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## Microkinetics of oxygenate formation in the Fischer-Tropsch reaction

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### Abstract

Microkinetics simulations are presented on the intrinsic activity and selectivity of the Fischer-Tropsch reaction with respect to the formation of long chain oxygenated hydrocarbons. Two different chain growth mechanisms are compared: the carbide chain growth mechanism and the CO insertion chain growth mechanism.

The microkinetics simulations are based on quantum-chemical data on reaction rate parameters of the elementary reactions steps of the Fischer-Tropsch reaction available in the literature.

Because the overall rate constant of chain growth remains too low the CO insertion chain growth mechanism is not found to produce higher hydrocarbons, except for ethylene and acetaldehyde or the corresponding hydrogenated products. According of the carbide mechanism available quantum-chemical data are consistent with high selectivity to long chain oxygenated hydrocarbon production at

low temperature. The anomalous initial increase with temperature of the chain growth parameter observed at such conditions is reproduced. It arises from the competition between the apparent rate of C-O bond activation to produce “CH<sub>x</sub>” monomers to be inserted into to the growing hydrocarbon chain and rate of chain growth termination.

The microkinetics simulations data enable analysis of selectivity changes as a function of critical elementary reaction rates as rate of activation of C-O bond of CO, insertion rate of CO into the growing hydrocarbon chain or rate constant of methane formation. Simulations show that changes in catalyst site reactivity affect elementary reaction steps differently. This has opposing consequences for oxygenate production selectivity, so that an optimizing compromise has to be found.

The simulation results are found to be consistent with most experimental data available today.

It is concluded that Fischer-Tropsch type catalysis has limited scope to produce long chain oxygenates with high yield, but there is an opportunity to improve yield of C<sub>2</sub> oxygenates.

## 1. Introduction:

In addition to hydrocarbons the Fischer-Tropsch reaction, which is an important conversion step in the overall process that converts coal or natural gas into liquid hydrocarbon fuels, can also produce oxygenates<sup>1-3</sup>. The selectivity towards their formation strongly depends on reaction conditions as well as the

catalytic material used. To produce oxygen containing hydrocarbons from synthesis gas (a mixture of CO and H<sub>2</sub>) instead of by selective oxidation of the corresponding hydrocarbons may have advantages in terms of raw materials used or processing requirements. In heterogeneous catalysis the oxygenated long hydrocarbon chain product can be formed through two essentially different reaction processes, that are excellently reviewed in references<sup>4, 5</sup>.

CO can become initially hydrogenated to methanol and the methanol undergoes aldol type reactions that lead to mixture of branched alcohols. The main investigated catalysts for this process are modified methanol catalysts, based on Cu, promoted by ZnO, Cr<sub>2</sub>O<sub>3</sub> or additional additives to catalyze formation of higher alcohol oligomers<sup>6</sup>.

Alternative catalyst systems to be considered here are based on the Fischer-Tropsch reaction. In this reaction instead of becoming hydrogenated CO initially decomposes into an adsorbed "CH<sub>x</sub>" intermediate that initiates an oligomerisation reaction. Oxygenate formation arises from the insertion reaction of CO in the growing adsorbed hydrocarbon chain. A transition metal component of such catalysts, that has been extensively studied, is Rh<sup>7, 8</sup>.

We will present results of microkinetics simulations that address the improvement of selectivity of oxygenate formation versus that of hydrocarbon formation, which is a key issue with respect to the application of this catalytic system.

In order to study the microkinetics of this reaction two main competitive mechanistic proposals for the hydrocarbon chain growth reaction have to be considered.<sup>9</sup> The most generally accepted is the carbide mechanism.<sup>10</sup> According to this mechanism chain growth occurs by consecutive insertion  $\text{CH}_x$  intermediates. This is different from the alternative proposal, originally by Pichler and Schulz<sup>11</sup> that proposes hydrocarbon growth through CO molecule insertion into the growing hydrocarbon chain. There is no consensus on which of the two mechanisms is preferred. For a recent analysis we refer to the literature.<sup>12, 13</sup> To decide between the two mechanistic options of chain growth is practically important because it provides different criteria for catalyst composition and structure choices to optimize CO conversion rates and product selectivity.

These criteria we will compare with experimental information as mainly summarized in the two review papers<sup>4, 5</sup>.

All of the known Fischer-Tropsch catalysts produce oxygenates, but with widely varying selectivities, that not only depend on the catalyst material, but also strongly on reaction conditions.<sup>14</sup>,

Important additional questions with respect to the optimization of the catalyst relate to structure dependence, role of promoters and the use of alloys.

The microkinetics simulations to be presented are based on consideration of the complete set elementary reaction steps leading to such products. An earlier study based also on such an approach is by Storsaeter et al.<sup>15</sup> Since several

elementary reaction steps compete, the microkinetics simulations will have to be solved without making a priori assumptions on rate controlling steps. For this reason the ordinary differential equations that follow from the kinetics schemes used will be solved directly using the ordinary differential equations (ODE) suite which comes with the software program Matlab<sup>®</sup>.

The simulation strategy is similar as we used in previous papers<sup>12, 13</sup>, that however only considered hydrocarbon formation and did not include oxygenate formation as will be done here.

The experimental distribution of Fischer-Tropsch hydrocarbon chains shows approximately ASF (Anderson-Schulz-Flory) distribution.<sup>3, 16</sup> When the product distribution is plotted as a function of hydrocarbon chain length an exponential distribution is found. It implies that the chain growth rate is independent of hydrocarbon chain length beyond a particular chain length that is typically for C<sub>3</sub> and higher chain length. The slope of this distribution plot gives chain growth probability  $\alpha$  (see also Eq. 1). We have used this property also in the simulations by electing the microkinetics chain growth parameters to be independent of chain length.

The molecular data on reaction intermediates and activation energies of elementary reaction steps will be based on published quantum-chemical data, that we have extensively reviewed elsewhere for the carbide mechanism<sup>12, 13</sup> and for the CO insertion chain growth mechanism in ref.<sup>21</sup>. The input data used can be

considered representative for Co, Ru or Rh metal surfaces of different structure. For consistency the microkinetics elementary reaction rate data have been adapted to confirm with the overall thermodynamics of the relevant Fischer-Tropsch products.

Different surface topologies change significantly the relative rate constants of CO activation versus that of methane formation, chain growth termination and C-C bond formation.

In the case of the chain growth reaction through CO insertion Cheng et. al.<sup>17</sup> for stepped and non-stepped Co (0001) surfaces and in a later paper we demonstrated that most of the additional published quantum-chemical data lead to the conclusion that this reaction mechanism can be excluded<sup>13, 21</sup>. However recently an interesting paper by Saeys et.al.<sup>18</sup> appeared that demonstrated a high sensitivity of key activation energy parameters to surface coverage. Of special interest is their suggestion that at high coverage lateral effects decrease the activation barriers for CO insertion into the growing hydrocarbon chain substantially, which would favour high chain growth according to this reaction route. This is important because simulations indicate<sup>12</sup> that long chain hydrocarbon selectivity is consistent with a high coverage of CO. For this reason we took the high surface coverage reaction energy data of Saeys et. al.<sup>18</sup> calculated for the Co(0001) surface as the default values for the CO insertion chain growth reaction.

In the microkinetics simulations to be presented here we will calculate selectivity and CO conversion rates at practical conditions. We will be interested in catalyst performance changes as a consequence of different choices of rate parameters that reflect catalyst composition as well as structure.

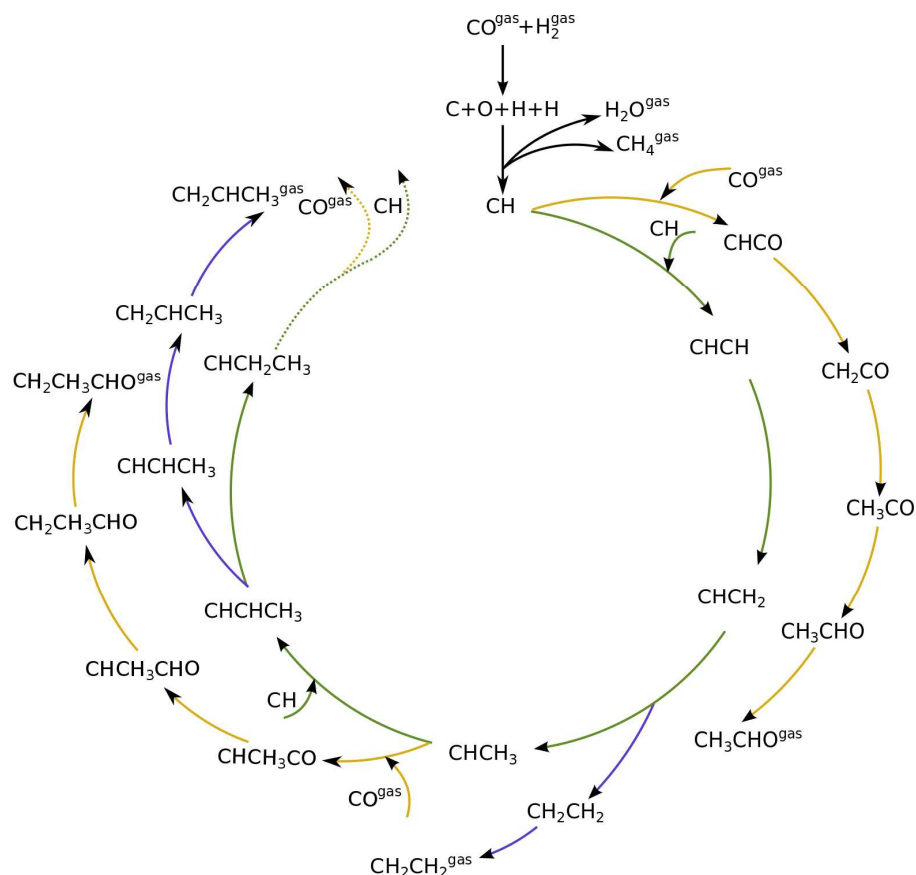
It will appear that selectivity to long chain oxygenate formation depends on the balance of several elementary rate constants that sometimes counteract. In the discussion and conclusion section the optimum microkinetics relations between elementary rate constants will be discussed. Through quantum-chemistry this can be related to composition and catalyst structure requirements, which provide a basis to compare theory with experiment in the Conclusion: comparison of theory and experiment Section.

## 2. Method

Microkinetics model descriptions including the mechanistic schemes in terms of the complete set of elementary reactions and their corresponding rate parameters for both the carbide chain growth mechanism as well as CO insertion mechanism studied in this report are presented in this section.



## 2.1 Carbide chain growth mechanism



**Figure 1** Mechanistic scheme for the Fischer-Tropsch reaction implemented for the formation of olefins as well as oxygenates. When the reaction intermediate does not have the “gas” label it is considered to be chemisorbed.

Figure 1 shows a schematic presentation of the kinetic model according to the carbide chain growth model explored in the present work. Mechanistic pathways leading to the formation of up to C<sub>3</sub> olefin and oxygenates can be seen in the figure. Based on previous work<sup>13, 19</sup> the CH<sub>ads</sub> monomer is considered as the building block that gets incorporated into the growing chain. The chain growth pathways are green color coded in the figure. Oxygenate termination pathways via a CO insertion step are represented by yellow and elementary steps leading to the termination of olefins

are shown in blue.  $\text{CH}_{\text{ads}}$  monomer, which is formed by the hydrogenation of carbon from the directly dissociated CO, is considered to be the building block for subsequent chain growth.

There are three prerogatives for the initial  $\text{CH}_{\text{ads}}$  monomer. It can undergo further hydrogenation steps desorbing as methane. Another path for it is the coupling with CO to form CHCO. This species further goes through three hydrogenation steps to terminate as acetaldehyde. The final option for  $\text{CH}_{\text{ads}}$  monomer is to couple with another  $\text{CH}_{\text{ads}}$  species leading the pathway towards chain growth. This CHCH species on the surface can now go through a hydrogenation step to form  $\text{CHCH}_2$ . Further addition of a hydrogen atom to the primary carbon leads to the termination of the chain as an olefin, ethylene in this case. Addition of the hydrogen atom to the secondary carbon atom leads it towards further chain growth. This alkylidene type of chain can either terminate into a corresponding aldehyde by going through CO insertion and subsequent hydrogenation steps; recombination of this with CH leads it to either termination into an olefin or towards further chain growth. The work presented here includes the formation of olefins and oxygenates up to a chain length of  $\text{C}_{50}$ .

As discussed elsewhere, another important technical aspect of first principle microkinetics simulations is that simulations are to be done including production of hydrocarbon chains of sufficient length so as to prevent spurious cut-off effects that result from reversibility of all the chain growth reactions included.<sup>20</sup> The chain growth parameter  $\alpha$  for oxygenate formation and alkane formation has to be the

same, which can be used as a test criterion for convergence of the simulations when

Figure 2 shows the relative adsorption energies and the activation barriers for various intermediates leading to the formation of propionaldehyde. Based on available quantum chemical data we have constructed the energy profiles of this reaction. Formation of all longer hydrocarbons as well as oxygenates is considered to be homologous and proceeds through insertion of a CH species in agreement with the chain growth model proposed before for Ru.<sup>19</sup> CH<sub>ads</sub> is the monomer that is incorporated into the growing adsorbed hydrocarbon chain. This mechanism corresponds to the generally accepted carbide mechanism in which CH<sub>x</sub> species is the surface species to be inserted into the growing hydrocarbon chain. The reaction energy diagrams of all higher carbon number products (hydrocarbons as well as oxygenates) have similar elementary reaction rate parameters, so that the product distribution may be expected to correspond to the logarithmic ASF distribution with chain growth parameter  $\alpha$  independent of the chain length.

