A Quantum-Chemical DFT Study of Direct and H- and C-assisted CO Dissociation on the $\chi$-Fe$_5$C$_2$ Hägg Carbide

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SI-1A: Adsorption Energies for CO adsorption on Hägg carbide surfaces

**Table S1**: CO adsorption on the five most stable Hägg carbide surfaces in various configurations and their corresponding adsorption energies. Adsorption modes found are Top (either on Fe or on C), Bridged, 3-fold (either on Fe-only or on 2Fe and 1C), 4-fold (either on Fe-only, like 2B or on 3Fe and 1C), 5-fold, and 6-fold

| Surface  | Mode       | Adsorption Energies (kJ/mol) |
|----------|------------|------------------------------|
| (010)$_{0.25}$ | Bridged  | 181 kJ/mol                     | 4-fold (2B$_3$) | 194 kJ/mol                     | Top (on 1 C) | 77 kJ/mol                     |
| (111)$_{0.0}$ | Top      | 92 kJ/mol                     | 3-fold (on 2 Fe and 1C) | 112 kJ/mol                     | 4-fold (on 3Fe and 1C) | 121 kJ/mol                     |
| (100)$_{0.0}$ | Top      | 189 kJ/mol                     | 3-fold            | 187 kJ/mol                     | 5-fold (B$_5$) | 174 kJ/mol                     |
| (111)$_{0.5}$ | Bridged  | 202 kJ/mol                     | 4-fold (2B$_3$) | 180 kJ/mol                     | 6-fold (B$_5$) | 147 kJ/mol                     |
| (100)$_{0.287}$ | Bridged | 186 kJ/mol                     | 3-fold            | 194 kJ/mol                     | 5-fold (B$_5$) | 230 kJ/mol                     |
SI-1B: Adsorption geometries for CO adsorption on Hägg carbide surfaces

Table S2: Adsorption geometries for CO on various Hägg carbide surfaces. Corresponding adsorption energies can be found in table 1 SI-1A.

| Surface   | Adsorption Geometry | Adsorption Geometry | Adsorption Geometry |
|-----------|---------------------|---------------------|---------------------|
| (010)_{0.25} | Bridged             | 4-fold (2B₃)       | Top (on 1C)         |
|           |                     |                     |                     |
| (11\bar{1})_{0.0} | Top                 | 3-fold (on 2Fe, 1C) | 4-fold (on 3Fe, 1C) |
|           |                     |                     |                     |
| (100)_{0.0}  | Top                 | 3-fold              | 5-fold (B₅)         |
| Plane     | Structure       | 4-fold (2B₃) | 6-fold (B₅) |
|-----------|-----------------|--------------|-------------|
| (111)₀.₅  | Bridged         |              |             |
| (100)₀.₂₈⁷ | Bridged         |              |             |

The images show different views of the structures at the specified planes.
SI-2A: Structural information on the direct CO dissociation reactions on Hägg carbide surfaces

**Table S3** Geometries of the IS, TS and FS for direct CO dissociation on various Hägg carbide surfaces

| Surface   | Initial state | Transition state | Final state |
|-----------|---------------|------------------|-------------|
| (010)_{0.25} | CO            | C--O             | C + O       |
| (010)*_{0.25} |               |                  |             |
| (11̅1)_{0.0} |               |                  |             |
SI-2B: Structural information on the H-assisted CO dissociation via CHO on Hägg carbide surfaces

Table S4 Geometries of the IS, TS and FS for H-assisted CO dissociation via a CHO intermediate on various Hägg carbide surfaces

| Surface    | Initial state | Transition state | Final state |
|------------|---------------|------------------|-------------|
| (010)_{0.25} | ![Initial state](image1) | ![Transition state](image2) | ![Final state](image3) |
| (010)_{*0.25} | ![Initial state](image4) | ![Transition state](image5) | ![Final state](image6) |
**SI-2C: Structural information on the H-assisted CO dissociation via COH on Hägg carbide surfaces**

