Oxidative Coupling of Methane: A Microkinetic Model Accounting for Intraparticle Surface-Intermediates Concentration Profiles

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ABSTRACT: A microkinetic model for oxidative coupling of methane (OCM) has been developed that comprises a reaction network of 39 gas-phase and 26 catalytic elementary steps. It has been implemented in a heterogeneous reactor model that explicitly accounts for the interactions between gas phase and surface species. Concentration gradients arising from mass transport limitations are found to develop inside the catalyst pellet for all intermediates (i.e., surface and gas-phase) even under an intrinsic kinetics regime for the molecules and clearly affect the C₂ selectivity. Special attention has been devoted to the reduction of the number of adjustable parameters in the model and the a priori determination of thermodynamic as well as kinetic parameters. A contribution analysis is conducted in order to elucidate the complex reaction pathways in OCM that lead to the desired products. Apart from the methyl radicals that couple to an extent of almost 70% in the void space between the pellets, the catalyst pellet accounts for the majority of molecules and radicals conversion, which are produced on the surface and further interact either in the catalyst pores or with other surface species. Almost 95% of CH₄ consumption and more than half of the C₂H₆ production take place inside the catalyst pellet. A similar analysis is applied to understand the effect of various textual properties of catalysts on the performance of OCM, for example, increasing the catalyst porosity is found beneficial for the C₂ yield, as long as a sufficient CH₄ activation takes place, so that the coupling pathway is promoted over the heterogeneous oxidation of CH₄.

1. INTRODUCTION

The oxidative coupling of methane (OCM) is a heterogeneous catalyzed gas-phase reaction.¹ The catalyst produces methyl radicals, which can further react through gas-phase reactions in the catalyst pores as well as in the void space between the catalyst pellets.²⁻³ More specifically, methyl radicals can either couple to form ethane or can be oxidized toward carbon oxides via a branched-chain reaction mechanism.⁴ The reaction has been extensively investigated since the first relevant publications in the early 80s⁵⁻⁶ but has still not reached industrial implementation.

An efficient way to extract knowledge from the large experimental data sets that have been generated over various OCM catalyst formulations is via a microkinetic analysis, which accounts for the gas-phase reactions, the fundamental catalytic surface chemistry, and the interaction between both.⁷ Incorporating such a microkinetic model into an advanced reactor model, which considers all relevant transport phenomena, can lead to a deeper understanding and optimization of the investigated reaction, especially in the case of OCM, given its recognized dual homogeneous—heterogeneous nature.⁸⁻¹⁰ Aparicio et al.¹¹ were one of the first to conduct a microkinetic analysis of OCM kinetics data to gain a mechanistic insight in the occurring chemistry. Wolf²¹ and Buyevskaya et al.¹² discriminated between various elementary step models that considered different heterogeneous reaction pathways for methane activation, surface oxidation by gas-phase oxygen and consecutive reaction steps of methyl radicals and ethane, supported by transient experiments on MgO and Sm₂O₃. More recently, Su et al.¹³ developed a thermodynamically consistent microkinetic model with which an upper bound of 28% for C₂ yield was calculated. Similarly, Simon et al.¹⁴ applied various physicochemical relations and thermodynamic constraints to calculate the parameters of a microkinetic model that was used to describe data over a La₂O₃ catalyst. Sinev¹⁵ has studied extensively the oxidative transformations of light alkanes. Early on, the interaction of radicals with the surface was investigated,¹⁶⁻¹⁷ wherein a Polanyi correlation was applied to determine the activation energies of the various proposed heterogeneous steps by postulating an analogy with equivalent homogeneous steps. The key role of surface hydroxyl groups was discussed, while a kinetic model accounting for surface interactions and diffusion of oxygen, hydrogen, and hydroxyl ions in the oxide lattice was developed to account for the participation of lattice oxygen in methane oxidation.¹⁸ More recently, the author’s findings were consolidated in an elaborate microkinetic model that was able to describe qualitatively various experimental observations.

In the work of Couwenberg et al.,¹² it was established that the participating gas-phase intermediates are highly reactive and lead to irreducible mass transport limitations for the latter. This effectively means that the pellet size necessary to consider the internal concentration gradients negligible is so small that it would lead to unacceptable pressure drop in the catalyst bed. As a result, during the determination of OCM kinetics these transport limitations have to be explicitly considered. The existence and importance of such gradients was also stressed, although not directly accounted for, in the work of Sinev.¹⁹ A one-dimensional heterogeneous reactor model was specifically...
developed by Couwenberg et al.\textsuperscript{22,23} for this purpose, that is, to adequately describe the interactions between the elementary catalytic reactions and the gas-phase reactions. The model was successfully applied to investigate the effects of the reactive intermediates on conversions, selectivities, and yields over Li/MgO and Sn/Li/MgO catalysts. Subsequently, Sun et al.\textsuperscript{24} expanded the surface reaction network by enhancing the detail in which deep oxidation reactions were represented and by the introduction of reversible reaction steps. Additionally, the application of catalyst descriptors was introduced in the model to facilitate knowledge extraction from high-throughput experiments. More recently, in the work of Thybaut et al.\textsuperscript{25} the surface network was further elaborated, including reaction steps for the description of the heterogeneous oxidation of ethylene. Moreover, a theoretical study was conducted so as to optimize C\textsubscript{2} product yields varying various operating conditions and catalyst texture properties.