Activation entropies have been chosen to be different from zero only for reactions between gas phase and solid. Further details about the actual prefactors used and their calculation details can be found in the supplementary information file accompanying this article. Readsorption from gas phase is ignored in the simulations.

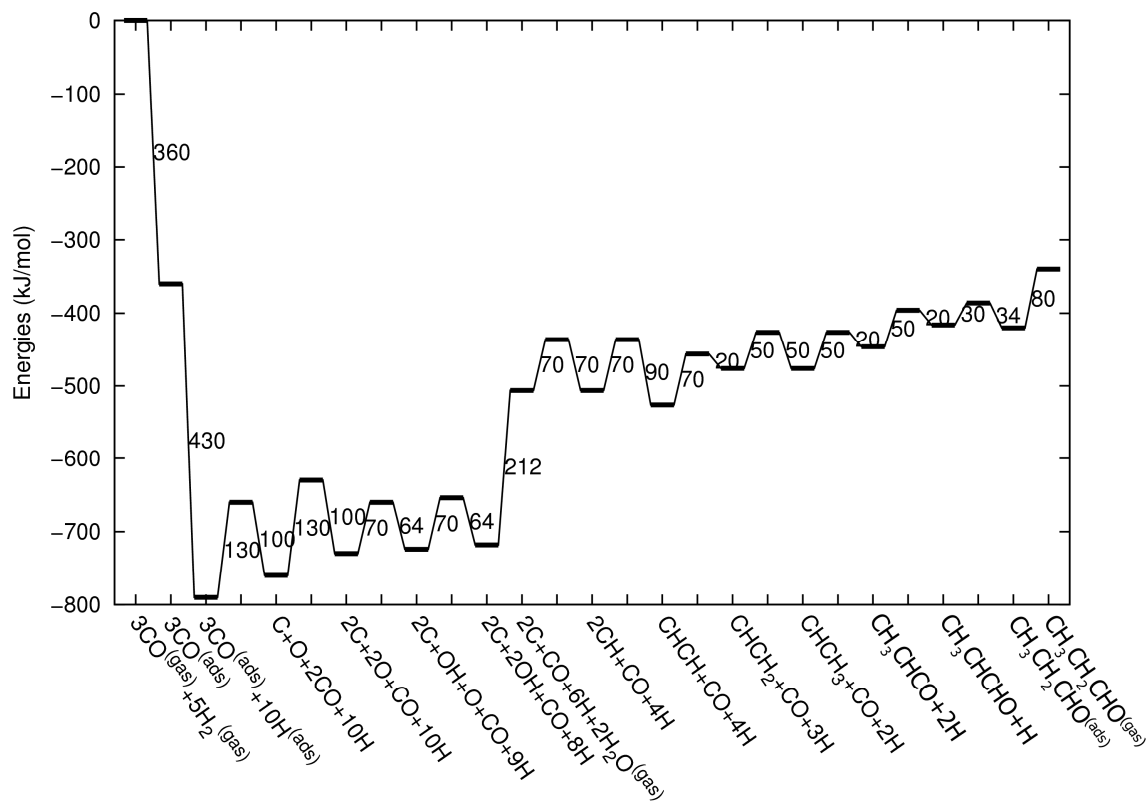
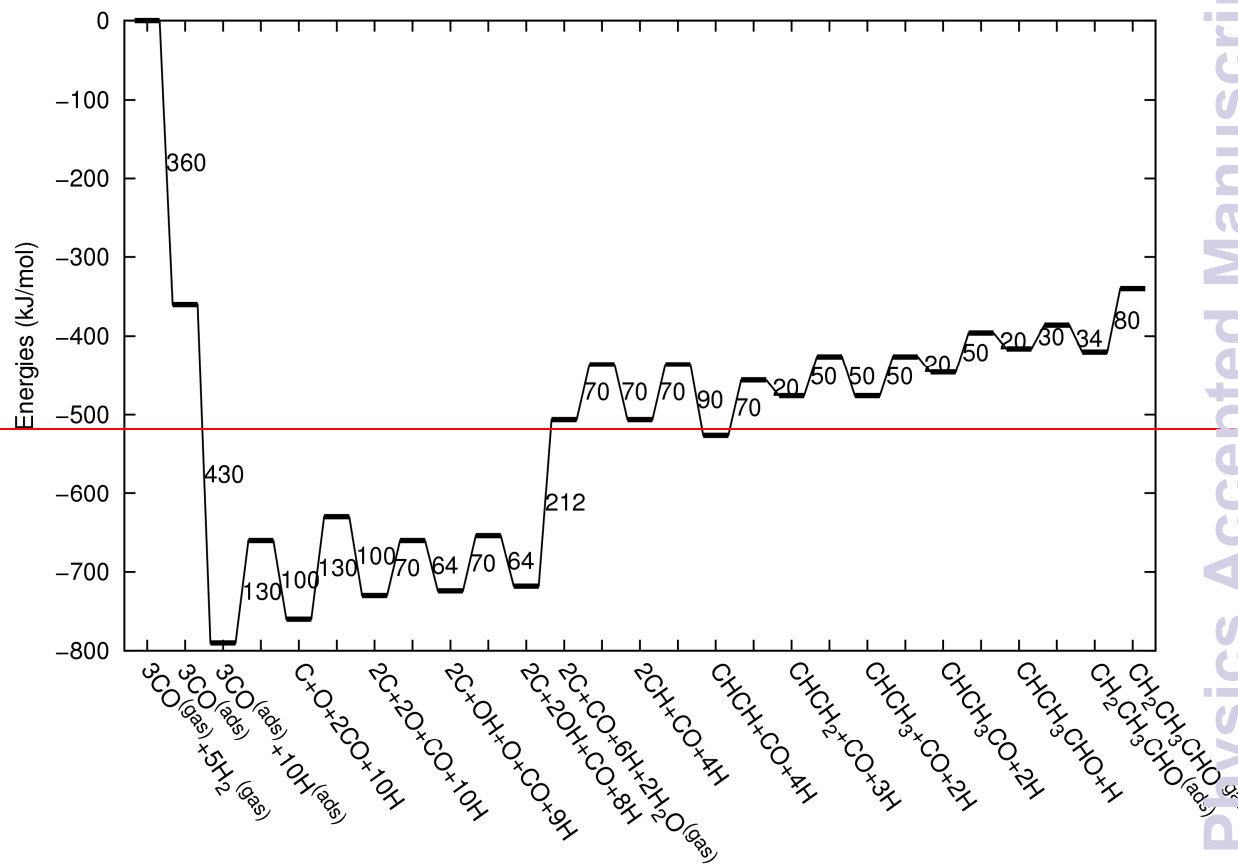
The rate constants used in the microkinetics schemes are based on activation energies available from recent DFT quantum-chemical calculations reviewed in ref.<sup>21</sup> Activation energies of elementary reaction rate constants and relative energies of surface intermediates will depend on surface structure as well as catalyst composition. In the simulations we have selected default values that are representative for reactive Co or Ru surfaces. Variation of parameters as the activation energies of the CO dissociation reaction or the CH<sub>ads</sub> to methane transformation reaction represent different choices of surface or composition.

Quantum-chemical data based on DFT computations cannot be expected to be more accurate than 10 kJ/mol. For this reason absolute values of predicted elementary reaction rates in comparison to experiment maybe expected to have a significant error. In microkinetics studies the systematic errors that lead to the inaccuracies of the quantum-chemical calculations lead sometimes to approximate cancellations, which reduces the error in predicted temperature maxima in such simulations. So may errors in energies of adsorption cancel errors in activation energies.

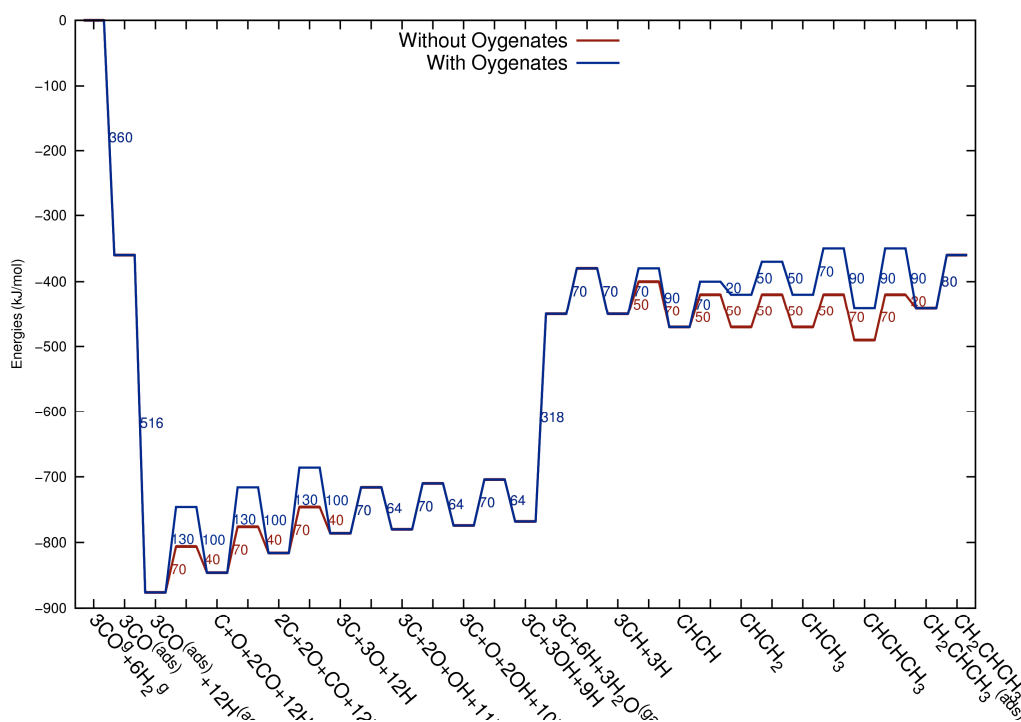
In the comparative kinetic studies considered here we have maintained most of the reaction energy data invariant, but have changed reaction rate data of elementary reaction steps of interest by altering the activation energies substantially more than 10 kJ/mol. The results obtained should be considered qualitative in an absolute sense, but reliable in a comparative sense.

Figure 3 shows the energy diagrams for the production of propylene as well as higher olefins when the oxygenate products are included in the model and when there is no oxygenate production. An important reference to the quantum-chemical data is Kapur et.al.<sup>22</sup>. For a review we refer to Van Santen et. al.<sup>21</sup>.

The energy diagram when no oxygenates are produced is the same as used earlier.<sup>12, 13</sup> As in previous simulations we have chosen H<sub>2</sub>O formation to be a relatively fast reaction.



**Figure 2** Reaction energy diagram, with default values of activation energies and reaction energies for the formation of propionaldehyde as a function of progress of the reaction. Reaction intermediate energies and relative stabilities with respect to gas phase are given. For additional details we refer to Supplementary Information.

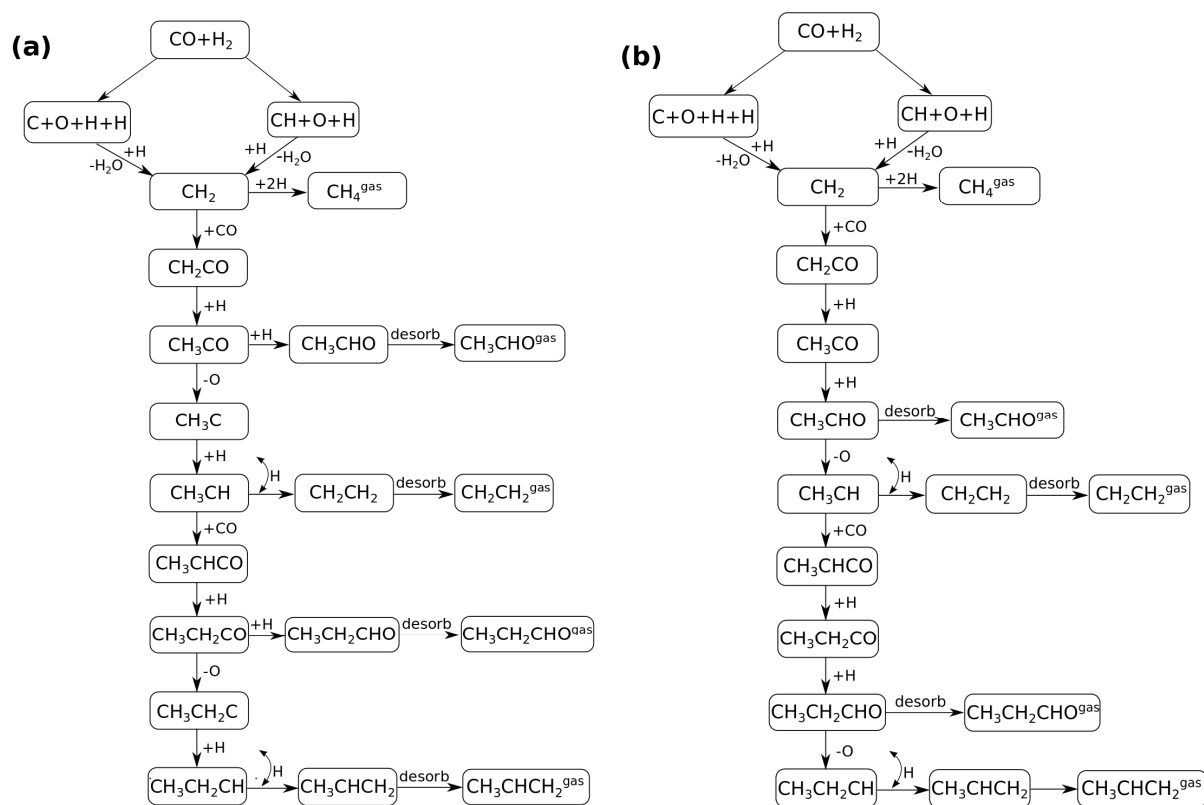


**Figure 3** Reaction energy diagram for the formation of propylene when the product selectivity is biased towards the production of oxygenates (blue line) and when the oxygenates are not included in the model (red line). Default values for (activation) energies are used in the diagram. Energies are given with respect to gas phase. For additional details we refer to Supplementary Information.