**Table S5** Geometries of the IS, TS and FS for H-assisted CO dissociation via a COH intermediate on various Hägg carbide surfaces

| Surface     | Initial state | Transition state | Final state |
|-------------|---------------|------------------|-------------|
| (010)$_{0.25}$ | ![Image](image1.png) | ![Image](image2.png) | ![Image](image3.png) |
|             | ![Image](image4.png) | ![Image](image5.png) | ![Image](image6.png) |
| (010)*$_{0.25}$ | ![Image](image7.png) | ![Image](image8.png) | ![Image](image9.png) |
SI-2D: Structural information on the (H)/C-assisted CO dissociation on the (11\(\overline{1}\))\(_{0.0}\) surface

Table S6 Geometries of the IS, TS and FS for C-assisted CO dissociation via a CCO, CHCO, and CCOH intermediate on the (11\(\overline{1}\))\(_{0.5}\) Hägg carbide surface.

| Intermediate species | Initial state | Transition state | Final state |
|----------------------|---------------|------------------|-------------|
| CCO                  |               |                  |             |
| CCHO                 |               |                  |             |
SI-3A: Derivation rate equation for direct and H-assisted C-O bond scission

For the direct CO dissociation, we assume that the CO molecule obeys the Langmuir-Hinshelwood mechanism, therefore the first step in the mechanism is adsorption of the CO molecule. The second step is the dissociation of the CO molecule to C and O.

\[
\text{CO} + * \rightleftharpoons \text{CO}^* \quad (1)
\]
\[
\text{CO}^* + * \rightarrow \text{C}^* + \text{O}^* \quad (2)
\]

We assume that CO adsorption is in equilibrium and very fast compared to the CO dissociation, therefore, K is defined as:

\[
K = \frac{k^{+1}}{k^{-1}} = \frac{\theta_{\text{CO}}}{\theta_*} \cdot \frac{P_{\text{CO}}}{P_0}
\]

where \( \theta_{\text{CO}} \) and \( \theta_* \) stand for the CO coverage and free sites, respectively, adding up to unity. \( \frac{k^{+1}}{k^{-1}} \) is the ratio between the forward and backward rate constants of the adsorption. Therefore, we can write:

\[
\theta_{\text{CO}} = \frac{K P_{\text{CO}}}{1 + K P_{\text{CO}}} \quad \text{and} \quad \theta_* = \frac{1}{1 + K P_{\text{CO}}}
\]

Meanwhile \( K^0 \) can be calculated as follows:

\[
K^0 = e^{-\frac{\Delta G^0}{kT}}
\]

\[
\Delta G^0 = E_{\text{ads}} - \Delta \mu (T, P_0)
\]

Where \( \Delta G^0 \) is the standard Gibbs free energy for CO adsorption, \( k \) is the Boltzmann constant, \( T \) the temperature and \( P_0 \) the standard pressure. \( \Delta \mu (T, P_0) \) is the chemical potential of CO in the gas phase. Here, \( T = 500 \text{ K} \) and \( P = 3 \times 10^5 \text{ Pa} \), corresponding to low coverage of CO that were used in our study.

To take changes in entropy (S) and enthalpy (H) into account, \( \Delta \mu_{\text{CO}} \) and \( \Delta \mu_{\text{H}} \) were determined using the NIST thermodynamic tables and the abovementioned values for temperature and pressure in the following formula:

\[
\Delta \mu_{\text{CO}/H}(T, P^0) = -TS(T, P^0) + (H(T, P^0) - H(0 K, P^0))
\]

We have applied a value for \( \Delta \mu_{\text{CO}} \) of 91.59 kJ/mol and a value for \( \Delta \mu_{\text{H}} \) of 62 kJ/mol in our paper.

