_{hcp}$ | $2.16 \times 10^{-7}$ |
| $CH_2O$ | -0.85 | $C_{bri}$-hcp-$O_{bri}$ | $1.26 \times 10^{-9}$ |
| CHOH | -2.94 | $C_{hcp}$ | $5.73 \times 10^{-12}$ |
| $CH_3O$ | -2.81 | $O_{hcp}$ | $8.12 \times 10^{-4}$ |
| $CH_2OH$ | -1.58 | $C_{bri}$ | $2.07 \times 10^{-12}$ |
| HCOO | -3.06 | $O_{top}$-$O_{top}$ | $1.34 \times 10^{-11}$ |
| COOH | -2.24 | $C_{top}$-hcp-$O_{bri}$ | $1.14 \times 10^{-13}$ |
| $H_2O$ | -0.28 | $O_{top}$ | $2.48 \times 10^{-21}$ |

**Table S3.** Activation energies ($\Delta E_{act}$ in eV) and reaction energies ($\Delta H$ in eV) of forward reactions and distance of C-O, C-H or O-H ($d$ in Å) at the TSs for various elementary steps in CO methanation on Co (0001). $\Delta E_{act}$ and $\Delta H$ are calculated with respected to separate adsorbed states. * and X* denote the vacant site and adsorbed X species, respectively. The calculated rates ($r$ in $s^{-1}site^{-1}$) of various elementary steps in the microkinetic study at 503 K, 1atm and $H_2$/CO ratio of 2 are also listed.

| Reactions | $\Delta E_{act}$ | $\Delta H$ | $d$ | $r$ |
|---|---|---|---|---|
| $CO*+*=C*+O*$ | 2.35 | 0.67 | 1.83 | $2.51\times10^{-14}$ |
| $CO*+H*=CHO*+*$ | 1.23 | 1.08 | 1.30 | $6.17\times10^{-6}$ |
| $CO*+H*=COH*+*$ | 1.85 | 0.85 | 1.33 | $8.88\times10^{-8}$ |
| $CHO*+*=CH*+O*$ | 0.68 | -0.73 | 1.78 | $3.12\times10^{-6}$ |
| $COH*+*=C*+OH*$ | 1.58 | 0.09 | 2.02 | $3.01\times10^{-13}$ |
| $CHO*+H*=CHOH*+*$ | 1.17 | 0.43 | 1.37 | $2.21\times10^{-9}$ |
| $COH*+H*=CHOH*+*$ | 0.70 | 0.66 | 1.45 | $2.38\times10^{-7}$ |
| $CHO*+H*=CH_2O*+*$ | 0.45 | 0.23 | 1.58 | $1.80\times10^{-6}$ |
| $CH_2O*+*=CH_2*+O*$ | 0.70 | -0.65 | 1.82 | $1.50\times10^{-6}$ |
| $CHOH*+*=CH*+OH*$ | 0.67 | -0.89 | 1.88 | $1.10\times10^{-8}$ |
| $CHOH*+H*=CH_2OH*+*$ | 0.67 | 0.26 | 1.55 | $8.00\times10^{-8}$ |
| $CH_2O*+H*=CH_3O*+*$ | 0.58 | -0.38 | 1.58 | $1.22\times10^{-7}$ |
| $CH_2O*+H*=CH_2OH*+*$ | 1.07 | 0.46 | 1.38 | $8.75\times10^{-9}$ |
| $CH_2OH*+*=CH_2*+OH*$ | 0.53 | -0.84 | 1.98 | $8.87\times10^{-8}$ |
| $CH_3O*+*=CH_3*+O*$ | 1.38 | -0.42 | 1.90 | $1.35\times10^{-7}$ |
| $C*+H*=CH*+*$ | 0.72 | -0.32 | 1.69 | $3.26\times10^{-13}$ |
| $CH*+H*=CH_2*+*$ | 0.55 | 0.31 | 1.61 | $3.13\times10^{-6}$ |
| $CH_2*+H*=CH_3*+*$ | 0.54 | -0.16 | 1.74 | $4.72\times10^{-6}$ |
| $CH_3*+H*=CH_4+2*$ | 1.04 | 0.04 | 1.60 | $4.85\times10^{-6}$ |
| $CO*+O*=CO_2+2*$ | 1.37 | 1.03 | 1.63 | $1.74\times10^{-6}$ |
| $O*+H*=OH*+*$ | 1.22 | 0.28 | 1.33 | $6.01\times10^{-6}$ |
| $OH*+H*=H_2O*+*$ | 1.49 | 0.60 | 1.51 | $7.11\times10^{-10}$ |
| $2OH*=H_2O*+O*$ | 0.57 | 0.32 | 1.41 | $3.05\times10^{-6}$ |
| $CO*+OH*=COOH*+*$ | 1.31 | 0.94 | 1.43 | $1.22\times10^{-10}$ |
| $COOH*=CO_2+H*$ | 1.00 | -0.19 | 1.43 | $1.22\times10^{-10}$ |
| $CHO*+O*=HCOO*+*$ | 0.66 | -0.29 | 1.82 | $6.02\times10^{-8}$ |
| $HCOO*=CO_2+H*$ | 0.94 | 0.24 | 1.37 | $6.02\times10^{-8}$ |

