Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Microkinetics of oxygenate formation in the Fischer-Tropsch reaction

Supplementary information

Details of the molecular microkinetics simulations

In this section, we provide further details on the molecular microkinetics simulations employed in this study. This section is divided into two subsections. Subsection S1 details the methods used for the calculation of the elementary rate constants, while subsection S2 explains the microkinetics rate expressions and the corresponding ordinary differential equations in both the carbide chain growth mechanism and the CO insertion chain growth mechanism.

Section S1: Methods used for calculation of the elementary rate constants

The reaction energy profile shown in Figures 2 and 3 of main text 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 a gain in entropy in the product desorption and loss in entropy for reagent adsorption. In the present study, product re-adsorption is not included.

The rates of CO and H_2 adsorption are calculated using the expression (S1.1) below.

$$W_{ads} = \frac{P A_{site} \sigma S}{\sqrt{2\pi m k_B T}} \qquad \text{(S1.1)}$$

Here, A_{site} is the area of a single adsorption site, P is the partial gas pressure and T, temperature (in Kelvin). Except for the subsection 3.1.2 in the main paper in which the effect of the reagent partial pressure on the final rate of the reaction is explored, the total pressure is 20 bar with H_2:CO pressure ratio of 3:1. Values of 10^{-2} and 10^{-5} are used for the sticking coefficient S of CO and H_2 respectively.The rates of CO and H_2 desorption are calculated using Equation S2 below.

$$W_{des} = \frac{k_B T}{h} \frac{Q^{\ddagger}}{Q} \exp\left[-\frac{E_{bar}}{k_B T}\right] \qquad \text{(S1.2)}$$

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.

$$Q^{\ddagger}_{trans} = \frac{A_{site} 2\pi m k_B T}{h^2} \tag{S1.3}$$

The rotational partition function is calculated using

$$Q^{\ddagger}_{rot,2D} = \frac{1}{\sigma} \frac{T}{\theta_{rot}} \tag{S1.4}$$

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:

$$Q_{vib} = \prod_i \left[\tilde{Q}_i \exp\left[-\frac{\mathrm{h}\omega_i}{2k_B T} \right] \right] \tag{S1.5}$$

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

$$\tilde{Q}_i = \frac{1}{1 - \exp\left[-\frac{\mathrm{h}\omega_i}{k_B T} \right]} \tag{S1.6}$$

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. The elementary reaction steps leading up to the production of C_3 olefin and aldehyde products are listed below. The rate parameters for higher olefins and oxygenates are homologous to the respective C_3 products formation. In columns 2 and 3, the first number indicates the forward rate, while the second number indicates the reverse rate. Please note the reversible and unidirectional reactions.

Reaction	**υ (s^{-1})**	**Activation Barrier (kJ/mol)**
CO (gas) 👎 CO (ads)	*,10^{16}	0,120
H_2 (gas) 👎 H (ads) + H (ads)	*,10^{16}	0, 86
CO 👎 C + O	10^{13}, 10^{13}	130, 100
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}	130, 130
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}	70, 90
CHCH + H 👎 $CHCH_2$	10^{13}, 10^{13}	70, 20
$CHCH_2$ + H 👎 $CHCH_3$	10^{13}, 10^{13}	50, 50
$CHCH_3$ + CH 👎 $CHCHCH_3$	10^{13}, 10^{13}	70, 90
$CHCHCH_3$ + H 👎 CH_2CHCH_3	10^{14}, 10^{13}	90, 90
CH_2CHCH_3 (ads) ✂ CH_2CHCH_3 (gas)	10^{16}	80
$CHCH_3$ + CO 👎 $CHCH_3CO$	10^{13}, 10^{13}	50, 20
$CHCH_3CO$ + H 👎 $CHCH_3CHO$	10^{13}, 10^{13}	50, 20
$CHCH_3CHO$ + H 👎 CH_2CH_3CHO	10^{14}, 10^{13}	30, 34
CH_2CH_3CHO (ads) ✂ CH_2CH_3CHO (gas)	10^{16}	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 S1.1.

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

The reactions highlighted in brown colored text are the elementary reactions whose rates are varied to evaluate their effect on the final reactivity.