## 2.2. CO insertion chain growth mechanism

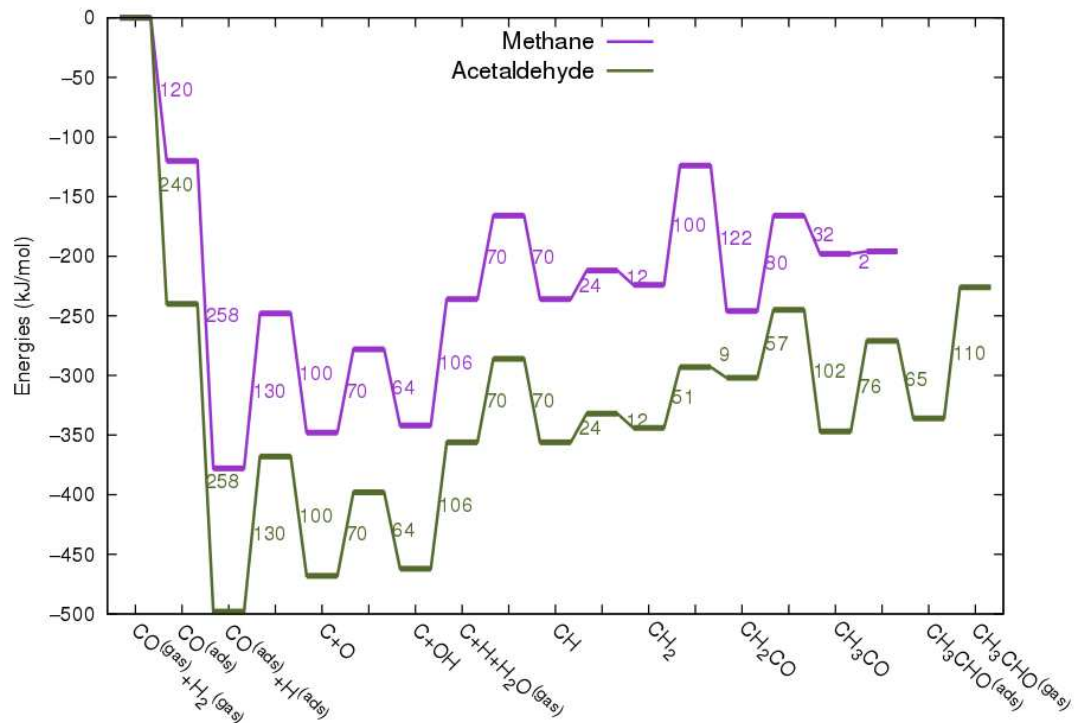
In figure 4 the two reaction mechanistic schemes studied for the CO insertion chain growth mechanism are shown. They differ by a choice of which oxygen containing surface intermediate cleaves its bond. In scheme (a) the C-O bond cleaves in the  $\text{CH}_3\text{CO}$  species, in scheme (b) this occurs in the aldehyde molecule. Which of the two steps occur determines the competitive reaction steps with chain growth. While in case (a) rapid hydrogenation of  $\text{CH}_3\text{CO}$  would cause interference

with high chain growth rate, in case (b) this would be the desorption of aldehyde. The corresponding reaction diagrams shown in figures 5 and 6 have been constructed using the high coverage data of Saeys and co-workers on Co(0001).<sup>18</sup> Since their data are not complete and do not close the catalytic reaction cycle we have used representative data from available literature.<sup>12, 21</sup>



**Figure 4** Fischer-Tropsch reaction mechanistic schemes used in the microkinetics simulations to model the chain growth via CO insertion. The difference in the schemes (a) and (b) is in the C-O bond scission step. In scheme (a) C-O bond cleavage takes place before the formation of surface aldehyde, whereas in scheme (b) C-O bond cleaves after the formation of surface aldehyde and before it desorbs from the surface.





**Figure 5** Reaction energy diagram for the formation of methane and acetaldehyde via CO insertion chain growth model. Formyl route of CO activation leading to CH species from CO is included in the simulations but is not implied here. Higher oxygenates formation is homologous to the rate of formation of acetaldehyde. The last steps in methane formation reaction energy diagram concern  $CH_{3,ads}$  and  $CH_{4,ads}$  formation. Part of the reaction energies data is adapted from Saeys et al.<sup>18</sup> Default values for (activation) energies have been used. Energies are given with respect to gas phase. For additional information we refer to Supplementary Information.

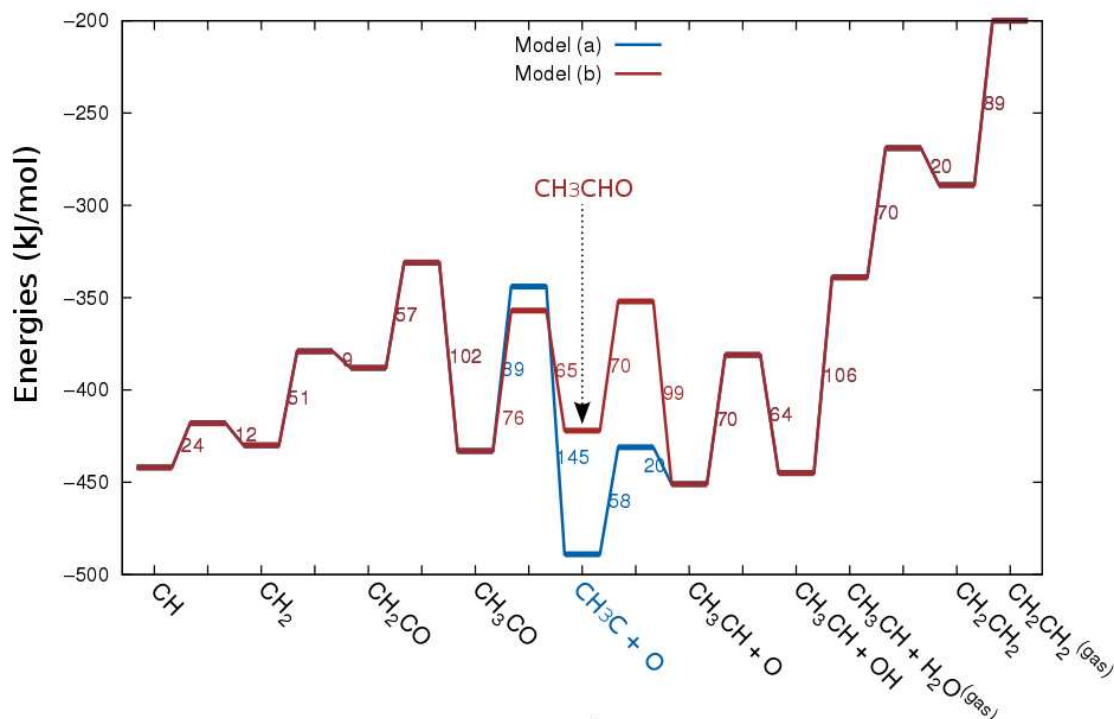


Figure 6 Reaction energy diagram for the formation of ethylene via CO insertion chain growth mechanism. Higher olefin formation is homologous to the rate of formation of ethylene. This energy diagram corresponds to the scheme shown in figure 4(a) and 4(b). Reaction energies data is adapted from Saeys et al.<sup>18</sup>. Default values for the (activation) energies have been used. Energies are given with respect to gas phase. For additional information we refer to Supplementary Information.

### 3 RESULTS AND DISCUSSION

The results to be presented enable us to address the relative importance of the hydrogen activated CO versus the path of C-O bond cleavage through direct CO activation and the validity of the different mechanistic proposals of the formation of oxygenated higher hydrocarbons.

We will analyze in subsections 3.1 oxygenate formation according to the carbide mechanism and in subsections 3.2 oxygenate and olefin formation according to the CO insertion chain growth mechanism.

The issue of hydrogen activated C-O bond cleavage<sup>23-27</sup> is especially relevant to the carbide mechanism of the Fischer-Tropsch reaction and will be discussed in

subsection 3.1.1. In the carbide chain growth mechanism chain growth proceeds by intermediate formation of “CH” that we identified previously as the monomer species inserted into the growing hydrocarbon chain.<sup>13</sup>

As we have reviewed elsewhere<sup>12, 28</sup> Fischer-Tropsch catalysis transition metals as Ru<sup>29</sup> or Co<sup>30, 31</sup>, or oxygenate production on Rh<sup>32, 33</sup> is strongly particle size dependent. CO consumption rate and chain growth parameter  $\alpha$  steeply decrease when transition metal particle sizes decrease below a few nanometers. This can be ascribed to the requirement of step-edge type sites, which are not present on the small particles<sup>61</sup>.

. The step-edge sites provide low barriers for CO activation, reduce rate of methane formation and chain growth termination.

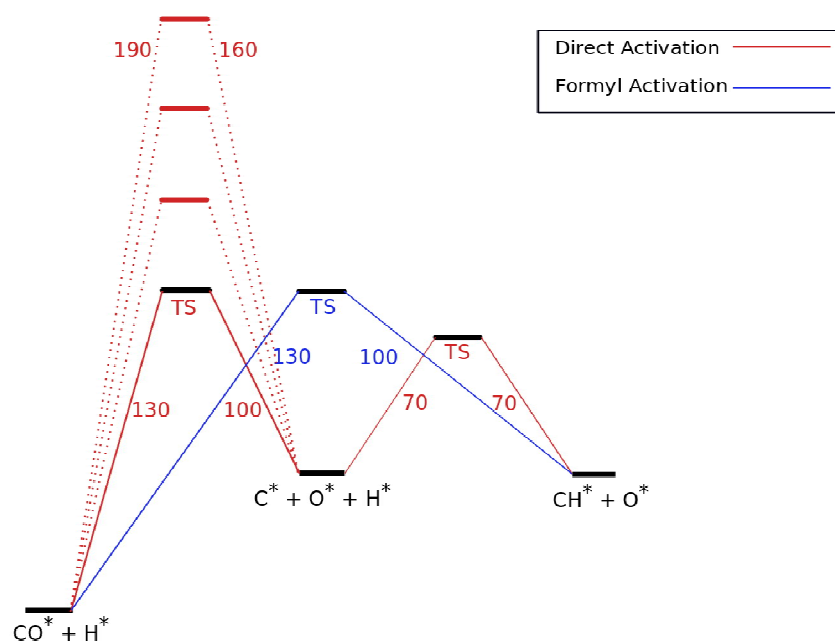
In the simulations to be presented CO activation barriers as well as hydrogenation barriers of CH<sub>x</sub> formation have been varied to simulated changes in surface structure of the catalysts and to provide a prediction of optimum site structure. The choice of metal tunes such effects. Activation barriers for C-O bond cleavage will be higher on Co or Rh than Ru<sup>34</sup>., whereas the M-C bond strengths tend to be stronger on Ru than Rh or Co<sup>34</sup> and hence the relative chain growth termination and methanation elementary rate constants. On the same surface site the activation energy for C-O bond activation on Rh is lower than that of Co, which makes Rh a more attractive catalyst material for oxygenate formation<sup>35</sup>.

Microkinetics simulations are indispensable because of the sometimes counteracting effects of reaction parameter changes when site structure or composition changes.

### ***3.1 Oxygenate formation according to the carbide chain growth mechanism***

#### ***3.1.1 Formyl vs. Direct path of CO activation***

Fischer Tropsch synthesis originates at the activation step of CO to give C<sub>1</sub> monomer which incorporates itself into the growing chain. The mechanism of CO dissociation has important kinetic consequences on the overall rate of FT reaction. Two mechanisms which are discussed in the literature<sup>9, 24, 36, 37</sup> are (i) direct dissociation of CO<sub>ads</sub> to give surface species C<sub>ads</sub> and O<sub>ads</sub> and (ii) formyl path of CO activation where adsorbed hydrogen reacts with adsorbed CO to give an unstable COH or HCO type of species which readily dissociates to give CH<sub>ads</sub> and O<sub>ads</sub>. Here we have employed microkinetics simulations to investigate the role of formyl path of CO activation in the overall reaction rate of the FT reaction.



**Figure 7** Reaction mechanistic scheme and reaction barriers used to investigate the competition of direct vs. hydrogen assisted or formyl path of CO dissociation. The mechanism until  $\text{CH}_{\text{ads}}$  formation is only shown. Numbers shown are respective barriers in kJ/mol. In red the activation barriers of the direct CO dissociation path are given. The high barriers of CO dissociation refer to surface terrace sites. The second barrier of the direct CO dissociation path concerns  $\text{C}_{\text{ads}}$  to  $\text{CH}_{\text{ads}}$  transformation. The black curve denotes the hydrogen activated CO dissociation reaction energy path. The transition state energy is that for the overall reaction energy of formyl intermediate formation and consecutive C=O bond cleavage.