The rate for CO dissociation can be written as
\[ r = k_2 \theta_{CO} \theta_* = \frac{k_2 P_{CO}}{(1 + k P_{CO})^2}, \]

where

\[ k_2 = \nu_f e^{\frac{E_f}{RT}}. \]

In this formula, \( \nu_f \) and \( E_f \) stand for the pre-exponential factor and the forward reaction energy barrier for the CO dissociation reaction, as found in table 2.

For the H-assisted CO dissociation pathway, the following reactions have to be taken into account.

\[
\begin{align*}
\text{CO} + * & \quad \text{CO}^* \quad (1) \\
\text{H}_2 + 2* & \quad \text{2H}^* \quad (2) \\
\text{CO}^* + \text{H}^* & \quad \text{CHO}^* + * \quad \text{CH}^* + \text{O}^* \quad (3,4) \\
\text{CO}^* + \text{H}^* & \quad \text{COH}^* + * \quad \text{C}^* + \text{OH}^* \quad (5,6)
\end{align*}
\]

Reactions 3, 4 and 5, 6 are composed out of 2 lumped elementary reaction steps. The equations for the coverages are now as follows:

\[
\begin{align*}
\theta_{CO} = \frac{K_1 P_{CO}}{1 + K_1 P_{CO} + \sqrt{K_2 P_{H2}}} \quad \theta_H = \frac{\sqrt{K_2 P_{H2}}}{1 + K_1 P_{CO} + \sqrt{K_2 P_{H2}}} \quad \text{and} \quad \theta_* = \frac{1}{1 + K P_{CO} + \sqrt{K_2 P_{H2}}}
\end{align*}
\]

Now, the reaction rate can be defined as

\[ r = k_{r_{ls}} \theta_{CO} \theta_H \equiv k_{r_{ls}} \theta_{CHO} \theta_* = \frac{k_{r_{ls}} K_1 P_{CO} \sqrt{K_2 P_{H2}}}{(1 + K_1 P_{CO} + \sqrt{K_2 P_{H2}}^2)}, \]

Where \( k_{r_{ls}} \) is the rate constant for the rate limiting step, which is defined as

\[ k_{r_{ls}} = \nu_f e^{\frac{E_{r_{ls}}}{RT}}. \]

\( E_{r_{ls}} \) is defined as the (lumped) reaction barrier, where the \( \Delta E \) of reaction 3 and 4 was taken for the CHO pathway and the \( \Delta E \) of reaction 5 and 6 was taken for the COH pathway.

\( K_1 \) is defined as

\[
K_1 = \frac{e^{\left(\frac{\Delta G^0}{k_b T}\right)}}{P_0} = \frac{e^{\left(\frac{E_{ads} - \Delta \mu_{CO}}{k_b T}\right)}}{P_0}
\]
SI-3B: Derivation rate equation for C-CO assisted C-O bond scission

For the direct C-CO dissociation, we assume that the CO molecule obeys the Langmuir-Hinshelwood mechanism, therefore the first step in the mechanism is adsorption of the CO molecule. The second step is the reaction of the CO with a C from the surface, termed the C_s. After the formation of this intermediate species, dissociation of the CO molecule results in the formation of C_sC and O. Because we are using both regular empty sites and C from the surface, it is necessary to introduce a dual site model. In this model we denote the regular sites as θ_s and the C from the surface as θ_C.

\[
\begin{align*}
\text{CO} + * & \rightleftharpoons \text{CO}^* \quad (1) \\
\text{CO}^* + \text{C}_s & \rightleftharpoons \text{C}_s\text{CO} + * \quad (2) \\
\text{C}_s\text{CO} + * & \rightarrow \text{C}_s\text{C} + \text{O}^* \quad (3)
\end{align*}
\]

\[
\theta_s + \theta_{CO} = 1 \quad \& \quad \theta_{C_sCO} + \theta_{C_s} = 1
\]

For the regular sites we get the following equations for the coverage:

\[
\theta_{CO} = K_1 P_{CO} \theta_s = \frac{K_1 P_{CO}}{1 + K_1 P_{CO}}
\]

\[
\theta_s = \frac{1}{1 + K_1 P_{CO}}
\]