Section S2: 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 Table S1 above, the kinetics is described using the following set of coupled ordinary differential equations for carbide mechanism:

$$\frac{d\Theta_{CO}}{dt} = k_{CO}^{ads}\Theta_v - k_{CO}^{des}\Theta_{CO} - k_{CO}^{diss}\Theta_{CO}\Theta_v + k_{CO}^{rec}\Theta_C\Theta_O - k_{CHCH_3CO}^{form}\Theta_{CHCH_3}\Theta_{CO} + k_{CHCH_3CO}^{rev}\Theta_{CHCH_3CO}\Theta_v$$

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

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

$$\begin{aligned}\frac{d\Theta_H}{dt} = {} & k_{H_2}^{ads}\Theta_v\Theta_v - k_{H_2}^{des}\Theta_H\Theta_H - k_{OH}^{form}\Theta_O\Theta_H + k_{OH}^{diss}\Theta_{OH}\Theta_v - k_{H_2O}^{des}\Theta_{OH}\Theta_H \ldots\ldots \\ & - k_{CH}^{form}\Theta_C\Theta_H + k_{CH}^{rev}\Theta_{CH}\Theta_v - k_{CH_2}^{form}\Theta_{CH}\Theta_H + k_{CH_2}^{rev}\Theta_{CH_2}\Theta_v \ldots\ldots\ldots \\ & - k_{CH_3}^{form}\Theta_{CH_2}\Theta_H + k_{CH_3}^{rev}\Theta_{CH_3}\Theta_v - k_{CH_4}^{form}\Theta_{CH_3}\Theta_H + k_{CH_4}^{rev}\Theta_{CH_4}\Theta_v \ldots\ldots\ldots \\ & - k_{CHCH_2}^{form}\Theta_{CHCH}\Theta_H + k_{CHCH_2}^{rev}\Theta_{CHCH_2}\Theta_v - k_{CHCH_3}^{form}\Theta_{CHCH_2}\Theta_H + k_{CHCH_3}^{rev}\Theta_{CHCH_3}\Theta_v \ldots\ldots \\ & - k_{CH_2CHCH_3}^{form}\Theta_{CHCHCH_3}\Theta_H + k_{CH_2CHCH_3}^{rev}\Theta_{CH_2CHCH_3}\Theta_v - k_{CHCH_3CHO}^{form}\Theta_{CHCH_3CO}\Theta_H + k_{CHCH_3CHO}^{rev}\Theta_{CHCH_3CHO}\Theta_v \ldots\ldots \\ & - k_{CH_2CH_3CHO}^{form}\Theta_{CHCH_3CHO}\Theta_H + k_{CH_2CH_3CHO}^{rev}\Theta_{CH_2CH_3CHO}\Theta_v\end{aligned}$$

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

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

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

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

$$\frac{d\Theta_{OH}}{dt} = k_{OH}^{form}\Theta_{O}\Theta_{H} - k_{OH}^{diss}\Theta_{OH}\ \Theta_{v} - k_{H_2O}^{desorp}\Theta_{H}\ \Theta_{OH}$$

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

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

$$\begin{aligned}\frac{d\Theta_{CHCH_3}}{dt} = {} & k_{CHCH_3}^{form}\Theta_{CHCH_2}\Theta_{H} - k_{CHCH_3}^{rev}\Theta_{CHCH_3}\Theta_{v}\ldots\ldots \\ & - k_{CHCHCH_3}^{form}\Theta_{CHCH_3}\Theta_{CH} + k_{CHCHCH_3}^{rev}\Theta_{CHCHCH_3}\Theta_{v}\ldots\ldots \\ & - k_{CHCH_3CO}^{form}\Theta_{CHCH_3}\Theta_{CO} + k_{CHCH_3CO}^{rev}\Theta_{CHCH_3CO}\Theta_{v}\end{aligned}$$

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

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

$$\frac{d\Theta_{CHCH_3CO}}{dt} = k_{CHCH_3CO}^{form}\Theta_{CHCH_3}\Theta_{CO} - k_{CHCH_3CO}^{rev}\Theta_{CHCH_3CO}\Theta_{v} - k_{CHCH_3CHO}^{form}\Theta_{CHCH_3CO}\Theta_{H} + k_{CHCH_3CHO}^{rev}\Theta_{CHCH_3CHO}\Theta_{v}$$

$$\frac{d\Theta_{CHCH_3CHO}}{dt} = k_{CHCH_3CHO}^{form}\Theta_{CHCH_3CO}\Theta_{H} - k_{CHCH_3CHO}^{rev}\Theta_{CHCH_3CHO}\Theta_{v} - k_{CH_2CH_3CHO}^{form}\Theta_{CHCH_3CHO}\Theta_{H} + k_{CH_2CH_3CHO}^{rev}\Theta_{CH_2CH_3CHO}\Theta_{v}$$