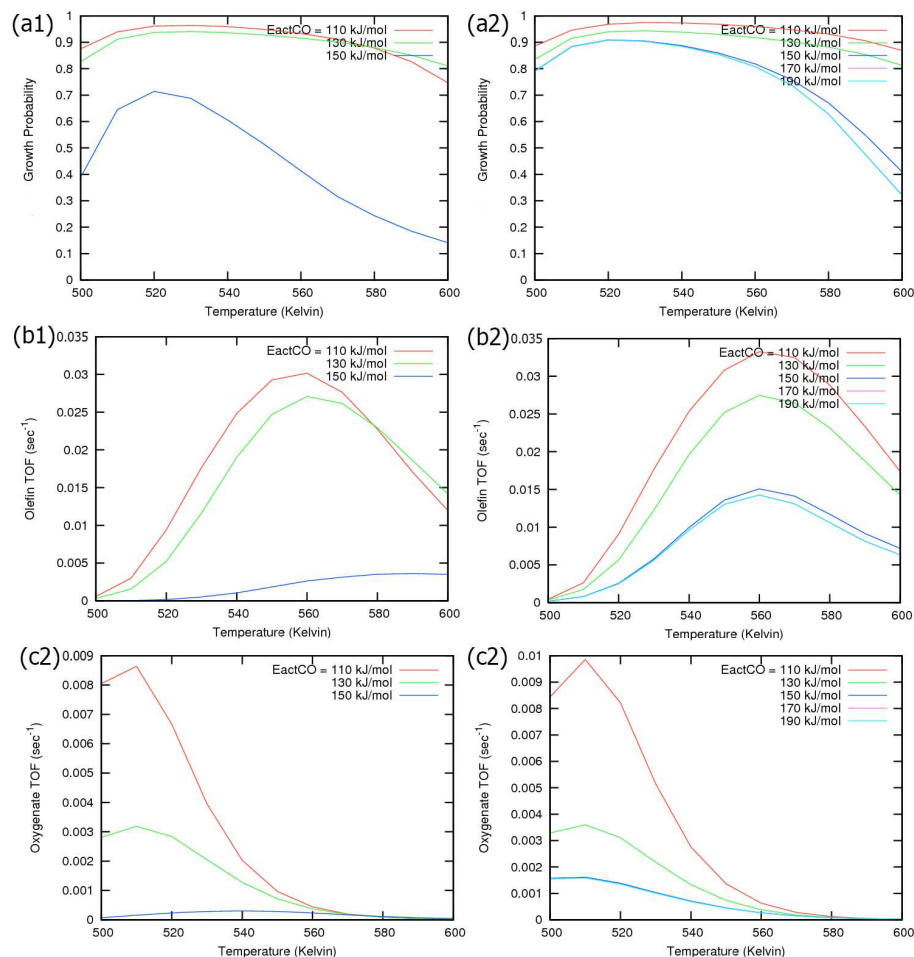
Figure 7 shows the reaction energy diagram of the kinetic model constructed which includes both the direct and the hydrogen assisted paths of CO dissociation. The reaction scheme of direct CO dissociation and hydrogen activated C-O bond cleavage is based on calculations of Ru.<sup>26, 27, 38, 39</sup> In the simulations to be presented the activation energy of direct CO activation will be varied with respect to that of the hydrogen activated case.

Earlier we argued<sup>26</sup> that in contrast to direct CO activation, the C-O bond cleavage path through intermediate CHO formation is relatively surface structure independent. On the dense Ru(0001) surface the corresponding low barrier of CH

formation will make this route the preferred one<sup>27</sup>, but on reactive step-edge sites direct CO activation will become the preferred elementary reaction.

When there is direct CO dissociation, the CH<sub>ads</sub> surface species is formed in two steps: CO dissociation to give C<sub>ads</sub> and O<sub>ads</sub> and the subsequent hydrogenation of C to give CH<sub>ads</sub> (red lines in figure 7). In the hydrogen activated CO dissociation path CH<sub>ads</sub> is the direct product. Transformation of CO<sub>ads</sub> to CH<sub>ads</sub> takes place through intermediate formyl formation and subsequent C=O bond cleavage. In figure 7 and the simulations the two relevant transition states and relative energy of the formyl intermediate have been taken together into a single transition state.

Calculated chain growth probability  $\alpha$  and Turn Over Frequencies (TOFs) for olefin and oxygenate yield are compared in figure 8 for the two models when CO activation only goes through direct dissociation (figures 8(a1), 8(b1), 8(c1)) and when the formyl path of CO activation is included in the simulation (figures 8(a2), 8(b2), 8(c2)). The activation barrier for direct CO dissociation is varied within a range from 110 kJ/mol to 170 kJ/mol while keeping the formyl path barrier constant at 130 kJ/mol. The thermodynamics between these two competing pathways is the same and is endothermic by 30 kJ/mol.



**Figure 8 Microkinetics Simulations in competition between direct and hydrogen activated C-O bond cleavage. CO gas pressure is  $P_{\text{CO}} = 0.5$  MPa and  $\text{H}_2$  gas pressure is  $P_{\text{H}_2} = 1.5$  MPa. (a) Chain growth probability (a) (b) Olefin TOF ( $\text{sec}^{-1}$ ) and (c) Oxygenate TOF ( $\text{sec}^{-1}$ ) are compared when there is (1) no formyl path of CO activation (left) and when (2) formyl path is included (right).**

Figures 8a and 8b compare simulated chain growth parameters  $\alpha$ , rates of  $\text{C}_2^+$  olefin and rate of  $\text{C}_2^+$  oxygenate formation as a function of temperature. The rates of product formation are normalized per unit “C” consumed.

In figures 8a we observe a step decrease in  $\alpha$  and  $\text{C}_2^+$  yield when the activation energy of direct CO activation exceeds 130 kJ/mol, whereas in figure 8b this decrease is absent since hydrogen activated C-O bond cleavage is included, that remains fixed at the overall activation energy of 130 kJ/mol.

At the lower activation energies, representative of CO activation on step-edge sites, we observe high chain growth as well as a high CO consumption rate. At the higher activation energies of CO it starts to compete with hydrogen activated CO dissociation, which becomes then dominating. Then with our chosen parameters chain growth parameter  $\alpha$  initially remains relatively high, but decreases steeply with temperature when total  $C_2^+$  yield becomes maximum.

Initially at low temperature the selectivity towards oxygenate formation exceeds that of hydrocarbon formation, but this selectivity rapidly declines with temperature, The latter is due to the high activation barrier of CO insertion compared to the activation energy of alkene chain growth termination.

The dominating production of oxygenates at low temperature, and decrease of oxygenate selectivity with temperature is in agreement with experimental observations on nanoparticles of Ru<sup>40</sup>.

Of interest also is the agreement between these experimental results and the anomalous initial increase in chain growth parameter  $\alpha$  with temperature. Whereas usually chain growth parameter  $\alpha$  decreases with temperature we observe in the simulations that it increases with temperature, when also low temperature oxygenate formation is included.

This maximum in  $\alpha$  value as a function of temperature is due to the need to dissociate the C-O bond to form the “CH” intermediate that is to be inserted into the growing hydrocarbon chain. This unique behavior of chain growth parameter  $\alpha$  is nicely illustrated by consideration of the course grained kinetics expressions for  $\alpha$



that one deduces for the case of only oxygenate formation (Eq.5) versus that for alkene formation (Eq.4) . They follow from the general lumped kinetics expression for  $\alpha$ <sup>9</sup>:

$$\text{Eq 1} \quad \alpha = \frac{k(n, n-1)\theta_{c_1}}{k(n, n-1)\theta_{c_1} + k_t^O + k_t^H}$$

In Eq 1,  $k(n, n-1)$  is the lumped kinetics rate constant of “C<sub>1</sub>” insertion into the growing hydrocarbon chain,  $\theta_{c_1}$ , the surface concentration of “C<sub>1</sub>” and  $k_t^O$  and  $k_t^H$  the respective lumped kinetics rate constants of chain growth termination to give oxygenate or hydrocarbon. As Eq.2 indicates  $k_t^O$  is proportional to  $\theta_{CO}$ , the surface coverage of CO:

$$\text{Eq.2} \quad k_t^O = k_t^O \theta_{CO}$$

As we have shown previously<sup>12</sup>, an elegant expression can be deduced

for  $\theta_{c_1}$ , when the transformation rate of adsorbed CO to “C<sub>1</sub>”,  $k_{CO}^{diss}$

controls the rate of CO consumption. This is the Fischer-Tropsch monomer formation kinetics limit, which applies to most of the practical catalysts. With the chosen activation energy for CO activation in this section this limit also applies to the low temperature simulations.

$$\text{Eq 3} \quad \theta_{c_1} = \left[ \frac{(k_t^O + k_t^H)k_{CO}^{diss}\theta_{CO}(1-\theta_{CO})}{(k(n, n-1))^2} \right]^{1/3}$$

When one substitutes expressions Eqs 2 and 3 into expression Eq.1 one deduces two different limiting expressions for  $\alpha$ . One finds in case oxygenate formation

dominates Eq 4 and for only hydrocarbon formation Eq 5.

$$\text{Eq. 4a} \quad \alpha^0 = \left(1 + \left(\frac{k_t^2 \theta_{CO}}{k(n, n-1)k_{CO}^{diss} (1-\theta_{CO})}\right)^{1/3}\right)^{-1}$$

$$\text{Eq 4b} \quad = \left(1 + \left(\frac{k_t^2 \theta_{CO}}{k(n, n-1)k_{CO}^{diss} K_{ads} P_{CO}}\right)^{1/3}\right)^{-1}$$

$$\text{Eq. 5a} \quad \alpha^H = \left(1 + \left(\frac{k_t^2}{k(n, n-1)k_{CO}^{diss} \theta_{CO} (1-\theta_{CO})}\right)^{1/3}\right)^{-1}$$

$$\text{Eq. 5b} \quad = \left(1 + \left(\frac{k_t^2 (1 + K_{ads} P_{CO})^2}{k(n, n-1)k_{CO}^{diss} K_{ads} P_{CO}}\right)^{1/3}\right)^{-1}$$

In Eq. 4b and 5b  $K_{ads}$  is the equilibrium constant of CO adsorption and  $P_{CO}$  the CO partial pressure.

The low initial value of  $\alpha$  at low temperature may arise when surface vacancies have to be created for CO dissociation. However, when the activation energy of the termination reactions is high, this will dominate the temperature dependence and  $\alpha$  shows regular behaviour and decreases with temperature. The mathematical condition for the occurrence of a maximum in  $\alpha$  with temperature is given by:

$$\text{Eq.6} \quad E_{act}^{CO} + E_{ads}^{CO} > 2\bar{E}_t - E_{n, n-1} \quad (\theta_{CO} \approx 1)$$

Eq.6 applies exactly to the case of Eq.4 and to the case of Eq.5 in the high pressure limit.  $\bar{E}_t$  denotes the respective activation energies for chain growth termination and  $E_{n, n-1}$  the activation energy of the chain growth rate constant.

The sum of activation energy of CO dissociation and adsorption energy of CO ( $E_{CO}^{ads}$ ), that defines the apparent activation energy of a CO covered surface, has to

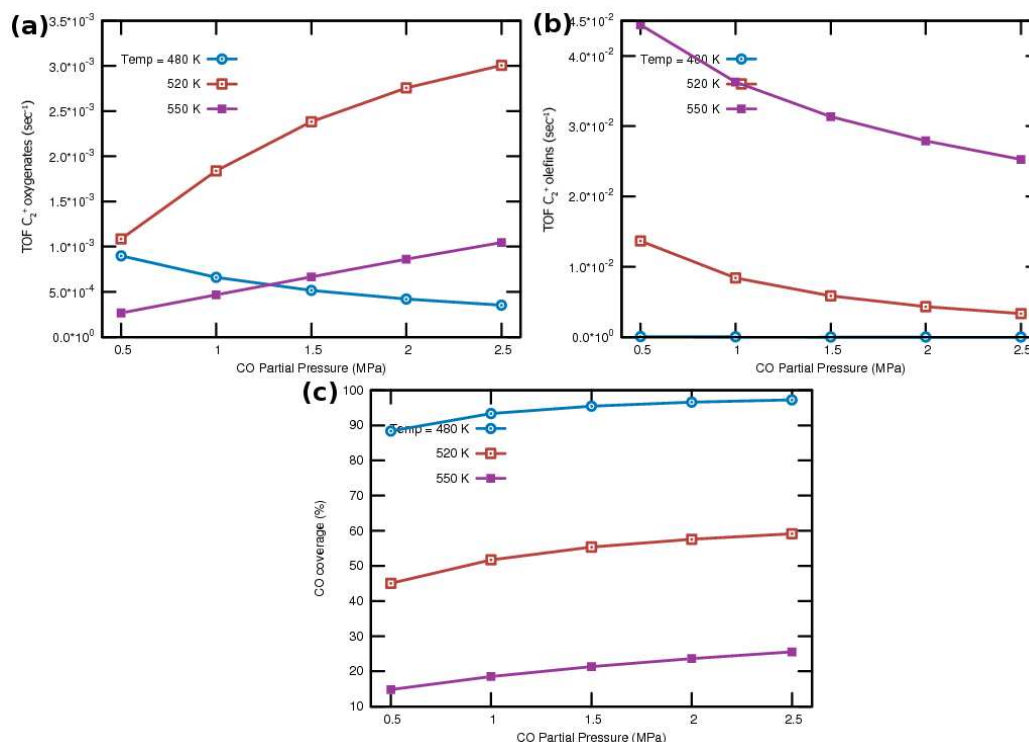
be relatively large and the activation energy of the termination reactions should not be too high.

