

# Supplementary Materials: Investigation of C<sub>1</sub>+C<sub>1</sub> Coupling Reactions in Cobalt-Catalyzed Fischer-Tropsch Synthesis by a Combined DFT and Kinetic Isotope Study

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## S1: The calculation method of free energy

Firstly, the equation to calculate the free energy is defined as shown.

$$G = E + E_{ZPE} + \Delta H^0(0 \rightarrow T) - TS + RT \ln\left(\frac{P}{P^0}\right)$$

Where  $G$  is free energy,  $E$  refers to electronic energy determined by DFT,  $E_{ZPE}$  is zero-point energy.  $H$  is enthalpy.  $S$  is entropy.  $T$  is temperature.  $P$  is the pressure.

$$E_{ZPE} = \sum_{i=1}^{3N-6(5)} \frac{N_A h \nu_i}{2}$$

Where  $N_A$  and  $h$  refers to Avogadro's number and Planck's constant, and  $\nu_i$  and  $N$  are the frequency of the normal mode and the number of atoms, respectively.

The evaluation of enthalpy ( $H$ ) and entropy ( $S$ ) are shown below.

The standard entropies of gas-phase species have three contributions from translational, rotational and vibrational modes. The detailed equations to calculate the entropy has been reported by Dumesic et.al<sup>2</sup> and can use the data from the handbook. The enthalpy of gas phase species also has three contributions.

$$\Delta H(T) = H_{tran} + H_{rot} + \Delta H_{vib}$$

$$\Delta H(T) = \frac{5}{2}RT + \frac{3}{2}RT \text{ (or } RT \text{ for linear molecules)} + R \sum_i^{3N-6} \frac{x_i T}{e^{x_i} - 1}$$

Where  $x_i = \frac{h\nu_i}{k_B T}$ ,  $k_B$  refers to the Boltzmann constant,  $\nu_i$  is normal-mode vibrational frequency.

As for the adsorbates, the enthalpy ( $H$ ) is equal to the internal energy ( $U$ ) with neglecting the  $PV$  contributions. For strongly adsorbed species, the frustrated translational and rotational modes are treated as special cases of vibrational modes. Accordingly, the entropy and the internal energy is evaluated according to the following equations.

$$\Delta U^0(0 \rightarrow T) = U_{vib} = R \sum_i^{3N} \frac{x_i T}{e^{x_i} - 1}$$

$$S = S_{vib} = R \sum_i^{3N} \left( \frac{x_i}{e^{x_i} - 1} - \ln(1 - e^{-x_i}) \right)$$

Where  $x_i = \frac{hc}{k_B T \lambda_i}$ ,  $c$  and  $k_B$  refer to speed of light and Boltzmann constant,  $1/\lambda_i$  is wavenumber corresponding to each vibrational frequency.

## Reference

(1) Cortright, R. D.; Dumesic, J. A., Kinetics of heterogeneous catalytic reactions: Analysis of reaction schemes. In *Adv Catal*, Academic Press: 2001; Vol. Volume 46, pp 161-264.

## S2: The formulas for KIE calculation<sup>1</sup>

Reaction rate is given:

$$r_{AB} = \frac{k_B T}{h} \exp\left(\frac{\Delta S^{0TS-IS}}{R}\right) \exp\left(-\frac{\Delta H^{0TS-IS}}{k_B T}\right) n_A n_B \quad (S1.1)$$

Kinetic isotope effect (KIE) is described as:

$$\frac{k_H}{k_D} = \frac{A_H \Omega_H}{A_D \Omega_D} \quad (S1.2)$$

Zero-point energy (ZPE) contribution to KIE (H/D) is:

$$\frac{\Omega_H}{\Omega_D} = \exp\left((-1) \frac{((ZPE_H^{TS} - ZPE_H^{IS}) - (ZPE_D^{TS} - ZPE_D^{IS}))}{k_B T}\right) \quad (S1.3)$$

Entropic contribution to KIE (H/D) (Pre-exponential factor) is obtained by:

$$\frac{A_H}{A_D} = \exp\left(\frac{((S_H^{TS} - S_H^{IS}) - (S_D^{TS} - S_D^{IS}))}{R}\right) \quad (S1.4)$$

$\Delta H$  is approximated by the energy  $\Delta E$ , which is calculated from DFT. The barriers without zero-point correction are identical for H and D, so the barrier term in the KIE only includes the zero-point energy corrections. The  $k_B T/h$  term is neglected because it does not change for H and D. Besides, the coverage term ( $n_A n_B$ ) is assumed to be identical for H and D.

All the zero-point energy and entropy are calculated from DFT.

$TS$  transition state

$IS$  initial state

$T$  reaction temperature

$k_B$  Boltzmann constant

$R$  ideal gas constant

## References

(1) Ojeda, M.; Li, A. W.; Nabar, R.; Nilekar, A. U.; Mavrikakis, M.; Iglesia, E. *J Phys Chem C* 2010, 114, 19761.

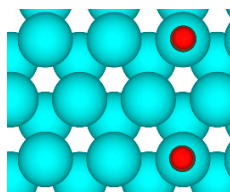


Figure S1: The stable configuration of two CO spectators on the surface

**Table S1:** Frequencies for the calculation of kinetic isotope effects

$\text{CH}_2^* + \text{CO}^* \rightarrow \text{CH}_2\text{CO}^{*+}$															
<b>IS-H</b>	3002	2716	1782	1377	817	584	499	396	388	344	310	286	259	159	88
<b>IS-D</b>	2204	1980	1782	1011	632	479	425	389	356	307	281	251	239	159	88
<b>TS-H</b>	3002	2950	1854	1349	920	856	515	483	462	386	361	182	129	59	
<b>TS-D</b>	2221	2136	1853	992	718	637	481	443	404	348	322	169	128	59	
$\text{CH}^* + \text{CH}^* \rightarrow \text{CHCH}^{*+}$															
<b>IS-H</b>	3022	3010	760	742	670	652	628	607	434	399	359	312			
<b>IS-D</b>	2224	2214	607	593	576	560	509	492	399	372	332	294			
<b>TS-H</b>	3049	3043	891	835	658	647	587	584	423	410	164				
<b>TS-D</b>	2242	2239	704	597	566	556	513	483	380	368	157				
$\text{CH}^* + \text{HCO}^* \rightarrow \text{CHHCO}^{*+}$															
<b>IS-H</b>	2998	2883	1429	1268	849	805	674	601	535	453	386	287	197	171	107
<b>IS-D</b>	2205	2118	1421	972	655	635	567	520	488	425	354	286	188	159	106
<b>TS-H</b>	3008	2943	1362	1255	942	800	617	541	535	400	346	285	194	135	
<b>TS-D</b>	2209	2165	1351	958	750	583	533	507	459	353	313	283	190	134	