In the present work, the aforementioned OCM model is further elaborated on the reactor as well as on the microkinetic level. Intraparticle concentration profiles for the surface intermediates are, for the first time, also accounted for explicitly, in addition to those already implemented for gas phase molecules and radicals. The implementation of the former is necessary given the reversibility of the reactions between gas phase and surface species and the importance of this interaction on products’ yield. In parallel, a considerable expansion of the surface network has been implemented to more adequately describe the complex OCM chemistry. Special attention is devoted to the a priori determination of the majority of surface network parameters, among others, by applying thermodynamic consistency within catalytic cycles. The effects of transport limitations are discussed, while an experimental data set derived from testing of a Sn/Li/MgO catalyst is used to validate the model. Via contribution analysis, the complex OCM reaction pathway is elaborated to gain a more detailed understanding of the relation between catalyst performance and properties.

2. REACTOR MODEL

2.1. Continuity Equations. In order to adequately account for the irreducible transport limitations of radicals, a heterogeneous model that explicitly distinguishes between a solid phase and a fluid phase has been adopted. The solid phase contains pores in which reactants, products and intermediates diffuse toward and away from active sites and in which they can also react with each other. The two phases considered in the model (i.e., the porous solid and the fluid) will be denoted as the intraparticle and the interstitial phase respectively. Mass transfer by molecular diffusion from the interstitial phase to the gas—solid interface occurs simultaneously with gas-phase reactions (eq 1 below). Also, mass-transport by internal diffusion in the catalyst pores occurs simultaneously with chemical reactions, in this case on the catalyst pores walls as well as in the gas phase in the catalyst pores (eq 2 below). No internal heat transport or external heat transfer gradients are considered, since the present model is developed for the assessment of data derived from laboratory-scale, intrinsic kinetic measurements. This entails that during experimental design appropriate criteria should be evaluated to ensure the lack of such limitations.\textsuperscript{26} Nonetheless, Hoebink et al.\textsuperscript{27} studied the design of industrial scale fixed bed OCM reactors and found that it is specifically external heat transfer limitations that play a more important role, as compared to internal thermal gradients.

The coordinate system applied in the continuity equations, in line with the work of Couwenberg et al.\textsuperscript{22},\textsuperscript{23} is illustrated in more detail in Figure 1. On the reactor scale a single coordinate, \( z \), going from 0 to \( L \), is employed. At the pellet scale, two different coordinates are used: \( \xi \) for the intraparticle phase starting from the center of the catalyst pellet to the external surface and \( r \) for the interstitial phase starting from the center of the interstitial phase to the gas—solid interface.

The respective continuity equations for all the components (i.e., molecules and radicals) in the reaction network that have to be integrated, together with the corresponding boundary conditions, are given as follows:

\[
\frac{F_e}{\varepsilon_iA_i} \frac{\partial C_{i,g}}{\partial z} = \frac{D_{bi}}{r} \frac{\partial}{\partial r} \left( r \frac{\partial C_{i,g}}{\partial r} \right) + R_{i,g}
\]

(1)

Intraparticle phase:

\[
-\frac{D_{i,i}}{\varepsilon_i^2} \frac{\partial}{\partial \xi} \left( \varepsilon_i \frac{\partial C_{i,i}}{\partial \xi} \right) = R_{i,i} + \varepsilon_i R_{i,g}
\]

(2)

Boundary conditions:

\[
z = 0 \wedge 0 < r < \frac{d_e}{2} \quad C_{i,g} = C_{i,0}
\]

(3)

\[
z > 0 \wedge r = 0 \quad \frac{\partial C_{i,g}}{\partial r} = 0
\]

(4)

\[
z > 0 \wedge r = \frac{d_e}{2} - a_{g} D_{i,i} \frac{\partial C_{i,i}}{\partial r} = a_{g} D_{i,i} \frac{\partial C_{i,i}}{\partial \xi}
\]

(5)

\[
\xi = 0 \quad \frac{\partial C_{i,i}}{\partial \xi} = 0
\]

(6)

\[
\xi = \frac{d_e}{2} \quad C_{i,g} = C_{i,e}
\]