$$\frac{d\Theta_{CH_2CH_3CHO}}{dt} = k_{CH_2CH_3CHO}^{form}\Theta_{CHCH_3CHO}\Theta_{H} - k_{CH_2CH_3CHO}^{rev}\Theta_{CH_2CH_3CHO}\Theta_{v} - k_{CH_2CH_3CHO}^{desorp}\Theta_{CH_2CH_3CHO}$$

$$\begin{aligned}\frac{d\Theta_{v}}{dt} = {} & -\frac{d\Theta_{CO}}{dt} - \frac{d\Theta_{C}}{dt} - \frac{d\Theta_{O}}{dt} - \frac{d\Theta_{H}}{dt} - \frac{d\Theta_{CH}}{dt} - \frac{d\Theta_{CH_2}}{dt} - \ldots\ldots\ldots \\ & \frac{d\Theta_{CH_3}}{dt} - \frac{d\Theta_{CH_4}}{dt} - \frac{d\Theta_{OH}}{dt} - \frac{d\Theta_{CHCH}}{dt} - \frac{d\Theta_{CHCH_2}}{dt} - \ldots\ldots\ldots\ldots \\ & \frac{d\Theta_{CHCH_3}}{dt} - \frac{d\Theta_{CHCHCH_3}}{dt} - \frac{d\Theta_{CH_2CHCH_3}}{dt} - \frac{d\Theta_{CHCH_3CO}}{dt} - \frac{d\Theta_{CHCH_3CHO}}{dt} - \frac{d\Theta_{CH_2CH_3CHO}}{dt}\end{aligned}$$

CO insertion Mechanism

Table S2 Elementary reactions and the respective barriers used in the microkinetics of Fischer-Tropsch Reaction based on the CO insertion mechanism. The elementary reaction steps leading up to the production of C_2 olefin and aldehyde products are listed below. The rate parameters for higher olefins and oxygenates are homologous to the respective C_2 products formation. In columns 2 and 3, the first number indicates the forward rate, while the second number indicates the reverse rate. Please note the reversible and unidirectional reactions.

Reaction	**υ (s^{-1})**	**Activation Barrier (kJ/mol)**
Elementary reactions common to mechanistic schemes shown in figures 4(a) and 4(b) of the main article		
CO (gas) 👎 CO (ads)	*, 10^{16}	*,120
H_2 (gas) 👎 H (ads) + H (ads)	*, 10^{16}	*, 86
CO 👎 C + O	10^{13}, 10^{13}	130, 100
CO + H 👎 CH + O	10^{13}, 10^{13}	130, 100
C + H 👎 CH	10^{13}, 10^{13}	70, 70
CH + H 👎 CH_2	10^{13}, 10^{13}	24, 12
CH_2 +H 👎 CH_3	10^{14}, 10^{13}	100, 122
CH_3 + H 👎 CH_4	10^{17}, 10^{13}	80, 32
CH_4 (ads) ✂ CH_4 (gas)	10^{13}	2
CH_2 + CO 👎 CH_2CO	10^{13}, 10^{13}	51, 9
CH_2CO + H 👎 CH_3CO	10^{13}, 10^{13}	57, 102
CH_3CO + H 👎 CH_3CHO	10^{14}, 10^{13}	76, 65
CH_3CHO (ads) ✂ CH_3CHO (gas)	10^{16}	110
CH_3CH 👎 CH_2CH_2	10^{14}, 10^{13}	70, 20
CH_2CH_2 (ads) ✂ CH_2CH_2 (gas)	10^{16}	89
O + H 👎 OH	10^{13}, 10^{10}	70, 64
OH + H ✂ H_2O (gas)	4.45×10^{16}	106
Elementary reactions specific for mechanistic scheme shown in figures 4(a) of the main article		
CH_3CO 👎 CH_3C + O	10^{13}, 10^{13}	89, 145
CH_3C + H 👎 CH_3CH	10^{13}, 10^{13}	58, 20
Elementary reaction specific for mechanistic scheme shown in figures 4(b) of the main article		
CH_3CHO 👎 CH_3CH + O	10^{13}, 10^{13}	70, 98

* The rates of adsorption are calculated using expression S1.1.