As can be readily verified from the parameter choices presented in section 2, Eq.6 will be usually satisfied. The anomalous temperature dependence of  $\alpha$  can be expected at low temperatures when the selectivity towards oxygenate formation dominates. The selectivity of oxygenate formation decreases with temperature since the apparent activation energy of  $k_t^O$  strongly increases with decreasing  $\theta_{CO}$  so that the rate constant of oxygenate formation is becomes overtaken by the rate constant of olefin termination. The physical reason for the appearance of the temperature maximum in  $\alpha$  is that at low temperature the surface is blocked by the high coverage with adsorbed CO. Once surface vacancies arise due to CO desorption, CO dissociation occurs and chain growth begins. As is especially seen in figure 8 a1 the maximum becomes more pronounced when the activation energy for CO dissociation increases.

Because of the very small additional effect on reaction yield of the inclusion of hydrogen activated C-O bond cleavage we take in the simulations that follow only the direct CO dissociation path into account and use a default value of 130 kJ/mol. This activation barrier of CO activation is representative of the activation barrier of CO on stepped Co or Ru surfaces of intermediate reactivity<sup>9</sup>, with not too high activation barrier of CO so that oxygenate formation will occur.

### 3.1.2 CO partial pressure dependence

Figures 9 show the CO partial pressure dependence as well as CO coverage for the case of only direct CO activation with activation energy of 130 kJ/mol.



**Figure 9**  $C_2^+$  (a) Oxygenate and (b) Olefin TOF ( $sec^{-1}$ ) as a function of CO partial pressures at three different temperatures. Also plotted (c) CO surface coverage.  $H_2$  partial pressure is maintained constant at 1.5 MPa.

One notes again the very different dependence of oxygenate and hydrocarbon yields as a function of temperature and in addition a very different CO partial pressure dependence. Figure 9a indicates that at very low temperature oxygenate yield is low and decreases with increasing partial pressure of CO. This is because CO dissociation is inhibited by the increased CO pressure. However at the higher temperatures the oxygenate yield increases and shows a maximum at the lower of the additional temperatures used. At the higher temperature hydrocarbon

formation takes over. At these temperatures the  $C_2^+$  yield of oxygenates has a positive order in CO pressure. The CO coverages have substantially decreased (see figure 9c), the positive order in partial pressure of CO arises to maintain a finite rate of the CO insertion termination reaction. At the temperatures selected in figure 9b one observes a uniform increase in  $C_2^+$  yield of hydrocarbons and the expected decrease in  $C_2^+$  yield as a function of CO partial pressure for olefin formation .

One notes from the surface coverages shown in table 1 that adsorbed CO is replaced by adsorbed “C<sub>2</sub>” intermediates when the temperature increases. The increasing rate of CO consumption with temperature reduces the surface coverage with CO . The temperature maxima in yields of oxygenate formation correspond with a CO surface coverage of approximately 0.5.

**Table 1 Steady state coverages (in ML) of the most dominantly present species at three different CO partial pressures corresponding to the results shown in figures 9. Three temperature ranges are shown in each case. ‘Others’ in the right hand most column shows the combined coverages of all other surface species other than those explicitly shown in other columns.**

| Temp  | pCO = 0.5 Mpa |        |                 |        |           |        |
|-------|---------------|--------|-----------------|--------|-----------|--------|
|       | CO            | C      | CH <sub>2</sub> | CHCH   | Vacancies | Others |
| 480 K | 0.8839        | 0.0025 | 0.0249          | 0.0786 | 0.0053    | 0.0048 |
| 520 K | 0.4502        | 0.0466 | 0.0551          | 0.3925 | 0.0359    | 0.0197 |
| 550 K | 0.1478        | 0.1602 | 0.0464          | 0.5515 | 0.0652    | 0.0289 |
| Temp  | pCO = 1.5 Mpa |        |                 |        |           |        |
|       | CO            | C      | CH <sub>2</sub> | CHCH   | Vacancies | Others |
| 480 K | 0.9546        | 0.0009 | 0.0094          | 0.0313 | 0.0019    | 0.0019 |
| 520 K | 0.5533        | 0.0285 | 0.0337          | 0.3591 | 0.0147    | 0.0107 |
| 550 K | 0.2131        | 0.1148 | 0.0332          | 0.5886 | 0.0314    | 0.0189 |
| Temp  | pCO = 1.5 Mpa |        |                 |        |           |        |
|       | CO            | C      | CH <sub>2</sub> | CHCH   | Vacancies | Others |

|       |        |        |        |        |        |        |
|-------|--------|--------|--------|--------|--------|--------|
| 480 K | 0.9726 | 0.0006 | 0.0057 | 0.0188 | 0.0012 | 0.0011 |
| 520 K | 0.5916 | 0.0223 | 0.0264 | 0.3423 | 0.0094 | 0.008  |
| 550 K | 0.2552 | 0.0968 | 0.028  | 0.582  | 0.0225 | 0.0155 |

### 3.1.3 Oxygenate selectivity as a function of various elementary rate constants

The effect of varying rate constants of methane formation on the selectivity of oxygenate formation is illustrated in figures 10, 11 and 12.

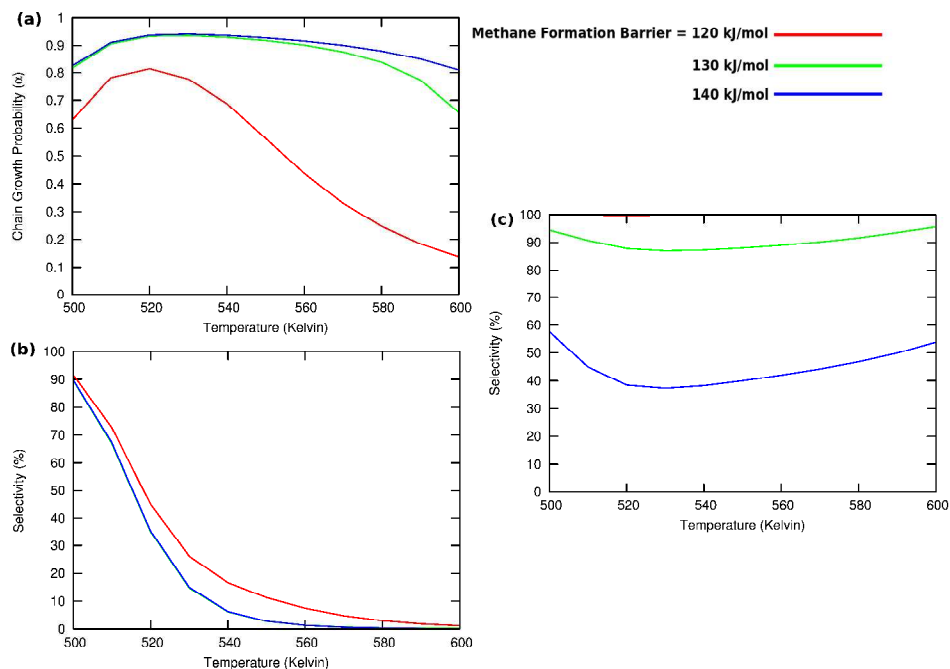
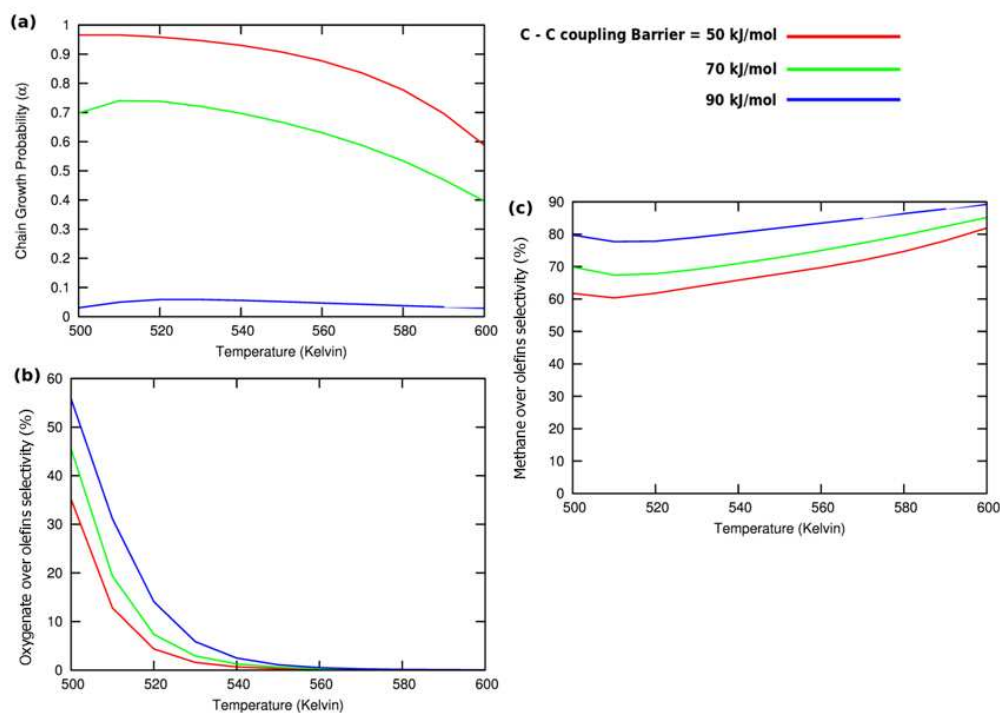


Figure 10 (a) Chain growth probability  $\alpha$  (b) Oxygenate over olefins selectivity and (c) Methane over olefins selectivity as a function of temperature for different values of Methane formation barriers.

The CO activation barrier in each case is  $E_{act}^{CO}=130$  kJ/mol, olefin termination activation energy change is  $E_{act}^{(R-CH)\rightarrow(R-CH_2)}=100$  kJ/mol and the change of activation energy for C-C coupling  $E_{act}^{(R-H)\rightarrow(R-CH_2)}=70$  kJ/mol. CO pressure is maintained at  $P_{CO} = 0.5$  MPa and  $H_2$  pressure is  $P_{H_2} = 1.5$  MPa.

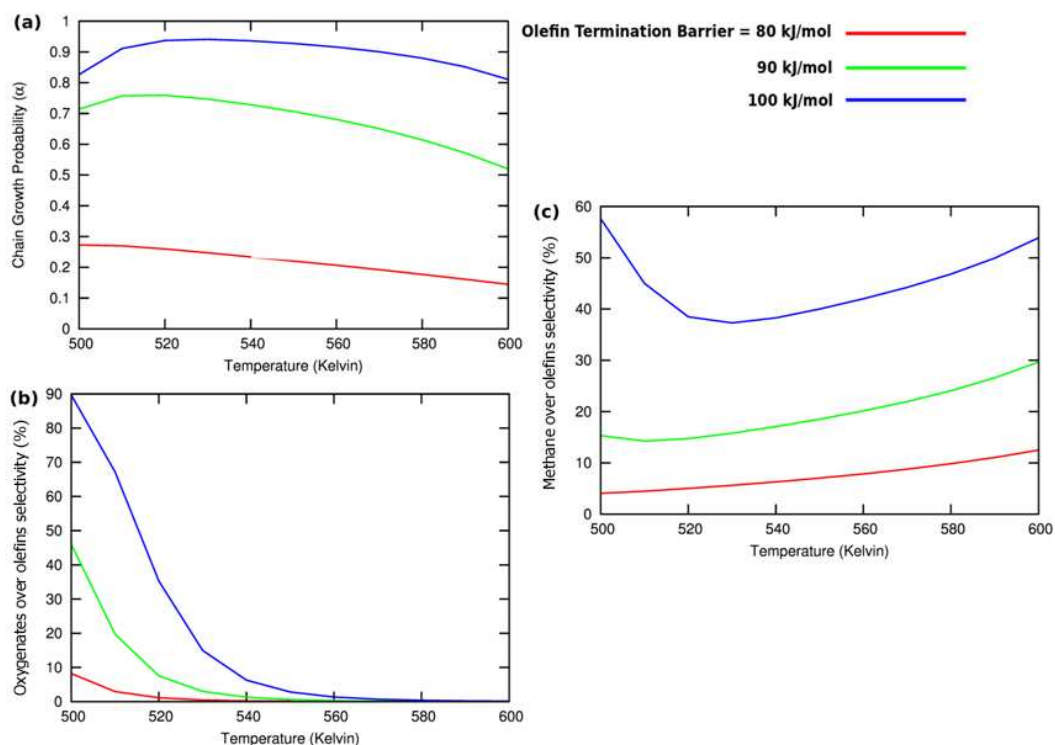


**Figure 11 (a) Chain growth probability (a) (b) Oxygenate over olefins selectivity and (c) Methane over olefins selectivity as a function of temperature for different values of C-C coupling barriers. The CO activation barrier in each case is  $E_{act}^{CO}=130$  kJ/mol, olefin termination barrier is  $E_{act}^{(R-CH)\rightarrow(R-CH_2)}=100$  kJ/mol and the barrier for Methane termination  $E_{act}^{CH_2\rightarrow CH_3}=130$  kJ/mol. CO pressure is maintained at  $P_{CO} = 0.5$  MPa and  $H_2$  pressure is  $P_{H_2} = 1.5$  MPa.**

Figure 10 illustrates competition between methane selectivity and selectivity of oxygenate formation. The relative rate of methane formation is altered by changing the activation energies of the transformation of “CH<sub>ads</sub>” to “CH<sub>2, ads</sub>”. This would correspond to a relative increase in the M-C bond energy for instance by an increase of surface metal atom coordinative unsaturation. The selectivity of oxygenate formation increases with increased methane selectivity. This is because chain growth through “CH<sub>ads</sub>” insertion competes with termination through CO insertion. As a consequence chain growth parameter  $\alpha$  decreases as can be observed from figure 10a.