(7)

where \( i \) ranges from 1 to \( N_{mol} + N_{rad} \). The concentrations of the molecules at the inlet of the catalyst bed are determined by the boundary condition of eq 3, which expresses that no pellet scale gradient occurs at this position. The other boundary conditions are given by eqs 4—7. The gas—solid interfacial surface area, \( a_{g} \), and the external surface area of the catalyst, \( a_{e} \), as used in eq 4, are not equal since during kinetic measurements the catalyst bed is, typically, diluted with an inert material. \( d_e \), that is, the characteristic dimension of the interstitial phase, represents the average distance between two catalyst pellets. The value of \( d_e \) can be calculated from the relation between the total gas-phase volume and the interfacial surface area, \( a_{g} \), in the reactor. Assuming that the reactor is filled with spherical particles of diameter \( d_p \) and accounting for the internal porosity of the bed, the diameter \( d_e \) of imaginary cylinders representing the gas phase volume in the reactor can be calculated as follows:

\[
\frac{d_e}{2} = \frac{d_p}{3} \left( 1 - \varepsilon_b \right)
\]

(8)

Moreover, if long cylindrical pores of uniform pore diameter are assumed for the catalyst, the average pore radius can be calculated according to...
2.2. Surface Intermediates. The balances for the surface species in the reaction network are an explicit part of the reactor model continuity equations and, as such, belong to the state variables of the mathematical set of equations presented above. In order to calculate the concentration of the surface intermediates, the pseudo-steady-state approximation is made, meaning that the net rates of formation of the surface species are considered equal to 0:

\[ \dot{R}_i = 0 \]

where \( i \) ranges from 1 to \( N_{\text{surf}} \). Additionally, the catalyst active site balance is accounted for via the following equation:

\[ \theta_\ast + \sum_{i=1}^{N_{\text{surf}}} \theta_i = 1 \]

with \( \ast \) representing the free site. The above equations complete the set of partial differential equations (PDE) presented in the previous paragraph and are solved simultaneously at each point of the intraparticle dimension \( \xi \) together with the rest of the equations to calculate the surface coverage by the considered species. The specific calculation way of \( R_{i,s} \) is presented in paragraph 3.3, while as will be described in more detail in paragraph 3.4, the obtained surface concentration is further utilized for the calculation of the net formation rates of molecules and radicals, \( R_{i,c} \), participating in the surface network that are required for eq 2.

2.3. Solution Procedure. The above-discussed set of second-order partial differential equations is integrated applying the method of orthogonal collocation. Orthogonal collocation belongs to the methods of weighted residuals and involves an approximation of the differential equations by a trial function. In this method, it is only necessary to evaluate the residuals at the collocation points. In the orthogonal collocation method these collocation points are chosen as the roots of orthogonal polynomials. The method is very suitable for the solution of two-point boundary-value problems. The trial function is then a set of orthogonal polynomials which satisfy the boundary conditions, while the roots to the polynomials determine the collocation points. The values of the solution at the collocation points can then be calculated from a set of algebraic equations.

More specifically, the equations of the current problem can be solved by discretization in the \( r \) and \( \xi \) direction using orthogonal collocation, and by subsequently applying a variable-step backward differentiation formula (BDF) integration method for the \( z \) direction. As such, the PDE set can be converted to a differential–algebraic one (DAE), with the number of model equations depending on the number of components, molecules, radicals, and surface species considered and on the number of collocation points chosen for the discretization of the interstitial and intraparticle dimensions. For the interstitial phase 4 collocation...
points suffice, while the intraparticle dimension is discretized using 7 points. A spherical coordinate system for the latter and a cylindrical coordinate system for the former phase are used, allowing the use of symmetrical polynomials as trial functions and, hence, automatically fulfilling the boundary conditions at \( r = 0 \) (eq 4) and \( r = \frac{x}{\xi} = 0 \) (eq 6). As such, the aforementioned number of collocation points represents the internal ones plus the right boundary. Twenty-four components are considered in total, fourteen of them being molecules, including inert \( N_2 \) and the remaining ten being radicals. Discretization of continuity eq 1, hence, leads to \( 3 \times 24 \) differential equations, while 24 algebraic ones result from eq 5 at the right boundary. Equation 2 is converted to \( 6 \times 24 \) algebraic equations, with 24 additional algebraic ones defined by eq 7 that represents again the right boundary.

Moreover, the balances of the 10 surface intermediates are considered for each intraparticle collocation point, meaning that eqs 10 and 11 contribute with 7 additional algebraic equations, correspondingly.

In total, 341 state variables, 72 of them being diatomic, \( \text{D} \), and \( \text{D}_{ij} \), are considered in total, fourteen of them being molecules, including inert \( N_2 \) and the remaining ten being radicals. Pre-exponential factors, and activation energies are compared to the other reactions, which is ascribed to the reduction of the number of adjustable parameters and the a priori determination of thermodynamic and kinetic parameters.

