

Mechanism and microkinetics of the Fischer-Tropsch Reaction

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Supplementary information

Section S1: Details of molecular microkinetics simulations

In this section, we provide further details on the molecular microkinetics simulations employed in this study. This section is divided into three subsections. Subsection S1A details the methods used for the calculation of the elementary rate constants, while subsection S1B explains the microkinetic rate expressions.

Section S1A: Methods used for calculation of the elementary rate constants

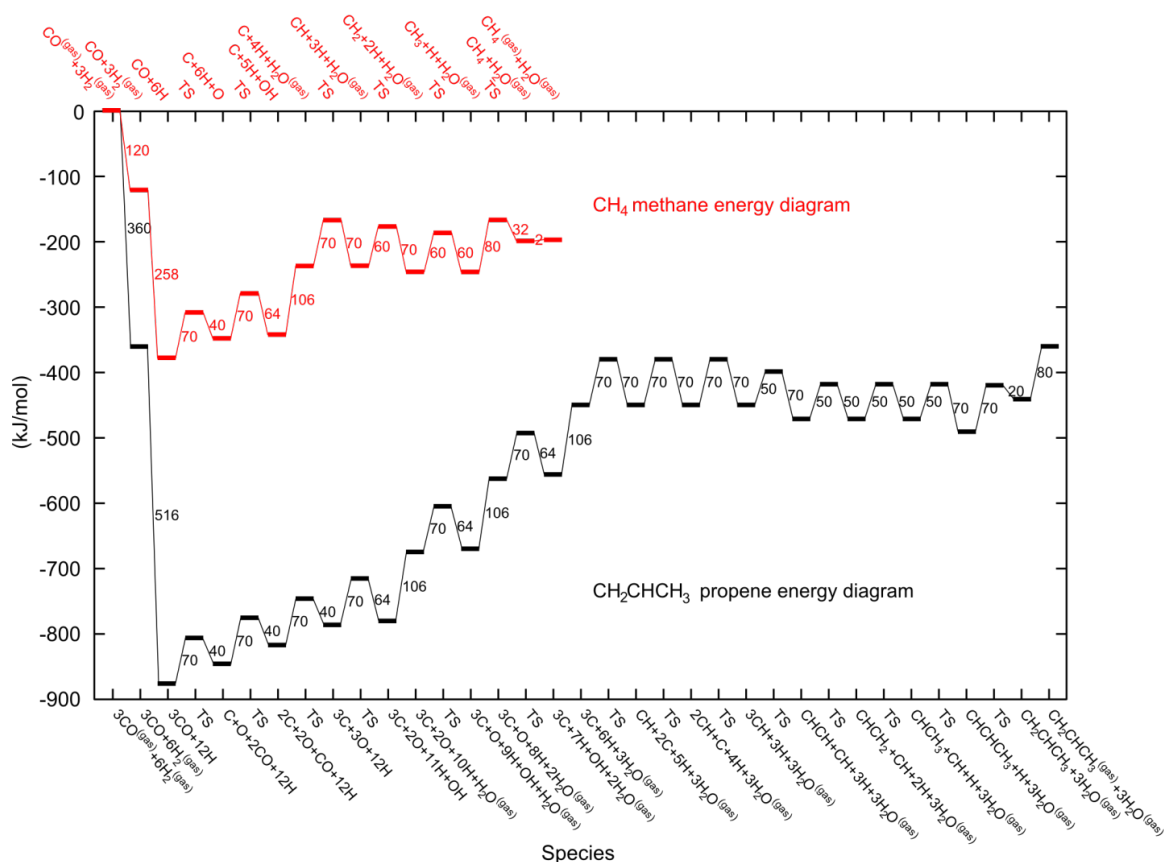


Figure S1: Reaction energy profile showing relative energies of the intermediates and their barriers leading to the formation of Methane and Propene⁵⁶.

The reaction energy profile shown in Figure S1 above illustrates the relative energies as well as the reaction energy barriers for each of the elementary reaction steps of Table S1.

The rate constants for elementary reactions are calculated using the Eyring transition state reaction rate expression. No change in entropy is assumed for the surface reactions. Hence a standard pre-factor of 10^{13} is used for the corresponding reactions. There is gain in entropy in the product desorption and loss in entropy for reagent adsorption. Product re-adsorption is not included.