Differential Equations corresponding to CO-insertion mechanism depicted in figure 4(a) of the main article and the elementary reactions shown in Table S2.

$$\frac{d\Theta_{CO}}{dt} = k_{CO}^{ads}\Theta_{v} - k_{CO}^{des}\Theta_{CO} - k_{CO}^{diss}\Theta_{CO}\Theta_{v} + k_{CO}^{rec}\Theta_{C}\Theta_{O} - k_{CH}^{formyl-forw}\Theta_{CO}\Theta_{H}\ldots\ldots$$
$$+ k_{CH}^{formyl-rev}\Theta_{CH}\Theta_{O} - k_{CH_2CO}^{form}\Theta_{CH_2}\Theta_{CO} + k_{CH_2CO}^{rev}\Theta_{CH_2CO}\Theta_{v}$$

$$\frac{d\Theta_{C}}{dt} = k_{CO}^{diss}\Theta_{CO}\Theta_{v} - k_{CO}^{rec}\Theta_{C}\Theta_{O} - k_{CH}^{form}\Theta_{C}\Theta_{H} + k_{CH}^{rev}\Theta_{CH}\Theta_{v}$$

$$\frac{d\Theta_{O}}{dt} = k_{CO}^{diss}\Theta_{CO}\Theta_{v} - k_{CO}^{rec}\Theta_{C}\Theta_{O} + k_{CH}^{formyl-forw}\Theta_{CO}\Theta_{H} - k_{CH}^{formyl-rev}\Theta_{CH}\Theta_{O}\ldots\ldots$$
$$- k_{OH}^{form}\Theta_{O}\Theta_{H} + k_{OH}^{diss}\Theta_{OH}\Theta_{v} + k_{CH_3C}^{form}\Theta_{CH_3CO}\Theta_{v} - k_{CH_3C}^{rev}\Theta_{CH_3C}\Theta_{O}$$

$$\frac{d\Theta_{H}}{dt} = k_{H_2}^{ads}\Theta_{v}\Theta_{v} - k_{H_2}^{des}\Theta_{H}\Theta_{H} - k_{OH}^{form}\Theta_{O}\Theta_{H} + k_{OH}^{diss}\Theta_{OH}\Theta_{v} - k_{H_2O}^{des}\Theta_{OH}\Theta_{H}\ldots\ldots$$
$$- k_{CH}^{form}\Theta_{C}\Theta_{H} + k_{CH}^{rev}\Theta_{CH}\Theta_{v} - k_{CH}^{formyl-forw}\Theta_{CO}\Theta_{H} + k_{CH}^{formyl-rev}\Theta_{CH}\Theta_{O} - k_{CH_2}^{form}\Theta_{CH}\Theta_{H} + k_{CH_2}^{rev}\Theta_{CH_2}\Theta_{v}\ldots\ldots\ldots$$
$$- k_{CH_3}^{form}\Theta_{CH_2}\Theta_{H} + k_{CH_3}^{rev}\Theta_{CH_3}\Theta_{v} - k_{CH_4}^{form}\Theta_{CH_3}\Theta_{H} + k_{CH_4}^{rev}\Theta_{CH_4}\Theta_{v}\ldots\ldots\ldots$$
$$- k_{CH_3CO}^{form}\Theta_{CH_2CO}\Theta_{H} + k_{CH_3CO}^{rev}\Theta_{CH_3CO}\Theta_{v} - k_{CH_3CHO}^{form}\Theta_{CH_3CO}\Theta_{H} + k_{CH_3CHO}^{rev}\Theta_{CH_3CHO}\Theta_{v}\ldots\ldots$$
$$- k_{CH_3CH}^{form}\Theta_{CH_3C}\Theta_{H} + k_{CH_3CH}^{rev}\Theta_{CH_3CH}\Theta_{v}$$

$$\frac{d\Theta_{CH}}{dt} = k_{CH}^{form}\Theta_{C}\Theta_{H} - k_{CH}^{rev}\Theta_{CH}\Theta_{v} + k_{CH}^{formyl-forw}\Theta_{CO}\Theta_{H} - k_{CH}^{formyl-rev}\Theta_{CH}\Theta_{O} - k_{CH_2}^{form}\Theta_{CH}\Theta_{H} + k_{CH_2}^{rev}\Theta_{CH_2}\Theta_{v}$$

$$\frac{d\Theta_{CH_2}}{dt} = k_{CH_2}^{form}\Theta_{CH}\Theta_{H} - k_{CH_2}^{rev}\Theta_{CH_2}\Theta_{v} - k_{CH_3}^{form}\Theta_{CH_2}\Theta_{H} + k_{CH_3}^{rev}\Theta_{CH_3}\Theta_{v} - k_{CH_2CO}^{form}\Theta_{CH_2}\Theta_{CO} + k_{CH_2CO}^{rev}\Theta_{CH_2CO}\Theta_{v}$$