A related effect is illustrated in figure 11. Now the activation barrier of the chain growth rate constant is varied. As in the previous case the selectivity of oxygenate formation is negatively affected when the chain growth rate constant is increased.

The selectivity of oxygenate formation is of course negatively affected when the olefin termination rate is increased (fig 12c). An increase of the rate constant of olefin termination will decrease  $\alpha$  (fig 12a), and it and the selectivity of oxygenate formation. As a consequence the selectivity of methane formation (fig 12c) will increase.



**Figure 12 (a) Chain growth probability (b) Oxygenate over olefins selectivity and (c) Methane over olefins selectivity as a function of temperature for different values of olefin termination barriers. The**

**CO activation barrier in each case is  $E_{act}^{CO}=130$  kJ/mol, C-C coupling barrier is  $E_{act}^{(R-H)\rightarrow(R-CH_2)}=70$  kJ/mol and the barrier for Methane termination  $E_{act}^{CH_2\rightarrow CH_3}=140$  kJ/mol. CO pressure is maintained at  $P_{CO}=0.5$  MPa and  $H_2$  pressure is  $P_{H_2}=1.5$  MPa.**



Table 2 of surface coverages shows that the surface coverages are hardly affected by variation of the hydrocarbon termination rate. This is expected as long as there is no change in rate controlling step, the inter conversion of CO to surface “CH” species.

**Table 2 Steady state coverages (in ML) of the most dominantly present species as a function of different olefin termination barriers corresponding to the results shown in figures 12. Three temperature ranges are shown in each case. ‘Others’ in the right hand most column shows the combined coverages of all other surface species other than those explicitly shown in other columns.**

| Temp = 480 K                  |        |        |                 |        |           |        |
|-------------------------------|--------|--------|-----------------|--------|-----------|--------|
| Olefin Term. Barrier (kJ/mol) | CO     | C      | CH <sub>2</sub> | CHCH   | Vacancies | Others |
| 80                            | 0.8876 | 0.0025 | 0.0244          | 0.0755 | 0.0053    | 0.0047 |
| 90                            | 0.8696 | 0.0027 | 0.0266          | 0.0911 | 0.0052    | 0.0048 |
| 100                           | 0.8681 | 0.0027 | 0.0267          | 0.0924 | 0.0052    | 0.0049 |
| Temp = 520 K                  |        |        |                 |        |           |        |
| Olefin Term. Barrier (kJ/mol) | CO     | C      | CH <sub>2</sub> | CHCH   | Vacancies | Others |
| 80                            | 0.4095 | 0.0469 | 0.0554          | 0.4365 | 0.0327    | 0.019  |
| 90                            | 0.4074 | 0.0469 | 0.0554          | 0.4387 | 0.0325    | 0.0191 |
| 100                           | 0.5403 | 0.0445 | 0.0526          | 0.2986 | 0.0431    | 0.0209 |
| Temp = 550 K                  |        |        |                 |        |           |        |
| Olefin Term. Barrier (kJ/mol) | CO     | C      | CH <sub>2</sub> | CHCH   | Vacancies | Others |
| 80                            | 0.1385 | 0.1576 | 0.0456          | 0.5692 | 0.0611    | 0.028  |
| 90                            | 0.1188 | 0.1508 | 0.0437          | 0.6081 | 0.0524    | 0.0262 |
| 100                           | 0.1749 | 0.1663 | 0.0481          | 0.5023 | 0.0772    | 0.0312 |

### **3.1.4. In summary:**

In the Fischer-Tropsch reaction the selectivity to produce long chain oxygenates versus olefins strongly depends on temperature and pressure. In agreement with experimental observations a low temperature and high partial pressure of CO<sup>40</sup> favours long chain oxygenate formation. Within the carbide mechanism increased oxygenate formation occurs at a cost of increased selectivity of methane formation. This is because CO insertion competes with “CH” insertion into the growing hydrocarbon chain. Low temperature experiments with Ru nanoparticles<sup>40</sup> indicate that long chain oxygenate production is possible with maximum CH<sub>4</sub> selectivity of 10%.

According to quantum-chemical calculations<sup>21</sup> the activation energy for CO insertion in the growing hydrocarbon chain is of the order of 50 kJ/mol and the overall activation energy to form the aldehyde 90 kJ/mol. The overall reaction of the CO insertion reaction is endothermic by 60 J/mol. The CO insertion reaction competes with the chain growth reaction by insertion of a “CH” monomer into the growing hydrocarbon chain. The activation barrier for this reaction is of the order of 50-70 kJ/mol.

We have used activation energies for CO insertion into the growing hydrocarbon chain and formation of final products by successive hydrogen addition steps representative for values as found in the literature from quantum-chemical calculations typical for metals as Co, Ru or Rh.<sup>21</sup>

We have varied the activation energies of some critical reaction steps in order to deduce chemical information to improve selectivity for long chain oxygenates.

When the activation energy for CO bond cleavage is low, the probability of long chain hydrocarbon formation is high. The relative rate of CO insertion is low because of its competition with CO dissociation. Hence there is an optimum in the chain growth probability versus oxygenate selectivity. The preference of Rh for oxygenate formation, but also its limited yield of higher oxygenated hydrocarbons is due to its relatively increased barrier of CO dissociation with respect to Co and Ru<sup>35</sup>. The competition between oxygenate formation selectivity and chain growth probability becomes even more apparent when we discuss the chain growth mechanism through CO insertion in the next section.

### ***3.2 Microkinetics according to the chain growth through CO insertion mechanism***

A high probability for chain growth requires that the rate of monomer insertion into the growing hydrocarbon chain is fast compared to the rate of the chain growth termination step. In the case of the carbide mechanism this implies the “CH” species that is inserted into the growing hydrocarbon chain is not rapidly removed as methane, but is rapidly inserted into the growing hydrocarbon chain. The monomer to be inserted into the growing hydrocarbon chain within the CO insertion chain growth mechanism is CO. A “C<sub>2</sub>O” intermediate is formed by

recombination of “CH<sub>x</sub>” with CO. The higher hydrocarbons result from insertion of CO into “C<sub>n</sub>” species that are generated by C-O bond cleavage of the “C<sub>n</sub>O” intermediate. Since the “C<sub>1</sub>” intermediate is only used to initiate the growing hydrocarbon chain, differently from the carbide chain growth mechanism, in this case high chain growth probability  $\alpha_{CO}$  does not require relatively fast CO dissociation. Instead of expression Eq.1 for  $\alpha$  according to the carbide mechanism, the coarse grained kinetics expression for chain growth  $\alpha_{CO}$  becomes Eq. 7<sup>21</sup>:

$$\text{Eq. 7} \quad \alpha_{CO} = \frac{k_p \theta_v k_f \theta_{CO}}{(k_t^H + k_f \theta_{CO})(k_t'' + k_p \theta_v)}$$

Long chain growth catalysis requires  $k_p$ , the elementary rate for C-O bond cleavage in the “C<sub>n</sub>O” intermediate, to be fast compared to  $k_t''$ , the elementary rate constant of chain growth termination with oxygenate as product.<sup>21</sup>  $k_f$  is the rate constant of CO insertion into the growing hydrocarbon chain “C<sub>n</sub>”.  $\theta_v$  is the vacancy surface concentration.

We have previously shown<sup>21</sup> that then available quantum-chemical data relevant to this mechanism, give too slow apparent rate constants for chain growth (determined by  $k_p$  and  $k_f$ ) compared to the rate constants of surface intermediate conversion to product,  $k_t^H$  and  $k_t''$ , for the CO insertion chain growth mechanism to give high chain growth probabilities.

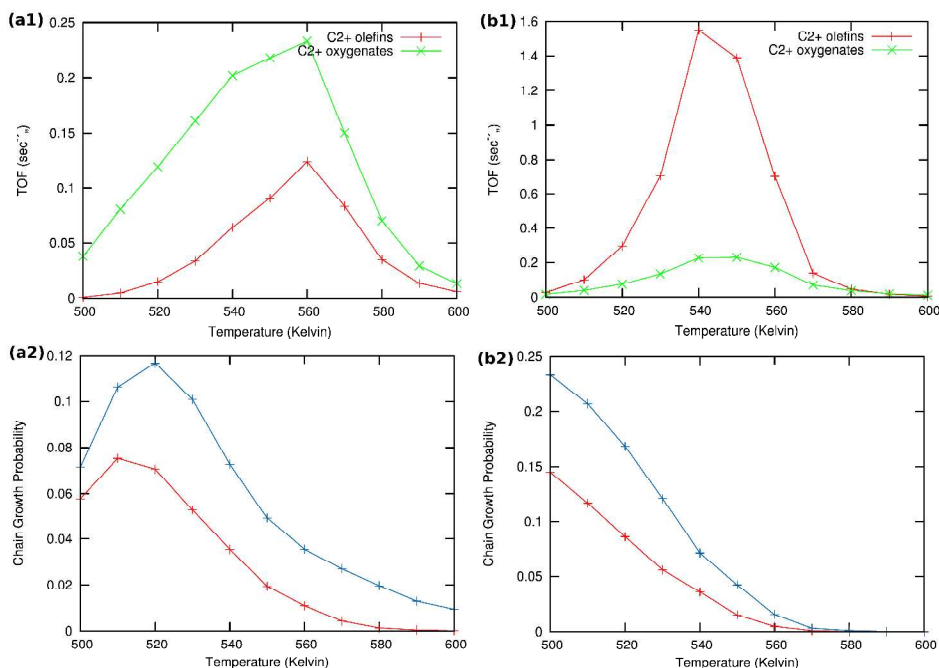
Recently it has been argued that the rate of chain growth within the CO insertion chain growth mechanism is underestimated in these microkinetics simulations because coverage dependent adsorbate-adsorbate interactions have been ignored<sup>18, 41</sup>. Indeed as the microkinetics simulations of the previous section

indicate at the Fischer-Tropsch condition the surface can be considered highly covered with reaction intermediates.

One can implement the consequences of such adsorbate –adsorbate interactions in microkinetics simulations by using the corresponding calculated values of the activation energies of the elementary reaction rate constants and reaction intermediates in the simulations<sup>42</sup>. Generally one expects elementary association reactions to have reduced activation energies, but bond cleavage reactions to have increased activation energies.

We will present here microkinetics simulations based on reaction intermediate adsorption energies and rate constant activation energy values of the Saeys group<sup>18</sup> that represent the case of a highly covered Co(0001) surface. Their data have been used to construct the two micro -mechanistic models of the CO insertion chain growth model shown in figures 4a and 4b .Since in the two respective cases the carbonaceous intermediates that are generated have very different relative stabilities the corresponding reaction energy diagrams are quite different.

Results of the microkinetics simulations for the CO insertion chain growth reaction with high coverage are shown in figures 13.



**Figure 13** Microkinetics results of the two mechanistic schemes depicted in figures 4a & 4b. Total TOFs and individual product yields are shown. Figures to the left (a1) & (a2) correspond to scheme in figure 4a and figures to the right (b1) & (b2) correspond to scheme 4b. In figure (a2) red curve shows the chain growth probability (a) with the default rate constants given in supplementary information file Table S2, and blue curves show the chain growth probability (a) with decreased rate constant of olefin desorption obtained by lowering the respective pre exponential values from  $10^{16}$  to  $10^{12}$ . In figure (b2) red curve shows the chain growth probability (a) with the default rate constants given in supplementary information file Table S2, and blue curves show the chain growth probability (a) with decreased rate constant of olefin desorption obtained by increasing the respective activation barriers from 70 kJ/mol to 100 kJ/mol.

Clearly no long chain hydrocarbons are formed, but C<sub>2</sub> formation is possible. In case (a) also a substantial amount of oxygenate is found. The results are consistent with many quantum-chemical results<sup>22, 43-47</sup> that indicate that C<sub>1</sub> and CO recombination can occur with relatively low activation barriers.

This recombination is essentially different from subsequent insertions of CO in the adsorbed longer hydrocarbon chains that has higher activation energies.

Selective C<sub>2</sub> formation without methane formation is a technologically important reaction.<sup>48</sup>

Next to the apparent activation energies of the overall C-C bond formation reaction, the other parameters that determine chain growth probability is the rate of constant  $k_t^H$  of the “C<sub>n</sub>” intermediate termination that produces the olefin product.

In order to test the sensitivity of the results in figures 13(a2) and 13(b2) we have compared values of the chain growth probabilities for decreased values of rate of desorption of the olefins. In case (a) the pre-exponential values of the olefin desorption rate has been decreased from  $10^{16}$  to  $10^{12}$ , in case (b) the activation barriers of olefin desorption rate has been increased from 70 kJ/mol to 100 kJ/mol.

As can be observed in the corresponding figures 13 the chain growth probabilities in both cases are slightly increased, but remain low. This confirms the conclusion that the CO insertion chain growth path mechanism will not lead to long chain hydrocarbon products.