3.1. Gas-Phase Reaction Network. The reaction network in the absence of catalyst has been adopted from the work of Chen et al.34 and consists of 39 reversible reactions among 13 molecules and 10 radicals as has been presented in the aforementioned work and more recently in the work by Sun et al.24 Typical gas-phase methanol oxidation networks derived from combustion chemistry comprise several hundreds of elementary steps.35 The current network was selected by reducing such comprehensive networks36,37 after conducting contribution and sensitivity analyses based on experimental data at typical OCM conditions. Moreover, the presently used gas-phase reaction network was validated with catalytic experimental data in the work of Couwenberg et al.23 over both a Li/MgO and a Sn/Li/MgO catalyst, where the contribution of the gas-phase network is high and low, respectively. The molecules considered are dihydrogen, water, hydrogen peroxide, dioxygen, methanol, carbon monoxide, carbon dioxide, ethyne, ethene, ethane, propene, and propane. The radicals are hydrogen and oxygen atoms, hydroxyl, hydrogen peroxy, formyl, methoxy radicals, and methyl, vinyl, ethyl, and propyl radicals. Pre-exponential factors and activation energies, as reported by Chen et al.,34 are utilized to calculate forward rate coefficients via the Arrhenius equation, while the rate coefficients for the backward directions are calculated by means of equilibrium coefficients and the equivalent forward rate coefficients. The equilibrium coefficients are calculated at a given temperature by using the thermodynamic database of CHEMKIN,38 which is interfaced to the simulation software used. All parameters of the gas-phase network, pre-exponential factors, and activation energies are fixed during regression using catalytic experimental data.

Finally, in order to adequately describe the total pressure behavior of the rate coefficients for the unimolecular reactions in the network has been taken into account explicitly. As described in detail by Chen et al.,39 the rate of these reactions shows a stronger pressure dependency compared to the other reactions, which is ascribed to the activation by collision with any other molecule (i.e., so-called third bodies). This falloff factor is, hence, a function of the concentration of these third bodies.

3.2. Catalytic Reaction Network. The elementary steps on the catalyst surface considered in the kinetic model are shown in Table 1. This set of reversible catalytic reactions is coupled to the gas-phase branched-chain reaction network described above via the reactor model equations presented in section 2.1. The complete kinetic model thus contains 26 catalytic and 39 gas-phase reactions in which 24 gas-phase, including inert \( N_2 \), and 11 surface components, including the active site, are involved.

The catalytic network describes methane activation on the catalyst surface by the dissociative oxygen adsorption (reaction C1), hydrogen abstraction of methane (reaction C2), and the regeneration of the active site (reactions C5 and C6). It accounts for CO2 generation through three reaction pathways: methyl radical scavenging followed by the sequential hydrogen abstraction from methoxy species on the catalyst (reactions C7–C13); the oxidation of CO adsorbed from the gas-phase (reactions C11–C13); and the heterogeneous oxidation of ethylene (reactions C14–C16). Given the average lattice constants of metal oxides typically used as OCM catalysts and the corresponding active site densities considered, second order surface reactions, such as the
Table 1. Catalytic Elementary Reactions Considered in the Oxidative Coupling of Methane

\[
\begin{align*}
O_2 + 2^* & \rightarrow 2O^* \quad (C1) \\
CH_4 + O^* & \rightarrow CH_3O + H^* \quad (C2) \\
C_2H_4 + O^* & \rightarrow C_2H_3 + OH^* \quad (C3) \\
C_2H_6 + O^* & \rightarrow C_2H_5 + OH^* \quad (C4) \\
2OH^* & \rightarrow H_2O^* + O^* \quad (C5) \\
H_2O^* & \rightarrow H_2O + \cdot \quad (C6) \\
CH_2O + O^* & \rightarrow CH_2O^* \quad (C7) \\
CH_3O^* + OH^* & \rightarrow CH_3O + H^* \quad (C8) \\
CH_4O^* + O^* & \rightarrow HCOO^* + OH^* \quad (C9) \\
HCOO^* + O^* & \rightarrow CO^* + OH^* \quad (C10) \\
CO^* + O^* & \rightarrow CO_2 + \cdot \quad (C11) \\
CO + \cdot & \rightarrow CO_2 \quad (C12) \\
CO_2 + \cdot & \rightarrow CO_3^* \quad (C13) \\
C_2H_4 + O^* & \rightarrow C_2H_2 + O^* \quad (C14) \\
C_2H_6O^* + O^* & \rightarrow C_2H_2O + OH^* \quad (C15) \\
C_2H_4O^* + O^* & \rightarrow CH_2O + CO + OH^* \quad (C16) \\
C_2H_5O + O^* & \rightarrow CH_2 + OH^* \quad (C17) \\
CH_3O + O^* & \rightarrow CH_2O + OH^* \quad (C18) \\
CH_2O + O^* & \rightarrow CH_2O + OH^* \quad (C19) \\
CH_4O^* + O^* & \rightarrow CH_3O + OH^* \quad (C20) \\
H_2 + O^* & \rightarrow H^* + OH^* \quad (C21) \\
H_2O_2 + O^* & \rightarrow H_2O + OH^* \quad (C22) \\
OH + O^* & \rightarrow O + OH^* \quad (C23) \\
H_2O^* + O^* & \rightarrow O + OH^* \quad (C24) \\
HO_2 + O^* & \rightarrow O_2 + OH^* \quad (C25) \\
HO_2 + O^* & \rightarrow OH + O^* \quad (C26)
\end{align*}
\]