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

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

$$\frac{d\Theta_{CH_2CO}}{dt} = k_{CH_2CO}^{form}\Theta_{CH_2}\Theta_{CO} - k_{CH_2CO}^{rev}\Theta_{CH_2CO}\Theta_{v} - k_{CH_3CO}^{form}\Theta_{CH_2CO}\Theta_{H} + k_{CH_3CO}^{rev}\Theta_{CH_3CO}\Theta_{v}$$

$$\frac{d\Theta_{CH_3CO}}{dt} = k_{CH_3CO}^{form}\Theta_{CH_2CO}\Theta_{H} - k_{CH_3CO}^{rev}\Theta_{CH_3CO}\Theta_{v} - k_{CH_3CHO}^{form}\Theta_{CH_3CO}\Theta_{H}\ldots\ldots$$
$$+ k_{CH_3CHO}^{rev}\Theta_{CH_3CHO}\Theta_{v} - k_{CH_3C}^{form}\Theta_{CH_3CO}\Theta_{v} + k_{CH_3C}^{rev}\Theta_{CH_3C}\Theta_{O}$$

$$\frac{d\Theta_{CH_3CHO}}{dt} = k_{CH_3CHO}^{form}\Theta_{CH_3CO}\Theta_{H} - k_{CH_3CHO}^{rev}\Theta_{CH_3CHO}\Theta_{v} - k_{CH_3CHO}^{desorp}\Theta_{CH_3CHO}$$

$$\frac{d\Theta_{CH_3C}}{dt}=k_{CH_3C}^{form}\Theta_{CH_3CO}\Theta_v-k_{CH_3C}^{rev}\Theta_{CH_3C}\Theta_O-k_{CH_3CH}^{form}\Theta_{CH_3C}\Theta_H+k_{CH_3CH}^{rev}\Theta_{CH_3CH}\Theta_v$$

$$\frac{d\Theta_{CH_3CH}}{dt}=k_{CH_3CH}^{form}\Theta_{CH_3C}\Theta_H-k_{CH_3CH}^{rev}\Theta_{CH_3CH}\Theta_v-k_{CH_2CH_2}^{form}\Theta_{CH_3CH}+k_{CH_2CH_2}^{rev}\Theta_{CH_2CH_2}$$

$$\frac{d\Theta_{CH_2CH_2}}{dt}=k_{CH_2CH_2}^{form}\Theta_{CH_3CH}-k_{CH_2CH_2}^{rev}\Theta_{CH_3CHO}\Theta_v-k_{CH_2CH_2}^{desorp}\Theta_{CH_2CH_2}$$

Differential Equations corresponding to CO-insertion mechanism depicted in figure 4(b) of the main article and the elementary reactions shown in Table S2.

$$\begin{aligned}\frac{d\Theta_{CO}}{dt}=&\,k_{CO}^{ads}\Theta_v-k_{CO}^{des}\Theta_{CO}-k_{CO}^{diss}\Theta_{CO}\Theta_v+k_{CO}^{rec}\Theta_C\Theta_O-k_{CH}^{formyl-forw}\Theta_{CO}\Theta_H\cdots\cdots\\&+k_{CH}^{formyl-rev}\Theta_{CH}\Theta_O-k_{CH_2CO}^{form}\Theta_{CH_2}\Theta_{CO}+k_{CH_2CO}^{rev}\Theta_{CH_2CO}\Theta_v\end{aligned}$$

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

$$\begin{aligned}\frac{d\Theta_O}{dt}=&\,k_{CO}^{diss}\Theta_{CO}\Theta_v-k_{CO}^{rec}\Theta_C\Theta_O+k_{CH}^{formyl-forw}\Theta_{CO}\Theta_H-k_{CH}^{formyl-rev}\Theta_{CH}\Theta_O\cdots\cdots\\&-k_{OH}^{form}\Theta_O\Theta_H+k_{OH}^{diss}\Theta_{OH}\Theta_v+k_{CH_3CH}^{form}\Theta_{CH_3CHO}\Theta_v-k_{CH_3CH}^{rev}\Theta_{CH_3CH}\Theta_O\end{aligned}$$

