Supporting Information for:

The Monomer Formation Model versus the Chain Growth Model of the Fischer-Tropsch Reaction

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Table of contents:

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

The reaction energy profile shown in Figure 1 in the main paper 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 H_2 adsorption are calculated using the expression (S1) below.

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

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 H_2:CO pressure ratio of 3:1. A sticking coefficient of 10^{-2} is used for CO and 10^{-5} is used for H_2. The rates of CO and H_2 desorption are calculated using Equation S2 below.

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

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 $\frac{k_B T}{h}Q^{\ddagger}_{trans}Q^{\ddagger}_{rot}$. The translational partition function is then calculated using the expression (S3) below.

$$Q^{\ddagger}_{trans} = \frac{A_{site}2\pi m k_B T}{h^2} \tag{S3}$$

The rotational partition function is calculated using

$$Q^{\ddagger}_{rot,2D} = \frac{1}{\sigma}\frac{T}{\theta_{rot}} \tag{S4}$$

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:

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

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

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

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

* The rates of adsorption are calculated using expression S1.
-- Readsorption 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:

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

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

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

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

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

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

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

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

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

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

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

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

$$\frac{d\Theta_{CHCH_3}}{dt} = k_{CHCH_3}^{form}\Theta_{CHCH_2}\Theta_{H} - k_{CHCH_3}^{rev}\Theta_{CHCH_3}\Theta_{v} - k_{CHCHCH_3}^{form}\Theta_{CHCH_3}\Theta_{CH} + k_{CHCHCH_3}^{rev}\Theta_{CHCHCH_3}\Theta_{v}$$

$$\begin{aligned}\frac{d\Theta_{CHCHCH_3}}{dt} = {} & k_{CHCHCH_3}^{form}\Theta_{CHCH_3}\Theta_{CH} - k_{CHCHCH_3}^{rev}\Theta_{CHCHCH_3}\Theta_{v} - k_{CH_2CHCH_3}^{form}\Theta_{CHCHCH_3}\Theta_{H} + \ldots\ldots\ldots \\ & k_{CH_2CHCH_3}^{rev}\Theta_{CH_2CHCH_3}\Theta_{v}\end{aligned}$$

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

$$\begin{aligned}\frac{d\Theta_{v}}{dt} = {} & -\frac{d\Theta_{CO}}{dt} - \frac{d\Theta_{C}}{dt} - \frac{d\Theta_{O}}{dt} - \frac{d\Theta_{H}}{dt} - \frac{d\Theta_{CH}}{dt} - \frac{d\Theta_{CH_2}}{dt} - \ldots\ldots\ldots \\ & \frac{d\Theta_{CH_3}}{dt} - \frac{d\Theta_{CH_4}}{dt} - \frac{d\Theta_{OH}}{dt} - \frac{d\Theta_{CHCH}}{dt} - \frac{d\Theta_{CHCH_2}}{dt} - \ldots\ldots\ldots \\ & \frac{d\Theta_{CH_2CH_2}}{dt} - \frac{d\Theta_{CHCH_3}}{dt} - \frac{d\Theta_{CHCHCH_3}}{dt} - \frac{d\Theta_{CH_2CHCH_3}}{dt}\end{aligned}$$

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 actual microkinetics simulations reported in the paper continue chain growth by including also the differential equations homologous to the ones for C_2 formation, for the formation of hydrocarbons longer than C_3 upto C_{100}.

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.

Section S2 List of Symbols

ASF	Anderson-Schulz-Flory
α	chain growth parameter
α_{BEP}	BEP proportionality parameter
A_x	pre-exponent of BEP rate constant expression of reaction x
BEP	Brønsted-Evans-Polanyi
β_x	BEP proportionality parameter of reaction x
θ_{CO}	surface coverage of CO
θ_{CO}^{ref}	surface coverage of CO with no reaction
θ_v	surface vacancy concentration
θ_1	surface coverage of CH_x
θ_2	surface coverage of C_2 hydrocarbon chain
θ_i	surface coverage of hydrocarbon chain with i carbon atoms
θ_t	total surface concentration of hydrocarbons
P_{CO}	partial pressure of CO
P_{H_2}	partial pressure of H_2
k_{ads}^{CO}	rate constant of CO adsorption
k_{des}^{CO}	rate constant of CO desorption
$k_{CO}^{CH_x}$	lumped rate constant of CO to CH_x transformation
k_{CC}^{f}	forward lumped rate constant of C-C bond formation
k_{cc}^{b}	reverse lumped rate constant of C-C bond formation

k_t^m	lumped rate constant of CH_x to methane transformation
k_t	lumped rate constant of chain growth termination
ΔE_{act}	change in activation energy
$\Delta E_{reaction}$	change in reaction energy
P_1	gas phase yield of CH_4
P_i	gas phase yield of hydrocarbon of chain length i
k_x	BEP rate constant expression of reaction x
E_x^0	default value of activation energy for reaction x
$E_{ads}(C)$	adsorption energy of C atom
R_{CO}	rate of total CO consumption
$R_{C_{2^+}}$	rate of hydrocarbon product formation with more than one carbon atom
C_{2^+}	concentration of hydrocarbons with more than one carbon atom
E_{act}^{CO}	activation energy of CO dissociation
E_{act}^{CC}	activation energy for the incorporation of CH monomer into growing chain
$E_{act}^{CH \rightarrow CH_2}$	activation energy for the hydrogenation of CH into CH_2
$E_{act}^{CHCH_2R \rightarrow CH_2CH_2R}$	activation energy to terminate alkenyl chain by hydrogenation
E_t^0	default value of activation energy of termination
E_f^0	default value of activation energy of chain growth reaction
E_d^0	default value of activation energy of CO dissociation
FT	Fischer-Tropsch
r	rate

R	gas constant
T	temperature
TOF	Turn Over Frequency
TS	transition state
$T_{max}(C_2^+)$	temperature of maximum C_2^+ yield`

Section S3 Supporting References (with more than 10 authors)

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