with \( N_{\text{gas}} \) being the number of gas-phase reactions. This equation is used both for the interstitial phase and for the contribution of the gas phase network in the intraparticle phase, as seen in eqs 1 and 2 respectively. The rate of an elementary step in the gas phase network is calculated through the law of mass action according to

\[
r_j = k_j N_{\text{gas}} \prod_{i=1}^{N_{\text{rad}}} C_i^{v_{ij}}
\]

(16)

where \( k_j \) is the rate coefficient of reaction \( j \). Equivalently, the rate of an elementary step in the catalytic reactions follows from the law of mass action. For example, the rate of catalytic reaction \( C2 \) is calculated according to

\[
r_{c2} = k_{14} C_{CH_4} \theta_{O_2} L_i
\]

(17)

All of catalytic reaction rates are calculated per internal surface area of the catalyst pellet and have to be multiplied with the specific surface area, \( S_p \), and the catalyst density, \( \rho_i \), so that they can be expressed per pellet volume. They are used for calculating the net production rates of surface species, \( R_{ij,s} \), according to

\[
R_{ij,s} = \sum_{j=1}^{C_{26}} v_{ij} R_j
\]

(18)

As mentioned, given the pseudosteady state approximation applied, net rates, \( R_{ij} \), are used for the determination of the surface coverages, \( \theta_j \), via eqs 10 and 11. However, in order to calculate the catalytic net production rate of molecules and radicals, \( R_{ij} \), used in eq 2, a separate procedure is followed, see section 3.4.

3.4. Global Catalytic Reaction Paths. Sixteen global reactions (a to p), built up from catalytic elementary steps, can be distinguished in this model and are presented in Table 2. These paths represent the number of independent catalytic cycles that exist in the considered surface network. Path a, for example, represents the catalytic formation of methyl radicals from methane. It can be seen that this path can be constructed from catalytic elementary steps 1, 2, 5, and 6 taking into account appropriate stoichiometry numbers, that is, 1, 4, 2, and 2. Moreover, after constructing in a similar way the combinations for all independent paths, it can be seen that
reaction C2 participates four times in global path a, while it is not involved in any other global path. Thus, the rate of global reaction a is equal to \( r_a = r_{C2}/4 \). This way of presenting a complex reaction network follows from the work of Temkin\(^43\) and allows a straightforward calculation of the net production rates of the molecules and radicals taking part in the surface network.\(^44\)

Similarly, paths b and c account for the catalytic formation of vinyl and ethyl radicals from ethylene and ethane, respectively. Path d shows the catalytic conversion of carbon monoxide into carbon dioxide, and path e describes the deep oxidation of ethylene. Likewise, the other paths describe \( \text{H-atom abstraction of the remaining gas-phase species, except for path m, which accounts for the scavenging of hydroperoxy radicals on the catalyst surface.} \)

Similar analogies to path a can be found for all of the other global paths according to the coefficients presented in Table S1 of the Supporting Information, resulting in the following rates:

\[
\begin{align*}
\text{a}. & \quad 4\text{CH}_4 + \text{O}_2 \rightleftharpoons 4\text{CH}_3^+ + 2\text{H}_2\text{O} \\
\text{b}. & \quad 4\text{C}_2\text{H}_4 + \text{O}_2 \rightleftharpoons 4\text{C}_2\text{H}_3^+ + 2\text{H}_2\text{O} \\
\text{c}. & \quad 4\text{C}_2\text{H}_6 + \text{O}_2 \rightleftharpoons 4\text{C}_2\text{H}_5^+ + 2\text{H}_2\text{O} \\
\text{d}. & \quad 2\text{CO} + \text{O}_2 \rightleftharpoons 2\text{CO}_2 \\
\text{e}. & \quad 4\text{CH}_3^+ + 7\text{O}_2 \rightleftharpoons 4\text{CO}_2 + 6\text{H}_2\text{O} \\
\text{f}. & \quad \text{C}_2\text{H}_4 + 3\text{O}_2 \rightleftharpoons 2\text{CO}_2 + 2\text{H}_2\text{O} \\
\text{g}. & \quad 4\text{C}_2\text{H}_5^+ + \text{O}_2 \rightleftharpoons \text{C}_2\text{H}_4 + 2\text{H}_2\text{O} \\
\text{h}. & \quad 4\text{CH}_3\text{O} + \text{O}_2 \rightleftharpoons 4\text{CHO} + 2\text{H}_2\text{O} \\
\text{i}. & \quad 4\text{CH}_3\text{O} + \text{O}_2 \rightleftharpoons 4\text{CHO} + 2\text{H}_2\text{O} \\
\text{j}. & \quad 4\text{CHO} + \text{O}_2 \rightleftharpoons 4\text{CO} + 2\text{H}_2\text{O} \\
\text{k}. & \quad 4\text{H}_2 + \text{O}_2 \rightleftharpoons 4\text{H}_2\text{O}_2 \\
\text{l}. & \quad 4\text{H}_2\text{O}_2 + \text{O}_2 \rightleftharpoons 4\text{H}_2\text{O}_2 + 2\text{H}_2\text{O} \\
\text{m}. & \quad 4\text{H}_2\text{O}_2 \rightleftharpoons 3\text{O}_2 + 2\text{H}_2\text{O} \\
\text{n}. & \quad 2\text{OH} + 2\text{O}_2 \rightleftharpoons 2\text{H}_2\text{O}_2 \\
\text{o}. & \quad 2\text{H}_2\text{O} + \text{O}_2 \rightleftharpoons 4\text{OH}^+ \\
\text{p}. & \quad 4\text{OH}^+ + \text{O}_2 \rightleftharpoons 4\text{O}^+ + 2\text{H}_2\text{O} \\
\end{align*}
\]