$$\begin{aligned}\frac{d\Theta_H}{dt}=&\,k_{H_2}^{ads}\Theta_v\Theta_v-k_{H_2}^{des}\Theta_H\Theta_H-k_{OH}^{form}\Theta_O\Theta_H+k_{OH}^{diss}\Theta_{OH}\Theta_v-k_{H_2O}^{des}\Theta_{OH}\Theta_H\cdots\cdots\\&-k_{CH}^{form}\Theta_C\Theta_H+k_{CH}^{rev}\Theta_{CH}\Theta_v-k_{CH}^{formyl-forw}\Theta_{CO}\Theta_H+k_{CH}^{formyl-rev}\Theta_{CH}\Theta_O-k_{CH_2}^{form}\Theta_{CH}\Theta_H+k_{CH_2}^{rev}\Theta_{CH_2}\Theta_v\cdots\cdots\cdots\\&-k_{CH_3}^{form}\Theta_{CH_2}\Theta_H+k_{CH_3}^{rev}\Theta_{CH_3}\Theta_v-k_{CH_4}^{form}\Theta_{CH_3}\Theta_H+k_{CH_4}^{rev}\Theta_{CH_4}\Theta_v\cdots\cdots\cdots\\&-k_{CH_3CO}^{form}\Theta_{CH_2CO}\Theta_H+k_{CH_3CO}^{rev}\Theta_{CH_3CO}\Theta_v-k_{CH_3CHO}^{form}\Theta_{CH_3CO}\Theta_H+k_{CH_3CHO}^{rev}\Theta_{CH_3CHO}\Theta_v\end{aligned}$$

$$\frac{d\Theta_{CH}}{dt}=k_{CH}^{form}\Theta_C\Theta_H-k_{CH}^{rev}\Theta_{CH}\Theta_v+k_{CH}^{formyl-forw}\Theta_{CO}\Theta_H-k_{CH}^{formyl-rev}\Theta_{CH}\Theta_O-k_{CH_2}^{form}\Theta_{CH}\Theta_H+k_{CH_2}^{rev}\Theta_{CH_2}\Theta_v$$

$$\frac{d\Theta_{CH_2}}{dt}=k_{CH_2}^{form}\Theta_{CH}\Theta_H-k_{CH_2}^{rev}\Theta_{CH_2}\Theta_v-k_{CH_3}^{form}\Theta_{CH_2}\Theta_H+k_{CH_3}^{rev}\Theta_{CH_3}\Theta_v-k_{CH_2CO}^{form}\Theta_{CH_2}\Theta_{CO}+k_{CH_2CO}^{rev}\Theta_{CH_2CO}\Theta_v$$

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

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

$$\frac{d\Theta_{CH_2CO}}{dt}=k_{CH_2CO}^{form}\Theta_{CH_2}\Theta_{CO}-k_{CH_2CO}^{rev}\Theta_{CH_2CO}\Theta_v-k_{CH_3CO}^{form}\Theta_{CH_2CO}\Theta_H+k_{CH_3CO}^{rev}\Theta_{CH_3CO}\Theta_v$$

$$\frac{d\Theta_{CH_3CO}}{dt} = k^{form}_{CH_3CO}\Theta_{CH_2CO}\Theta_H - k^{rev}_{CH_3CO}\Theta_{CH_3CO}\Theta_v - k^{form}_{CH_3CHO}\Theta_{CH_3CO}\Theta_H + k^{rev}_{CH_3CHO}\Theta_{CH_3CHO}\Theta_v$$

$$\frac{d\Theta_{CH_3CHO}}{dt} = k^{form}_{CH_3CHO}\Theta_{CH_3CO}\Theta_H - k^{rev}_{CH_3CHO}\Theta_{CH_3CHO}\Theta_v - k^{form}_{CH_3CH}\Theta_{CH_3CHO}\Theta_v + k^{rev}_{CH_3CH}\Theta_{CH_3CH}\Theta_O - k^{desorp}_{CH_3CHO}\Theta_{CH_3CHO}$$

$$\frac{d\Theta_{CH_3CH}}{dt} = k^{form}_{CH_3CH}\Theta_{CH_3CHO}\Theta_v - k^{rev}_{CH_3CH}\Theta_{CH_3CH}\Theta_O - k^{form}_{CH_2CH_2}\Theta_{CH_3CH} + k^{rev}_{CH_2CH_2}\Theta_{CH_2CH_2}$$

$$\frac{d\Theta_{CH_2CH_2}}{dt} = k^{form}_{CH_2CH_2}\Theta_{CH_3CH} - k^{rev}_{CH_2CH_2}\Theta_{CH_3CHO}\Theta_v - k^{desorp}_{CH_2CH_2}\Theta_{CH_2CH_2}$$

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.

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.