The microkinetics results of this section and previous sections reveal that one has to be careful to conclude the validity of the CO insertion mechanism for chain growth based on arguments that relate to a relation between surface concentration and transient kinetics as recently done by Kruse et.al.<sup>49</sup>. It can be clearly seen also from the simulations presented in section 3.1, that a high surface concentration of CO can be consistent with the carbide mechanism and is no proof of the CO insertion chain growth mechanism. This is consistent with the elegant demonstration by in-situ PM-RAIRS experiments by Beitel et.al.<sup>50, 51</sup> that CO adsorbed to step edges is consumed during Fischer-Tropsch reaction, which

illustrates that it is replaced by different species. We observe from our simulations that within the carbide mechanism CO is replaced by growing adsorbed hydrocarbons. Previously published quantum-chemical calculations of the chain growth at the stepped Ru(1121) surface<sup>52</sup> have shown that at the step-edges C atoms generated by CO dissociation upon addition of a hydrogen atom move from their four-fold adsorbed position within the step to three-fold position at the step-edge, that is also the site of the chain growth reaction. The movement away of the C atom from the internal part of the step to its edge, prevents deactivation of the step site.

We have reviewed elsewhere<sup>13</sup> the very elegant early experiment isotope labeling experiments by Biloen and Sachtler<sup>10</sup> and the work of Brady and Pettit<sup>53, 54</sup> and of Maitlis<sup>55, 56</sup>, that provide strong experimental support of the carbide chain growth reaction path.

#### **4. CONCLUSION ; COMPARISON OF THEORY AND EXPERIMENT**

In this section we will discuss the critical rate parameter relations that determine the selectivity of long chain oxygenate formation and we will relate this with available experimental results. For a comparison with experimental results we will mainly base ourselves on material reviewed in papers<sup>4, 5</sup>.



Direct comparison of the microkinetics simulations as presented here with experimental data of practical catalysts with often complex composition will have to remain speculative. We will therefore limit the discussion to a general comparison of trends in catalyst performance data with the microkinetics simulations results. Since we will mainly compare with experiments that concern alcohol production, we will consider the alcohols to be rapidly formed by consecutive hydrogenation once aldehyde is produced as the primary product.

Most of the experimental Fischer-Tropsch catalyst studies on oxygenate formation are based on Rh, Fe (carbide), Co, MoC<sub>2</sub> or MoS<sub>2</sub>. When not modified by added promoting components as alkali metals or additional transition metals, these materials produce only alkanes or alkenes except when Rh and Fe catalyst materials are used. We earlier referred to nanoparticle Ru catalysts<sup>40</sup> that also produce long chain oxygenates, but only in a very low temperature regime where syngas conversion has a low Turn Over Frequency.

Promotion substantially increases the oxygenate production of most of the catalysts, but oxygenate versus hydrocarbon selectivity rarely exceeds 50% (the catalysts of highest selectivity are Rh/ZrO<sub>2</sub> or Rh/TiO<sub>2</sub>) and is usually substantially less. Interesting with respect to the microkinetics simulation results of section 3.2 is that C<sub>1</sub> and C<sub>2</sub> oxygenate production is usually far in excess of that of C<sub>3</sub><sup>+</sup> oxygenates, except for MoC<sub>2</sub> or MoS<sub>2</sub> based systems, where it may become comparable. Clearly there is a significant scope for improvement.

According to the microkinetics simulations the relatively high overall barrier for C-C bond formation by the CO insertion chain growth mechanism makes this reaction route unsuitable for long hydrocarbon formation. One has to note however that the mechanism of  $C_2H_4O$  formation is similar to that in the carbide chain growth route.

Within the carbide mechanism the relatively low activation energy of the rate of chain growth and relatively high activation energy for CO insertion into the adsorbed growing hydrocarbon chain are consistent with the possibility of long chain oxygenate formation.

Long chain oxygenate product formation competes with the following reactions:

- a) methane (methanol) formation
- b) recombination of " $CH_x$ " with another " $CH_x$ " that produces ethylene or " $C_nH_y$ " with another " $CH_x$ " ( $n>1$ ) that produces alkene. These recombination steps are to be compared with reaction of  $CO_{ads}$  with " $CH_x$ " or " $C_nH_y$ "
- c) decomposition of " $CH_xCO$ " or " $C_nH_yCO$ " into " $CH_xC$ " or " $C_nH_yC$ " and " $O_{ads}$ "

Ad a)

The rate of methane formation depends on the relative rate of C-O bond cleavage to give " $CH_x$ " versus the rate of " $CH_x$ " hydrogenation to methane. Within the carbide mechanism methane formation from " $CH_x$ ", the building unit of the

chain growth reaction, competes with the rate of incorporation of “CH<sub>x</sub>” into the adsorbed growing hydrocarbon chain.

We have studied in section 3.1.1 the sensitivity of catalyst performance with respect to the activation barrier for C-O bond activation. As long as the CO activation barrier is low, as is the case on stepped reactive surfaces, the chain growth probability does not depend on the activation energy of C-O bond cleavage. The rate of CO consumption as well as chain growth probability then is controlled by the rate constant of chain growth termination<sup>12</sup>. This we have called precisely the Fischer-Tropsch chain growth kinetics limit case. Then the reactive catalyst center becomes covered with mainly hydrocarbon intermediates.

When the activation energy of C-O bond activation increases, for instance when a more reactive metal as Ru is replaced by Co or a less reactive surface is chosen with different step-edges, CO consumption rate and chain growth probability can become limited by the rate of “CH<sub>x</sub>” production. Then the rate of CO consumption becomes controlled by the elementary rate constant of C-O bond cleavage. This kinetics limit we have previously identified as the monomer formation kinetics limit<sup>12</sup>. It is in this kinetics regime that most Fischer-Tropsch catalysts operate<sup>13</sup>.

When the activation energy of CO activation increases further, the route towards C-O bond cleavage starts to compete with that of the hydrogen activated bond cleavage reaction. This is typically the situation for CO activation on the dense surfaces of Co, Rh or Ru or metal surfaces of low reactivity as for Ni.<sup>26</sup> Recently

Salmeron and al.<sup>57</sup> have demonstrated hydrogen activated for C-O bond cleavage on nanoparticles of Co.

Clearly direct CO activation to give “CH<sub>x</sub>” as well as hydrogen activated C-O bond cleavage contain hydrogen atom addition as an important step, so that kinetically the difference between the two is not essential but the apparent activation energy to produce CH<sub>x</sub>. We have found that on the reactive Rh(211) surface<sup>58</sup> that both reaction paths have the same apparent activation energies.

To produce oxygenate the rate of CO bond cleavage has to be reduced. C-O bond cleavage and CO insertion into “CH<sub>x</sub>” or longer adsorbed hydrocarbon fragments are competing reactions and will also compete with methanol formation.

Ad b

To produce long chain oxygenates we find that the overall activation barrier of C-O bond cleavage of the CO to “CH<sub>x</sub>” transformation reaction should not be too low, since otherwise competition with CO insertion into the growing hydrocarbon chain becomes too unfavourable. On the other hand the activation energy of CO activation should not be too high, otherwise no “CH<sub>x</sub>” species will be generated to be inserted into the growing hydrocarbon chain. Then “CH<sub>x</sub>” will be mainly converted into methane. In the extreme case of a very high activation energy of CO activation methanol will be formed, as for instance on the Cu methanol catalyst<sup>59</sup>.

On Ni the rate of CO activation is too low<sup>60</sup>, which makes it the preferred catalyst for methane formation. In order to compete with methane formation the upper bound to the activation energy of C-O bond cleavage has to be between 90 or 120 kJ/mol, dependent of the reactivity of the metal surface to hydrogenate surface “CH<sub>x</sub>” intermediates to methane. On dense surfaces that have a low M-C interaction energy the lower value applies, on the more open reactive surfaces the higher value. The lower bound for the activation barrier of C-O bond cleavage due to competition with the activation energy of CO insertion into the growing hydrocarbon chain to give the aldehyde is of the order of 90 kJ/mol. It is consistent with a high chain growth probability because within the carbide mechanism the apparent activation energies for C-C bond formation are in the regime between 50 and 70 kJ/mol.

The lower bound to the activation energy of C-O bond activation implies that the reactive stepped Ru surfaces are no suitable catalysts for oxygenate formation. This conclusion agrees with experiment<sup>40</sup> that indicates that only small nanoparticles, that may be expected to have a low concentration of step-edge sites<sup>61</sup>, show high long chain oxygenate selectivity at low temperature, but with very low CO consumption rate. Because of the increased CO activation barrier at a higher temperature less reactive Rh shows a higher oxygenate formation selectivity. A high selectivity can be maintained with acceptable turn over frequencies, however at a cost of longer chain oxygenates.

Alloys that combine a metal that bind CO strongly but do not activate C-O bond cleavage, as Ir, with a metal that dissociates CO with a activation energy, as

Co have been demonstrated to have significant selectivity towards formation of C<sub>2</sub> oxygenates, with minor coproduction of methanol<sup>5</sup>.

The additional condition that has to be satisfied in order to obtain long chain oxygenates is that termination through CO insertion is favourable compared to termination as alkene.

The quantum-chemistry of CO insertion has been studied extensively with the context of hydroformulation<sup>62</sup>. The availability of empty d-valence electron states of surface metals atoms of low energy that reduce repulsive interaction between the lone pair electrons of CO and the occupied C atoms of the reacting adsorbed hydrocarbon intermediate by electron donation to the metal atoms reduces the CO insertion barrier. Also Lewis acid activation of CO<sup>63</sup> lowers the activation energy of C-O bond cleavage. Possibly for these reasons addition of reducible metal oxide catalysts as Vanadium or Mn oxides to Rh show significantly enhanced yields of oxygenate formation<sup>63</sup>.

From scaling law arguments<sup>64</sup> it is known that the activation energies for hydrogen transfer reaction increase with an increase of the surface metal M-C bond energy. Since the intermediate to be hydrogenated to the olefin is an alkenyl or alkylidyne intermediate, to which a hydrogen atom has to be added<sup>13</sup> a stronger M-C bond will reduce the rate of hydrocarbon formation since the rate constant of chain growth termination will be decreased.

A larger M-C bond interaction will not only decrease the rate constant of methane formation, but also decrease the rate of C-C bond formation compared to

that of CO insertion. This is possibly the reason that promoted MoC<sub>2</sub> or MoS<sub>2</sub> based catalysts have been reported<sup>5</sup> to produce the highest fraction of linear C<sub>3</sub><sup>+</sup> oxygenates.

Ad c

Rh catalysts have been experimentally<sup>4, 5</sup> as well computationally<sup>21</sup> most extensively investigated with respect to oxygenate formation. We have shown in section 3.2 that according to the data of Saeys et al.<sup>18</sup> on Co, CO insertion into adsorbed CH proceeds with relative low barrier and that because of ease of cleavage of the C-O bond the main reaction product according to this reaction path is ethylene. Computational quantum-chemical data of comparable elementary reaction steps for C<sub>2</sub> oxygenate formation on different surfaces of Rh<sup>22</sup> summarized in ref 20 and Ru surfaces<sup>13</sup> are also available. They indicate that the recombination reaction of CO<sub>ads</sub> and “CH<sub>ads</sub>” reaction will readily occur on Rh, but show a higher activation energy barrier on Ru<sup>13</sup>. On Rh activation of the C-O bond of inserted CO has a substantially higher barrier than on Ru. Whereas the relative rate of methane formation from adsorbed “CH<sub>x</sub>” is faster on Rh than Ru (the M-C bond is stronger on the latter), with Rh CO insertion into CH<sub>x</sub> will more favourable compete with “CH<sub>x</sub>” recombination and the rate of bond cleavage of C=O will be suppressed<sup>37</sup>. Since of the three metals considered more reactive Ru has the stronger M-C bond the observation of low temperature long chain oxygenate formation is consistent

with the theoretical considerations. At higher temperatures Rh should be the better catalyst for shorter chain oxygenates.

Takeuchi et.al.<sup>33</sup> find that highly dispersed Co catalysts that are Sr promoted show enhanced production of C<sub>2</sub> oxygenates compared to prediction according to the ASF product distribution plot. But for hydrocarbon formation ethylene production is suppressed. It is suggested by Spivey et.al.<sup>4</sup> that this demonstrates preferred CO insertion into “CH<sub>x</sub>”. The recent observation by de Galvis et.al.<sup>48</sup> that at high temperature nanosized carbided Fe particles promoted by S and alkali are selective ethylene and propylene catalysts suggest that they are produced also through recombination of a “CH<sub>ads</sub>” and CO<sub>ads</sub> species. More reactive Fe compared to Co now rapidly catalyses C-O bond cleavage after the CO insertion reaction.

To conclude we will address the question whether significant improvements of the production of linear long chain oxygenates by further adaptation Fischer-Tropsch catalysis may be expected.

The low temperature nanoparticle Ru catalyzed reaction<sup>21</sup> illustrates that high chain growth oxygenate probability is possible. But CO consumption rate is too low to be of practical interest.

Important at the low temperature are the low relative overall rate constants of methane formation and CO insertion versus the overall rate constant of chain growth through CH<sub>x</sub> insertion.



A strong M-C bond will be beneficial since it will suppress methane formation., except that it will slow down C-C bond formation, that becomes endothermic when the M-C bond becomes too strong<sup>20</sup>.

The increased M-C bond energy will also lower the activation energy of C-O bond activation. Oxygenate formation is maximum when the rate constant of C-O bond activation of CO is approximately equal to the rate constant of the oxygenate termination reaction<sup>21</sup>.

Whereas this will be beneficial to the chain growth reaction it will decrease the oxygenate yield. The choice of a reaction center that is less electronegative will be beneficial, since a decrease of the M-O bond energy will decrease the elementary rate constants of CO activation and favour oxygenate formation.

As shown by Arakawa et.al.<sup>33, 65</sup> a small metal particle size will enhance the probability of oxygenate formation. On a small metal particle CO dissociation will have a low rate, but also the rate constant of chain growth, so that primarily C<sub>2</sub> oxygenates can be expected.