It are these rates, of the global reaction paths, that are utilized in the reactor continuity eq 2 for the intraparticle phase according to

\[
R_i,c = \sum_{j=0}^n v_j r_j \tag{20}
\]

3.5. Calculation of Surface Reaction Network Parameters. Microkinetic model parameters are classified into kinetic and catalyst descriptors. While the former are exclusively related to the reaction kinetics, independent of the catalyst used, the latter specifically account for the physical and chemical catalyst properties and represent the essential differences between the various candidate catalysts.\(^45,46\) Special attention has been devoted to incorporating catalyst descriptors into the microkinetic model for methane oxidative coupling, as described in Sun et al.\(^24\) The main advantage of this approach is that the developed model is capable of quantifying trends between catalyst activity and selectivity on the one hand and properties on the other hand. As a result, such a model allows addressing which catalyst descriptors and, hence, corresponding properties are the most relevant for the improvement of catalytic performance.

The implementation of thermodynamic relationships in a microkinetic model is one approach in relating model parameters to catalyst descriptors and simultaneously reducing the number of adjustable parameters. Thermodynamic relationships can be established between surface reaction enthalpies and analogous gas-phase reactions provided that the adsorption thermodynamics of the species involved can be adequately described or can be defined as adjustable parameter.\(^47\) Applying thermodynamic consistency through such thermodynamic cycles allows to express reaction enthalpies for various elementary steps as a function of a limited number of unknown parameters, which will then be obtained, for example, by regression. Similar approaches are widely used during the development of microkinetic models,\(^48,49\) which have successfully described experimental data from a wide variety of applications.\(^50,51\) For the case of OCM, as already mentioned, the work of Su et al.\(^14\) was among the first to ensure thermodynamic consistency across their considered surface network. In the Supporting Information, this methodology is elaborated based on the OCM microkinetic network applied in this work, so as to calculate the surface reaction enthalpies and corresponding activation energies of all surface steps.

On the other hand, collision theory is used to calculate the maximum value of the pre-exponential factors of all steps involving the collision of a molecule on the catalyst surface. These reactions are actually all of the adsorption steps, including the forward direction of reactions C7 and C14 that describe the capture of \( \text{CH}_2^+ \) and \( \text{C}_2\text{H}_4 \) on the surface, and all of the Eley–Rideal steps. In the current work, these maximum values for the adsorption steps were corrected by a factor, denoted as sticking coefficient. These factors represent the ratio of the number of the respective molecules or radicals actually adsorbing to a clean surface to the total number of them colliding with it. Since they vary depending on catalyst, they were all defined as catalyst descriptors, meaning they are part of the adjustable parameters of the model, as also seen in section 4.1. The collision frequencies were calculated according to the following equation:\(^52\)

\[
A_i = \frac{1}{n} \sqrt{\frac{RT}{2\pi M}} \tag{21}
\]

The remaining pre-exponential factor values, pertaining to reactions involving only surface species, have been left unchanged at their values as previously reported,\(^52,53\) which were calculated in those references via statistical thermodynamics and transition state theory.