For the surface C sites we get the following equations for the coverage:

\[
\theta_{C_sCO} = \frac{K_2 \theta_{CO} \theta_{C_s}}{\theta_s} = K_2 K_1 P_{CO} \theta_{C_s} = \frac{K_1 K_2 P_{CO}}{1 + K_1 K_2 P_{CO}}
\]

The rate for CO bond scission is expressed as:

\[
r = k_3 \theta_{C_sCO} \theta_s
\]

\[
r = k_3 \theta_{C_sCO} \theta_s = k_3 \frac{K_1 K_2 P_{CO}}{1 + K_1 K_2 P_{CO}} \frac{1}{1 + K_1 P_{CO}} = \frac{k_3 K_1 K_2 P_{CO}}{1 + K_1 P_{CO} + K_1 K_2 P_{CO} + K_1^2 K_2 P_{CO}^2}
\]
Where $K_1$, $K_2$ and $k_3$ are defined as follows:

$$K_1 = \frac{e^{\left(\frac{\Delta G^0}{k_B T}\right)}}{P_0} = \frac{e^{\left(\frac{E_{ads} - \Delta \mu_{CO}}{k_B T}\right)}}{P_0}$$

$$K_2 = \frac{e^{\left(\frac{\Delta G^0}{k_B T}\right)}}{P_0} = \frac{e^{\left(\frac{\Delta H_{fus}}{k_B T}\right)}}{P_0}$$

$$k_3 = 10^{13} e^{\left(\frac{\Delta E_{fus}}{-RT}\right)}$$

The following reactions were used for the H-assisted CCO dissociation:

1. $\text{CO} + * \rightleftharpoons \text{CO}^* \quad (1)$
2. $\text{H}_2 + 2* \rightleftharpoons 2\text{H}^* \quad (2)$
3. $\text{CO}^* + \text{C}_s \rightleftharpoons \text{C}_s\text{CO} + * \quad (3)$
4. $\text{C}_s\text{CO} + \text{H}^* \rightarrow \text{C}_s\text{CHO} + * \rightarrow \text{C}_s\text{CH} + \text{O}^* \quad (4,5)$
5. $\text{C}_s\text{CO} + \text{H}^* \rightarrow \text{C}_s\text{COH} + * \rightarrow \text{C}_s\text{C} + \text{OH}^* \quad (6,7)$

Reaction 4,5 and 6,7 are composed out of 2 lumped elementary reaction steps. The equations for the coverages are now as follows:

$$\theta_{CO} = \frac{K_1 P_{CO}}{1 + K_1 P_{CO} + \sqrt{K_2 P_{H_2}}} \quad \theta_H = \frac{\sqrt{K_2 P_{H_2}}}{1 + K_1 P_{CO} + \sqrt{K_2 P_{H_2}}} \quad \theta_* = \frac{1}{1 + K P_{CO} + \sqrt{K_2 P_{H_2}}}$$

$$\theta_{C_sCO} = \frac{K_3 K_{CO} P_{CO}}{1 + K_3 K_{CO} P_{CO} + K_3 K_4 K_{CO} P_{CO} \sqrt{K_2 P_{H_2}}} \quad \text{and} \quad \theta_{C_s} = \frac{1}{1 + K_3 K_{CO} P_{CO} + K_3 K_4 K_{CO} P_{CO} \sqrt{K_2 P_{H_2}}}$$

Now, the reaction rate can be defined as

$$r = k_{r_{ls}} \theta_{C_sCO} \theta_H = k_{r_{ls}} \theta_{C_5CH0} \theta_* = k_{r_{ls}} \theta_{C_sCOH} \theta_* = \ldots$$
SI-4: A graphical representation of $\Delta E_{\text{total}}$ and $\Delta \Delta E$ values

$$k_{\text{rel}} K_1 P_{CO} \sqrt{K_2 P_{H2}} \over (1+K_3 K_2 P_{CO} + K_3 K_4 K_2 P_{CO} \sqrt{K_2 P_{H2}})$$