**Table S4.** Adsorption energies ($\Delta E_{ads}$ in eV) of $CH_2O$ and CHOH, and the total energy difference $\Delta E$ between adsorbed CHOH and $CH_2O$ intermediates on various Co surfaces.

| Surfaces | $\Delta E_{ads}(CH_2O)$ | $\Delta E_{ads}(CHOH)$ | $\Delta E$ |
|---|---|---|---|
| Co(0001) | -0.85 | -2.94 | 0.21 |
| Co(10-10) | -0.94 | -2.92 | 0.32 |
| Co(11-20) | -1.23 | -3.04 | 0.48 |
| Co(10-12) | -1.37 | -3.14 | 0.53 |
| Step | -1.28 | -3.01 | 0.58 |
| Co(10-11) | -1.39 | -2.97 | 0.71 |

**Figure S1**. (a) The coverage of intermediates and (b) the reaction order as a function of temperature on Co(0001).

**Figure S2**. The effect of functionals on the adsorption energy $\Delta E_{ads}$ of the $C_1$-oxygenate intermediates on Co(0001).
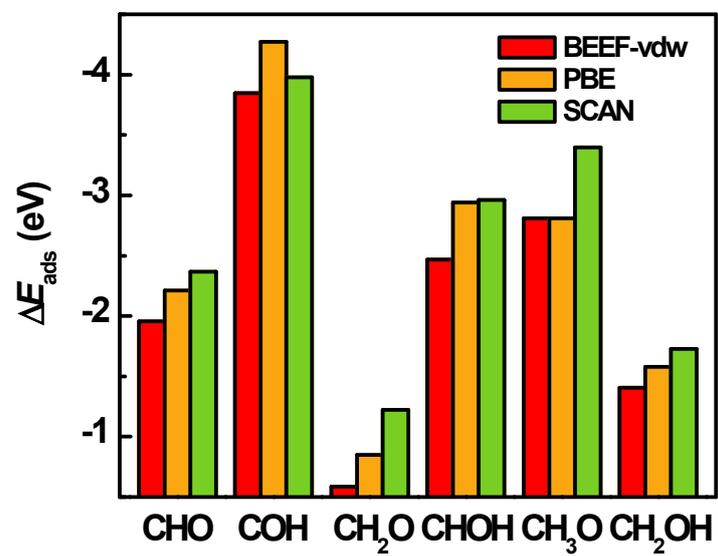
**Microkinetic Modeling**

The reaction rate constant ($k$) is given by the Eying equation based on the transition-state theory:

$$k = \frac{k_B T}{h} e^{\frac{-\Delta E_{act}}{k_B T}} \quad \ldots\ldots\ldots\ldots \tag{1}$$

where $k_B$, $T$, $h$ and $\Delta E_{act}$ represent the Boltzmann constant, absolute temperature, Planck constant and activation energy, respectively. The rate constant of adsorption ($k_{ads}$) is calculated by the following:

$$k_{ads} = \frac{S \cdot P \cdot A}{\sqrt{2\pi m k_B T}} \quad \ldots\ldots\ldots\ldots \tag{2}$$

where $S$, $P$, $A$ and m are the sticking coefficient, partial pressure of the adsorbed species, the area of the adsorption site and the molecular mass of adsorbed species, respectively. The value of $S$ is assumed to be one for all the species, since it is not very sensitive to the kinetic results.

The rate constant of desorption is calculated as

$$k_{des} = \frac{k_B T^3}{h^3} \frac{A(2\pi m k_B)}{\sigma \theta_{rot}} \exp(\frac{-E_{des}}{k_B T}) \quad \ldots\ldots\ldots\ldots \tag{3}$$

where $\sigma$, $\theta_{rot}$ and $E_{des}$ are the symmetry number, the characteristic temperature for rotation of adsorbed species and the activation energy of desorption.

Microkinetic simulations are performed by the MKMCXX program.[1] The reaction temperature ranges from 483 K to 573 K, and the total pressure is kept at 1 atm with $H_2$/CO ratio of 2. The degree of thermodynamic rate control $X_{RC,i}$ of step ($i$),[2] which can qualitatively determine the significance of single step ($i$) in the overall reaction, is defined as

$$X_{RC,i} = \frac{k_i}{r} \left( \frac{\partial r}{\partial k_i} \right)_{k_{j \neq i}, K_i} = \left( \frac{\partial \ln r}{\partial \ln k_i} \right)_{k_{j \neq i}, K_i}$$ ..................... (4)

where $k_i$, $K_i$ and $r$ are the rate constant, the equilibrium constant for elementary step $i$ and the reaction rate, respectively.

It is well-known that DFT methods do a poor job of treating CO adsorption on transition metal surfaces. Herein, we determined the CO adsorption energy of -1.30 eV from our experimental TPD data.[3] The CO adsorption energy is adjusted to experimental value by only adjusting the energy of gaseous CO, and the $\Delta G$ of surface reactions are preserved.

**References**

[1] I. A. W. Filot, R. A. van Santen, E. J. M. Hensen, *Angew. Chem. Int. Ed.* **2014**, *53*, 12746-12750.
[2] C. Stegelmann, A. Andreasen, C. T. Campbell, *J. Am. Chem. Soc.* **2009**, *131*, 8077-8082.
[3] J. W. Wu, J. Chen, Q. Guo, H. Y. Su, D. X. Dai, X. M. Yang, *Surf. Sci.* **2017**, *663*, 56-61.