In order to ensure thermodynamic consistency, as seen in the Supporting Information, the surface reaction network related
calculations require the knowledge of thermodynamic properties, namely of gas-phase reaction enthalpies. Additionally, in order to calculate the equilibrium coefficients of the gas-phase network, the Gibbs energy difference is needed, which in turn requires the gas-phase species molar entropies. It is assumed that the standard-state thermodynamic properties of all species are functions of temperature only, expressed in the form of polynomial fits. In particular the format used in the NASA chemical equilibrium code is applied, where seven coefficients are needed for each of two temperature ranges, above and below 1000 K:

\[
\frac{H}{RT} = \alpha_1 + \frac{\alpha_2}{2} T + \frac{\alpha_3}{3} T^2 + \frac{\alpha_4}{4} T^3 + \frac{\alpha_5}{5} T^4 + \frac{\alpha_6}{T} \quad (22)
\]

\[
\frac{S}{R} = \alpha_1 \ln T + \frac{\alpha_2}{2} T^2 + \frac{\alpha_3}{3} T^3 + \frac{\alpha_4}{4} T^4 + \alpha_7 \quad (23)
\]

Finally, the standard-state Gibb’s free energy is calculated according to

\[
G^\circ = H^\circ - TS^\circ \quad (24)
\]

The actual coefficients for the above equations for all the used species were taken from the database of the CHEMKIN software from Reaction Design.38

4. RESULTS AND DISCUSSION

4.1. Model Validation. The developed model was validated against an experimental data set on a Sn promoted Li/MgO catalyst. This data set has been elaborately discussed in previous publications, and will, therefore, not be further commented in the current work. In Figure 2, the simulated molar fractions are compared to the experimental ones, where it is seen that an overall satisfactory description of the data has been achieved with the proposed model. As described in detail previously, by implementing catalyst descriptors the microkinetic model can be applied on a library of catalysts rather than a single catalyst. Such an assessment of different catalysts has also been conducted and is presented elsewhere. Given the significant expansion of the surface kinetic network in the current work compared to the previous versions of the model, kinetic as well as catalyst, descriptors have been estimated to describe this data set. In Table 3, the estimated catalyst descriptors are given for the Sn/Li/MgO catalyst, while Table 4 presents the values of Polanyi parameters for the considered reactions families. More details on these parameters in relation to the surface network parameters are found in the Supporting Information and the previous publications. Moreover, in the work of Sun et al., a sensitivity analysis was presented to identify the most important descriptors in the microkinetic model. Considering the proposed methodology in studying the OCM reaction, wherein microkinetics are coupled with mass transport phenomena, the validation approach followed can be summarized as follows: The initial model developed by Couwenberg et al. considered a nonreversible surface network among a limited number of surface species. As such, an analytical solution of the set of equations describing the surface coverages was possible. Moreover, no intraparticle gradients were considered for the surface species in that work. The expansion of the surface reaction network as well as of the number of participating surface species and inclusion of reaction reversibility by Sun et al. necessitated the numerical determination of this coverage. The focus of that work was on the implementation of catalyst descriptors in the model and their validation with the Couwenberg data. Reaction reversibility, however, given the irreducible mass transport limitations of the radicals, should affect also surface coverage and, hence, OCM kinetics.

Table 3. Catalyst Descriptors Used in the Simulation of the Data Obtained on Sn/Li/MgO

<table>
<thead>
<tr>
<th>catalyst descriptor</th>
<th>unit</th>
<th>value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_1$</td>
<td>reaction enthalpy of H-atom abstraction of CH₄</td>
<td>(kJ mol⁻¹)</td>
</tr>
<tr>
<td>$D_2$</td>
<td>chemisorption enthalpy of O₂</td>
<td>(kJ mol⁻¹)</td>
</tr>
<tr>
<td>$D_3$</td>
<td>chemisorption enthalpy of CH₄O</td>
<td>(kJ mol⁻¹)</td>
</tr>
<tr>
<td>$D_4$</td>
<td>chemisorption enthalpy of CHO·</td>
<td>(kJ mol⁻¹)</td>
</tr>
<tr>
<td>$D_5$</td>
<td>chemisorption enthalpy of CO</td>
<td>(kJ mol⁻¹)</td>
</tr>
<tr>
<td>$D_6$</td>
<td>chemisorption enthalpy of CO₂</td>
<td>(kJ mol⁻¹)</td>
</tr>
<tr>
<td>$D_7$</td>
<td>chemisorption enthalpy of H₂O</td>
<td>(kJ mol⁻¹)</td>
</tr>
<tr>
<td>$D_8$</td>
<td>chemisorption enthalpy of C₂H₄O₂</td>
<td>(kJ mol⁻¹)</td>
</tr>
<tr>
<td>$D_9$</td>
<td>initial sticking probability of O₂</td>
<td></td>
</tr>
<tr>
<td>$D_{10}$</td>
<td>initial sticking probability of CH₃⁺</td>
<td></td>
</tr>
<tr>
<td>$D_{11}$</td>
<td>initial sticking probability of CH₄⁺</td>
<td></td>
</tr>
<tr>
<td>$D_{12}$</td>
<td>initial sticking probability of CO⁺</td>
<td></td>
</tr>
<tr>
<td>$D_{13}$</td>
<td>initial sticking probability of CO₂⁺</td>
<td></td>
</tr>
<tr>
<td>$D_{14}$</td>
<td>initial sticking probability of H₂O⁺</td>
<td></td>
</tr>
<tr>
<td>$D_{15}$</td>
<td>initial sticking probability of C₂H₄O₂⁺</td>
<td></td>
</tr>
<tr>
<td>$D_{16}$</td>
<td>density of active sites</td>
<td>(mol m⁻²)</td>
</tr>
</tbody>
</table>