The rates of CO and H₂ adsorption are calculated using the expression (S1) below.

$$W_{ads} = \frac{PA_{site}\sigma}{\sqrt{2\pi mk_B T}} \tag{S1}$$

Here, A_{site} is the area of a single adsorption site, P is the partial gas pressure and T , temperature (in Kelvin). The total pressure is 20 bar with H₂:CO pressure ratio of 3:1. A sticking coefficient of 10^{-2} is used for CO and 10^{-5} is used for H₂. The rates of CO and H₂ desorption are calculated using Equation S2 below.

$$W_{des} = \frac{k_B T}{h} \frac{Q^\ddagger}{Q} \exp\left[-\frac{E_{bar}}{k_B T}\right] \quad (S2)$$

Here, the partition functions Q and $Q^\ddagger$ of the initial state and the transition state respectively are calculated using $Q = Q_{trans} Q_{rot} Q_{vib}$. The pre-factor for desorption reduces to $\frac{k_B T}{h} Q_{trans}^\ddagger Q_{rot}^\ddagger$. The translational partition function is then calculated using the expression (S3) below.

$$Q_{trans}^\ddagger = \frac{A_{site} 2\pi m k_B T}{h^2} \quad (S3)$$

The rotational partition function is calculated using

$$Q_{rot,2D}^\ddagger = \frac{1}{\sigma} \frac{T}{\theta_{rot}} \quad (S4)$$

where σ is the symmetry number and θ_{rot} is the rotational temperature. The values for

these are tabulated for various small molecules. For hydrogen, θ_{rot} is 87.9 K and the symmetry number σ is 2. For CO, θ_{rot} is 2.73 K and the symmetry number σ is 1.

For all the other types of reactions for which the DFT calculated vibrational frequencies are available, the prefactors are calculated using the vibrational partition function which is given by expression (S5) below:

$$Q_{vib} = \prod_i \left[\tilde{Q}_i \exp\left[-\frac{\hbar \omega_i}{2k_B T}\right] \right] \quad (S5)$$

where $\tilde{Q}_i$ is defined as

$$\tilde{Q}_i = \frac{1}{1 - \exp\left[-\frac{\hbar \omega_i}{k_B T}\right]} \quad (S6)$$

Using the above mentioned expressions (S1) to (S6), the calculated prefactors are listed in Table S1, with the activation energies for the corresponding forward and reverse reactions. Formation of hydrocarbons of chain length $n \geq 2$ is treated in homologous fashion.

Table S1: List of prefactors and activation energies used in the calculation of the elementary rate constants. In columns 2 and 3, the first number indicates the forward rate, while the second number indicates the reverse rate.

Reaction	ν (s^{-1})	Activation Barrier (kJ/mol)
$CO(gas) \rightleftharpoons CO(ads)$	*	0,120
$H_2(gas) \rightleftharpoons H(ads) + H(ads)$	*	0, 86
$CO \rightleftharpoons C + O$	$10^{13}, 10^{13}$	70, 40
$C + H \rightleftharpoons CH$	$3.21 \times 10^{13}, 2.81 \times 10^{13}$	70, 70
$CH + H \rightleftharpoons CH_2$	$2.10 \times 10^{13}, 1.00 \times 10^{13}$	60, 70
$CH_2 + H \rightleftharpoons CH_3$	$1.25 \times 10^{14}, 4.53 \times 10^{13}$	60, 60
$CH_3 + H \rightleftharpoons CH_4$	$1.01 \times 10^{17}, 10^{13}$	80, 32
$CH_4(ads) \rightleftharpoons CH_4(gas)$	$10^{13}, --$	2, --
$CH + CH \rightleftharpoons CHCH$	$10^{13}, 10^{13}$	50, 70
$CHCH + H \rightleftharpoons CHCH_2$	$10^{13}, 10^{13}$	50, 50
$CHCH_2 + H \rightleftharpoons CHCH_3$	$10^{13}, 10^{13}$	50, 50
$CHCH_3 + CH \rightleftharpoons CHCHCH_3$	$10^{13}, 10^{13}$	50, 70
$CHCHCH_3 + H \rightleftharpoons CH_2CHCH_3$	$10^{13}, 10^{13}$	70, 20
$CH_2CHCH_3(ads) \rightleftharpoons CH_2CHCH_3(gas)$	$10^{17}, --$	80, --
$CHCH_2 + H \rightleftharpoons CH_2CH_2$	$10^{13}, 10^{13}$	70, 20
$CH_2CH_2(ads) \rightleftharpoons CH_2CH_2(gas)$	$10^{17}, --$	80, --
$O + H \rightleftharpoons OH$	$10^{13}, 10^{10}$	70, 64
$OH + H \rightleftharpoons H_2O(gas)$	$4.45 \times 10^{16}, --$	106, --

* The rates of adsorption are calculated using expression S1.