**Figure S1** Graphical representation of the $\Delta E_{\text{total}}$ and the $\Delta \Delta E$
SI-5: Kinetic parameters for Direct and H-assisted CO dissociation on the (510)\textsubscript{0.0} surface

We have combined the data from Pham \textit{et al.}\textsuperscript{1} with some of our own data (marked with *) in order to predict the rates of direct and H-assisted CO dissociation on the (510)\textsubscript{0.0} surface. As the adsorption energy of H\textsubscript{2} was not included in the work of Pham et al., we have calculated this value using the data in Table S5.1. We have determined the H\textsubscript{2} adsorption energy by using the reported total energy of an adsorbed H atom on the (510)\textsubscript{0.0} surface and subtracted the provided empty (510)\textsubscript{0.0} and our own value for the energy of H\textsubscript{2} in the gas phase (using the same VASP settings as employed by Pham et al.). The adsorption energies used in our kinetic model are shown in Table S5.2, evidencing that the estimated H\textsubscript{2} adsorption energy is within the range of the H\textsubscript{2} adsorption energies of the other surfaces. Table S5.3 shows the overall reaction energy for the C-O bond breaking and an estimation of the pre-exponential factors for the forward reaction.

| Adsorbate            | Adsorption energy (kJ/mol) |
|----------------------|-----------------------------|
| H\textsubscript{2} on (510)\textsubscript{0.0} | 148                         |
| H\textsubscript{2} on (100)\textsubscript{0.0} | 144\textsuperscript{2}     |
| H\textsubscript{2} on (001)\textsubscript{0.0} | 150\textsuperscript{*}     |
| H\textsubscript{2} on (110)\textsubscript{0.0} | 139\textsuperscript{2}     |
| H\textsubscript{2} on (100)\textsubscript{0.287} | 167\textsuperscript{7}    |
| CO on (510)\textsubscript{0.0} | 202\textsuperscript{7}    |

\textbf{Table S5.1} Total energies from DFT in eV for the empty (510)\textsubscript{0.0}, the (510)\textsubscript{0.0} with H adsorbed and the gas phase H\textsubscript{2}

| Total energy from DFT (eV)                      |
|------------------------------------------------|
| (510)\textsubscript{0.0} empty surface         | -460.246610\textsuperscript{7} |
| (510)\textsubscript{0.0} with H adsorbed       | -464.393222\textsuperscript{7} |
| H\textsubscript{2} gasphase                     | -6.7590177\textsuperscript{7}  |
Table S5.3 Overall reaction energy barrier for the direct and H-assisted C-O bond breaking and corresponding estimates for the pre-exponential factors for the forward reaction ($ν_f$)

| Reaction                          | (Overall) barrier for dissociation (kJ/mol) | $ν_f$   |
|-----------------------------------|---------------------------------------------|--------|
| CO → C + O                        | 127$^f$                                     | $1.0 \cdot 10^{13}$ |
| CO + H → CHO → CH + O             | 149$^f$                                     | $1.0 \cdot 10^{13}$ |
| CO + H → COH → CO + H             | 184$^f$                                     | $1.0 \cdot 10^{13}$ |

1. Pham, T. H.; Duan, X.; Qian, G.; Zhou, X.; Chen, D., CO activation pathways of Fischer–Tropsch synthesis on $\chi$-Fe5C2 (510): direct versus hydrogen-assisted CO dissociation. *The Journal of Physical Chemistry C* **2014**, *118* (19), 10170-10176.

2. Cao, D.-B.; Zhang, F.-Q.; Li, Y.-W.; Wang, J.; Jiao, H., Density functional theory study of hydrogen adsorption on Fe5C2 (001), Fe5C2 (110), and Fe5C2 (100). *The Journal of Physical Chemistry B* **2005**, *109* (2), 833-844.