The resulting conflicting dependencies on surface reactivity imply an optimum in oxygenate selectivity and CO consumption rate, that not necessarily has to coincide. This is confirmed by experiments with promoted Rh catalysts<sup>4</sup>, that give maximum oxygenate yield for the Vanadium promoted catalyst, but maximum selectivity of the TiO<sub>2</sub> promoted catalyst.

A computational study by Jennes et al.<sup>66</sup> indicates that reducible oxides promote a small charge deficit on the small Rh particles that enhances the M-C interaction

energy and reduce the interaction with oxygen. This appears to agree with experimental data on Vanadium promoted Rh catalysts<sup>67, 68</sup> that show decreased methane formation due to an increased M-C interaction.

The complex catalyst formulations developed so far lack optimum catalyst performance, due to excess hydrocarbon formation. Whereas further improvement of long chain oxygenate formation through Fischer-Tropsch type catalysis is unlikely, improvements in selectivity and yield of C<sub>2</sub> oxygenates should be possible.

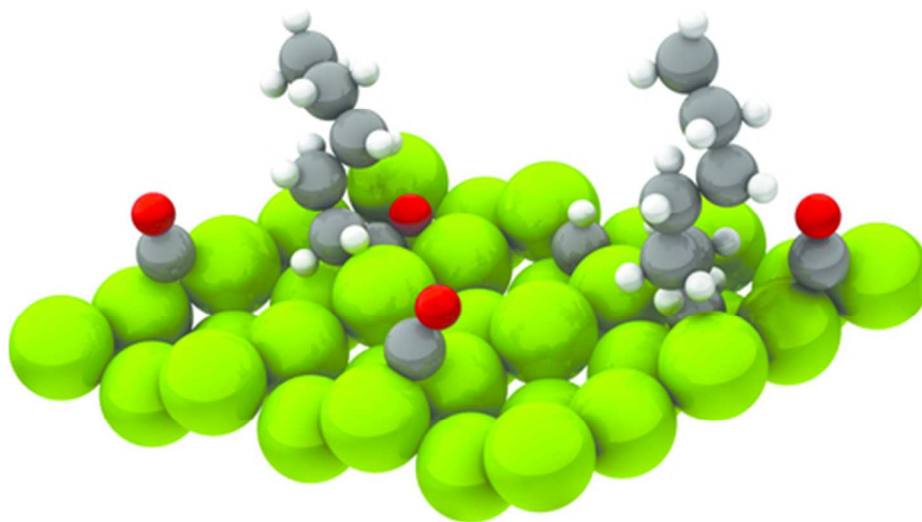
## 5. References

1. R. B. Anderson, H. Kölbl and M. Rálek, *The Fischer-Tropsch Synthesis*, Academic Press, 1984.
2. A. P. Steynberg and M. E. Dry, eds., *Fischer-Tropsch Technology*, Elsevier, Amsterdam, 2004.
3. H. H. Storch, N. Golumbic and R. B. Anderson, *The Fischer-Tropsch and Related Syntheses*, John Wiley & Sons, New York, 1951.
4. A. Egbebia. J. J. Spivey, *Chemical Society Reviews*, 2007, 36, 1514-1528.
5. S. K. Gangwal. V. Subramani, *Journal of Physical Chemistry*, 1986, 90, 4752-4758.
6. E. B. M. Doesburg, X. Xiaoding, J.J.F Scholten, *Catalysis Today*, 1987, 2.
7. T. Fukushima. M. Ichikawa, T. Yokohama, N. Kosugi, H. Kurodan, *Journal of Physical Chemistry*, 1986, 90.
8. V. Ponc, *Studies in Surface Science and Catalysis*, 1991, 64.
9. I. M. Ciobîcă. R. A. van Santen, E. van Steen, M. M. Ghouri, in *Advances in Catalysis*, ed. H. Knozinger. B.C. Gates, Academic Press, 2011, vol. 54, pp. 127-187.
10. P. Biloen and W. M. H. Sachtler, *Advances in Catalysis*, 1981, 30, 165-216.
11. H. Pichler and H. Schulz, *Chemie Ingenieur Technik*, 1970, 42, 1162-1174.
12. R. A. van Santen, A. J. Markvoort, M. M. Ghouri, P. A. J. Hilbers and E. J. M. Hensen, *Journal of Physical Chemistry C*, 2013, 117, 4488-4504.
13. R. A. van Santen, A. Markvoort, I. A. W. Filot, M. M. Ghouri and E. J. M. Hensen, *Physical Chemistry Chemical Physics*, 2013, 15, 17038 - 17063.
14. H. Schulz, in *Catalysis: From Principles to Applications*, eds. M. Beller, A. Renken and R. A. van Santen, Wiley-VCH, Weinheim, 2012.

15. S. Storsaeter, D. Chen and A. Holmen, *Surface Science*, 2006, 600, 2051-2063.
16. H. Kölbl, R.B. Anderson, M. Rálek, *The Fischer-Tropsch Synthesis*, Academic Press, 1984.
17. P. Hu, J.Cheng, P. Ellis, S. French, G. Kelly, C.M. Lok, *Journal of Physical Chemistry C*, 2008, 112.
18. M. Zhuo, A. Borgna and M. Saeys, *Journal of Catalysis*, 2013, 297, 217-226.
19. I. M. Ciobîcă, G. J. Kramer, Q. Ge, M. Neurock and R. A. van Santen, *Journal of Catalysis*, 2002, 212, 136-144.
20. A. J. Markvoort, R. A. Van Santen, P. A. J. Hilbers and E. J. M. Hensen, *Angewandte Chemie International Edition*, 2012, 51, 9015-9019.
21. R. A. van Santen and A. Markvoort, *ChemCatChem*, 2013, 5, 3384-3397.
22. N. Kapur, J. Hyun, B. Shan, J. B. Nicholas and K. Cho, *The Journal of Physical Chemistry C*, 2010, 114, 10171-10182.
23. O. R. Inderwildi, S. J. Jenkins and D. A. King, *Journal of Physical Chemistry C*, 2008, 112, 1305-1307.
24. J. W. Mirwald and O. R. Inderwildi, *Physical Chemistry Chemical Physics*, 2012, 14, 7028-7031.
25. M. Ojeda, R. Nabar, A. U. Nilekar, A. Ishikawa, M. Mavrikakis and E. Iglesia, *Journal of Catalysis*, 2010, 272, 287-297
26. S. Shetty, A. P. J. Jansen and R. A. van Santen, *Journal of the American Chemical Society*, 2009, 131, 12874-12875.
27. I. M. Ciobîcă and R. A. van Santen, *Journal of Physical Chemistry B*, 2003, 107, 3808-3812.
28. R. A. van Santen, I. M. Ciobîcă, E. van Steen and M. M. Ghouri, in *Advances in Catalysis*, eds. B. C. Gates and H. Knozinger, Academic Press, 2011, vol. 54, ch. 3, pp. 127-187.
29. J. Yang, J.M.G. Carballo, A. Holmen, S. García-Rodríguez, S. Rojas, M. Odeja, J.L.G. Fierro, *Journal of Catalysis*, 2011, 284, 102-108.
30. P. B. Radestake, J.P. Den Breejen, G.L. Bezemer, J.H. Bitter, V. Frøseth, A. Holmen, K.P. de Jong, *Journal of American Chemical Society*, 2009, 131, 7197-7203.
31. J. H. Bitter, G.L. Bezemer, H.P.C.E. Kuipers, H. Oosterbeek, J.E. Holewijn, X. Xu, F. Kapteijn, A.K. van Dillen, K.P. de Jong, *Journal of American Chemical Society*, 2006, 128.
32. K. Takeuchi, H. Arakawa, T. Matsuzaki, Y. Sugi, *Chemical Letters*, 1984, 13, 1607.
33. H. Arakawa, T. Hanaoka, T. Matsuzaki, Y. Sugi, K. Kanno, Y. Abe, *Catalysis Today*, 2000, 58, 271-280.
34. M. Neurock, R.A. van Santen, *Molecular Heterogenous Catalysis*, Wiley-VCH, 2006.
35. Z.-P. Liu, J.Chen, *Journal of American Chemical Society*, 2008, 130, 7929-7937.
36. C. H. Bartholomew and R. J. Farrauto, *Fundamentals of Industrial Catalytic Processes*, John Wiley & Sons, Inc., Hoboken, New Jersey, 2<sup>nd</sup> edn., 2005.

37. M. C. Valero and P. Raybaud, *Catalysis Letters*, 2013, 143, 1-17.
38. I. M. Ciobîcă and R. A. van Santen, *Journal of Physical Chemistry B*, 2002, 106, 6200-6205.
39. I. M. Ciobîcă, F. Frechard, R. A. van Santen, A. W. Kleyn and J. Hafner, *Chemical Physics Letters*, 1999, 311, 185-192.
40. Y. Guan, X.Y. Quek, R.A. van Santen, E.J.M. Hensen, *ChemCatChem*, 2011, 3, 1735-1738.
41. B. T. Loveless, C. Buda, M. Neurock and E. Iglesia, *Journal of American Chemical Society*, 2013, 135, 6107-6121.
42. J. W. Niemantsverdriet, R.A.van Santen, *Chemical Kinetics and Catalysis*, Plenum Press, 1995.
43. J. Cheng, X.-Q. Gong, P. Hu, C. M. Lok, P. Ellis and S. French, *Journal of Catalysis*, 2008, 254, 285-295.
44. Y. Choi and P. Liu, *Journal of The American Chemical Society*, 2009, 131, 13054-13061.
45. Y.-H. Zhao, K. Sun, X. Ma, J. Liu, D. Sun, H.-Y. Su and W.-X. Li, *Angewandte Chemie International Edition*, 2011, 50, 5335-5338.
46. M. Zhuo, K. F. Tan, A. Borgna and M. Saeys, *Journal of Physical Chemistry C*, 2009, 113, 8357-8365.
47. D.-B. Cao, Y.-W. Li, J. Wang and H. Jiao, *Journal of Molecular Catalysis A: Chemical*, 2011, 346, 55-69.
48. H. M. Torres, Galvis, J. H. Bitter, C. B. Khare, M. Ruitenbeek, A. I. Dugulan and K. P. de Jong, *Science*, 2012, 335, 835-838.
49. A. Bundhoo, J. Schweicher, A. Frennet, N. Kruse, D. Helen, F. Meunier, *Journal of physical Chemistry C*, 2010, 114, 2248-2255.
50. A. Laskov, G. A. Beitel, H. Oosterbeek, E. W. Kuipers, *Journal of Physical Chemistry*, 1996, 100, 12494-12502.
51. C. P. M. de Groot, G. A. Beitel, H. Oosterbeek, J. H. Wilson, *Journal of physical Chemistry B*, 1997, 101, 4035-4043.
52. I. M. Ciobîcă. S. Shetty, E. J. M. Hensen, R. A. van Santen, *Chemical Communications*, 2011, 47, 9822-9824.
53. R. Pettit. R. C. Brady III, *Journal of American Chemical Society*, 1981, 103, 1287-1289.
54. R. Pettit. R. C. Brady III, *Journal of American Chemical Society*, 1981, 102, 6181-6182.
55. R. Quyoum. P. M. Maitlis, H. C. Long and M. L. Turner, *Applied Catalysis A*, 1999, 186, 363-374.
56. P. M. Maitlis, V. Zanotti, *Catalysis Letters*, 2007, 122, 80-83.
57. S. Carencio. A. Tuxen, M. Chintapalli, C.-H. Chuang, C. Escudero, E. Pach, P. Jiang, F. Borondics, B. Beberwyck, A. P. Alivisatos, G. Thornton, W.-F. Pong, J. Guo, R. Perez, F. Besenbacher, M. Salmeron, *Journal of American Chemical Society*, 2013, 135, 2273-2278.
58. P. W. van Grootel, T.Zhu, I.A.W. Filot, S-G. Sun, R.A. van Santen, E.J.M. Hensen, *Journal of Catalysis*, 2013, 297, 227-235.

59. S. Lee, *Methanol Synthesis Technology*, CRC Press, 1989.
60. F. Abild-Pedersen, M.P. Andersson, I.N. Remediakis, T. Bligaard, G. Jones, J. Engbæk, O. Lytken, S. Horch, J.H. Nielsen, J. Sehested, J.R. Rostrup-Nielsen, J.K. Nørskov, I. Chorkendorff, *Journal of Catalysis*, 2008, 255, 6-12.
61. A. Hellman, K. Honkala, I.N. Remediakis, A. Logadottir, A. Carlsson, S. Dahl, C.H. Christensen, J.K. Nørskov, *Science*, 2005, 307, 555-558.
62. R. J. Hoffman, D.L. Thorn, *Journal of American Chemical Society*, 1978, 97.
63. M. Ichikawa, W.M.H. Sachtler, *Journal of Physical Chemistry*, 1986, 90, 4752-4758.
64. J. Greely, F. Abild-Pedersen, F. Studt, J. Rossmeisl, T.R. Munter, P.G. Moses, E. Skúlason, T. Bligaard, J.K. Nørskov, *Physical Review Letters*, 2007, 99, 016105-016109.
65. K. Takeuchi, H. Arakawa, T. Matsuzaki, Y. Sugi, *Chemical Letters*, 1989, 13.
66. J. R. Schmidt, G.R. Jenness, *ACS Catalysis*, 2013, 3, 2881-2890.
67. R. A. van Santen, T. Koerts, *Catalysis Letters*, 1990, 6, 49-57.
68. R. A. van Santen, T. Koerts, *Journal of Catalysis*, 1992, 134, 12-23.



Selective formation of long chain oxygenates from synthesis gas comes at a cost of increased methane formation.  
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