-- Adsorption of gas phase products not included in the simulations

Section S1B: Microkinetic rate expressions

The microkinetics model used in this work consists of reaction sites that form (111)-type hexagonal lattice. Only one reaction site is assumed per lattice unit cell. Rate equations are derived using a mean field approximation. Corresponding to the elementary steps shown in Figure 1 in the main paper, the kinetics is described using the following set of coupled differential equations:

$$\frac{d\Theta_{CO}}{dt} = k_{CO}^{ads} \Theta_v - k_{CO}^{des} \Theta_{CO} - k_{CO}^{diss} \Theta_{CO} \Theta_v + k_{CO}^{rec} \Theta_C \Theta_O$$

$$\frac{d\Theta_C}{dt} = k_{CO}^{diss} \Theta_{CO} \Theta_v - k_{CO}^{rec} \Theta_C \Theta_O - k_{CH}^{form} \Theta_C \Theta_H + k_{CH}^{rev} \Theta_{CH} \Theta_v$$

$$\frac{d\Theta_O}{dt} = k_{CO}^{diss} \Theta_{CO} \Theta_v - k_{CO}^{rec} \Theta_C \Theta_O - k_{OH}^{form} \Theta_O \Theta_H + k_{OH}^{diss} \Theta_{OH} \Theta_v$$

$$\begin{aligned} \frac{d\Theta_H}{dt} = & k_{H_2}^{ads} \Theta_v \Theta_v - k_{H_2}^{des} \Theta_H \Theta_H - k_{OH}^{form} \Theta_O \Theta_H + k_{OH}^{diss} \Theta_{OH} \Theta_v - k_{H_2O}^{des} \Theta_{OH} \Theta_H \dots \\ & - k_{CH}^{form} \Theta_C \Theta_H + k_{CH}^{rev} \Theta_{CH} \Theta_v - k_{CH_2}^{form} \Theta_{CH} \Theta_H + k_{CH_2}^{rev} \Theta_{CH_2} \Theta_v \dots \\ & - k_{CH_3}^{form} \Theta_{CH_2} \Theta_H + k_{CH_3}^{rev} \Theta_{CH_3} \Theta_v - k_{CH_4}^{form} \Theta_{CH_3} \Theta_H + k_{CH_4}^{rev} \Theta_{CH_4} \Theta_v \dots \\ & - k_{CHCH_2}^{form} \Theta_{CHCH} \Theta_H + k_{CHCH_2}^{rev} \Theta_{CHCH_2} \Theta_v - k_{CH_2CH_2}^{form} \Theta_{CHCH_2} \Theta_H + k_{CH_2CH_2}^{rev} \Theta_{CH_2CH_2} \Theta_v \dots \\ & - k_{CHCH_3}^{form} \Theta_{CHCH_2} \Theta_H + k_{CHCH_3}^{rev} \Theta_{CHCH_3} \Theta_v - k_{CH_2CHCH_3}^{form} \Theta_{CHCHCH_3} \Theta_H + k_{CH_2CHCH_3}^{rev} \Theta_{CH_2CHCH_3} \Theta_v \end{aligned}$$

$$\begin{aligned} \frac{d\Theta_{CH}}{dt} = & k_{CH}^{form} \Theta_C \Theta_H - k_{CH}^{rev} \Theta_{CH} \Theta_v - k_{CH_2}^{form} \Theta_{CH} \Theta_H + k_{CH_2}^{rev} \Theta_{CH_2} \Theta_v - k_{CHCH}^{form} \Theta_{CH} \Theta_{CH} + k_{CHCH}^{rev} \Theta_{CHCH} \Theta_v \dots \\ & - k_{CHCHCH_3}^{form} \Theta_{CHCH_3} \Theta_{CH} + k_{CHCHCH_3}^{rev} \Theta_{CHCHCH_3} \Theta_v \end{aligned}$$

$$\frac{d\Theta_{CH_2}}{dt} = k_{CH_2}^{form} \Theta_{CH} \Theta_H - k_{CH_2}^{rev} \Theta_{CH_2} \Theta_v - k_{CH_3}^{form} \Theta_{CH_2} \Theta_H + k_{CH_3}^{rev} \Theta_{CH_3} \Theta_v$$

$$\frac{d\Theta_{CH_3}}{dt} = k_{CH_3}^{form} \Theta_{CH_2} \Theta_H - k_{CH_3}^{rev} \Theta_{CH_3} \Theta_v - k_{CH_4}^{form} \Theta_{CH_3} \Theta_H + k_{CH_4}^{rev} \Theta_{CH_4} \Theta_v$$

$$\frac{d\Theta_{CH_4}}{dt} = k_{CH_4}^{form} \Theta_{CH_3} \Theta_H - k_{CH_4}^{rev} \Theta_{CH_4} \Theta_v - k_{CH_4}^{desorp} \Theta_{CH_4}$$

$$\frac{d\Theta_{OH}}{dt} = k_{OH}^{form} \Theta_O \Theta_H - k_{OH}^{diss} \Theta_{OH} \Theta_v - k_{H_2O}^{desorp} \Theta_H \Theta_{OH}$$

$$\frac{d\Theta_{CHCH}}{dt} = k_{CHCH}^{form} \Theta_{CH} \Theta_{CH} - k_{CHCH}^{rev} \Theta_{CHCH} \Theta_v - k_{CHCH_2}^{form} \Theta_{CHCH} \Theta_H + k_{CHCH}^{rev} \Theta_{CHCH_2} \Theta_v$$

$$\frac{d\Theta_{CHCH_2}}{dt} = k_{CHCH_2}^{form} \Theta_{CHCH} \Theta_H - k_{CHCH_2}^{rev} \Theta_{CHCH_2} \Theta_v - k_{CH_2CH_2}^{form} \Theta_{CHCH_2} \Theta_H + k_{CH_2CH_2}^{rev} \Theta_{CH_2CH_2} \Theta_v$$

$$\frac{d\Theta_{CH_2CH_2}}{dt} = k_{CH_2CH_2}^{form} \Theta_{CHCH_2} \Theta_H - k_{CH_2CH_2}^{rev} \Theta_{CH_2CH_2} \Theta_v - k_{CH_2CH_2}^{desorp} \Theta_{CH_2CH_2}$$

$$\frac{d\Theta_{CHCHCH_3}}{dt} = k_{CHCHCH_3}^{form} \Theta_{CHCH_2} \Theta_H - k_{CHCHCH_3}^{rev} \Theta_{CHCHCH_3} \Theta_v - k_{CHCHCH_3}^{form} \Theta_{CHCHCH_3} \Theta_{CH} + k_{CHCHCH_3}^{rev} \Theta_{CHCHCH_3} \Theta_v$$

$$\frac{d\Theta_{CHCHCH_3}}{dt} = k_{CHCHCH_3}^{form} \Theta_{CHCHCH_3} \Theta_{CH} - k_{CHCHCH_3}^{rev} \Theta_{CHCHCH_3} \Theta_v - k_{CH_2CHCH_3}^{form} \Theta_{CHCHCH_3} \Theta_H + \\ k_{CH_2CHCH_3}^{rev} \Theta_{CH_2CHCH_3} \Theta_v$$

$$\frac{d\Theta_{CH_2CHCH_3}}{dt} = k_{CH_2CHCH_3}^{form} \Theta_{CHCHCH_3} \Theta_H - k_{CH_2CHCH_3}^{rev} \Theta_{CH_2CHCH_3} \Theta_v - k_{CH_2CHCH_3}^{desorp} \Theta_{CH_2CHCH_3}$$

$$\begin{aligned} \frac{d\Theta_v}{dt} = & -\frac{d\Theta_{CO}}{dt} - \frac{d\Theta_C}{dt} - \frac{d\Theta_O}{dt} - \frac{d\Theta_H}{dt} - \frac{d\Theta_{CH}}{dt} - \frac{d\Theta_{CH_2}}{dt} - \dots\dots\dots \\ & \frac{d\Theta_{CH_3}}{dt} - \frac{d\Theta_{CH_4}}{dt} - \frac{d\Theta_{OH}}{dt} - \frac{d\Theta_{CHCH}}{dt} - \frac{d\Theta_{CHCH_2}}{dt} - \dots\dots\dots \\ & \frac{d\Theta_{CH_2CH_2}}{dt} - \frac{d\Theta_{CHCH_3}}{dt} - \frac{d\Theta_{CHCHCH_3}}{dt} - \frac{d\Theta_{CH_2CHCH_3}}{dt} \end{aligned}$$

Since these rate expressions are solved for a (111) type of hexagonal grid, the rate expressions involving the reaction of adsorbates on two sites are multiplied with the coordination number Z = 6. Parameters are assumed to be independent of lateral interactions.

The equations are solved using a stiff ODE solver (ode15s) in MATLAB.

In the simulations direct CO activation has thus been assumed, as found for highly reactive Ru surfaces, although there would be no essential difference if hydrogen activated dissociation had been considered as long as O_{ads} removal is fast, as is the case considered in the simulations. The only difference then is direct formation of CH, which in the present simulation occurs in two steps.

As can be seen from the above rate expressions, all the elementary reaction steps, excluding the product re-adsorption are considered reversible. This is a novel feature in our simulations as against conventional FT kinetics models where the chain growth steps are considered irreversible.