Table 4. Reaction Families and Corresponding Parameters Used in the Polanyi Relationships Considered in Methane Oxidative Coupling

<table>
<thead>
<tr>
<th>reaction family</th>
<th>α</th>
<th>$E_0$ (kJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>rf₁</td>
<td>H abstraction by Eley–Rideal reaction (steps C₂–C₄, C₁₇–C₂₅)</td>
<td>0.75</td>
</tr>
<tr>
<td>rf₂</td>
<td>H abstraction by surface reaction (steps C₈–C₁₀, C₁₅)</td>
<td>0.50</td>
</tr>
<tr>
<td>rf₃</td>
<td>Recombination of OH (step C₅)</td>
<td>0.65</td>
</tr>
<tr>
<td>rf₄</td>
<td>CO oxidation on the surface (step C₁₂)</td>
<td>0.26</td>
</tr>
<tr>
<td>rf₅</td>
<td>C–C cleavage on the surface (step C₁₆)</td>
<td>0.97</td>
</tr>
</tbody>
</table>
Hence, it is aim of the current work to specifically address this latter crucial aspect. In what follows, the insight acquired by the application of the current elaborate reactor and kinetic model will be focused on and the importance of considering such pellet scale phenomena will be quantified. Moreover, a detailed reaction pathway analysis is conducted to elucidate the relative importance of the homogeneous and heterogeneous network.

4.2. Concentrations Profiles. In the next paragraph, simulation results are presented to illustrate the existence of intraparticle and interstitial concentration gradients for the reactive intermediates. The effect and importance of surface coverage gradients in the catalyst pellet pores, which represents the main reactor model improvement of the current work, is addressed in the following one. The operating conditions at which this analysis has been performed are summarized in Table 5.

Table 5. Experimental Conditions Used for the Base Case Simulations

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_{\text{tot}}$</td>
<td>$1.13 \times 10^5$ Pa</td>
</tr>
<tr>
<td>$\text{CH}_4/\text{O}_2$</td>
<td>3.6 mol mol$^{-1}$</td>
</tr>
<tr>
<td>$T$</td>
<td>970 K</td>
</tr>
<tr>
<td>$W/F_{\text{G}}$</td>
<td>5.82 kg s mol$^{-1}$</td>
</tr>
<tr>
<td>$X_{\text{CH}_4}$</td>
<td>0.1032</td>
</tr>
<tr>
<td>$X_{\text{O}_2}$</td>
<td>0.3666</td>
</tr>
</tbody>
</table>

4.2.1. Molecules and Radicals. The reactivity of a component can be quantified by examining its lifetime, $\tau$, defined as the reciprocal of the pseudo-first-order rate coefficient, $k_i$, while the diffusion rate of the component can be compared to its consumption rate via the diffusion length, $\lambda_i$, that is calculated according to

$$\lambda_i = \sqrt{\frac{D_{ji}}{k_i}}$$

All of the quantities involved in these calculations are only available after integration of the set of differential equations presented above, since they depend on the local concentration of the components and their local consumption rates.

Looking at the reactants and products, it can be seen that for most of them no significant concentration gradients exist in the pellet coordinate. As shown in more detail in Table S2 of the Supporting Information, the diffusion lengths obtained for reactants and products exceed the pellet radius; for example, at the selected operating conditions, the diffusion lengths, of all radicals are, on average, $2-3$ orders of magnitude lower than the radius of the catalyst pellet; see Table S2 of the Supporting Information. Therefore, it can be ignored that the concentration of these two species recombine to form $\text{HO}_2^*$ radicals, being surface produced intermediates, have a much higher concentration in the catalyst pores as compared to the interstitial gas phase. However, approaching the catalyst surface, this concentration decreases significantly due to a net diffusion toward the interstitial phase. On the contrary, a surface terminated species, such as the $\text{HO}_2^*$ radical, presents a much higher concentration in the interstitial phase.

The radical quenching-mechanism is described here by including specific elementary steps (i.e., reactions C2S and C26), in contrast to the work of Couwenberg et al. where only a pseudohomogeneous reaction was considered. Nonetheless, the shape of the calculated profiles for $\text{HO}_2^*$ is in line with that work confirming the existence and important role of heterogeneous termination of gas-phase reactions. The above considerations indicate the strategic advantages of applying an elaborate reactor model, such as the one used in the present work, during kinetic modeling of experimental data aimed at the measurement of intrinsic OCM kinetics.

4.2.2. Surface Intermediates. Given the complex interplay between gas-phase and catalytic reactions during OCM, it can be speculated that the irreducible mass transport limitations for the reactive intermediates discussed in the previous section also affect catalyst surface coverages. This important phenomenon has not been systematically investigated till now in literature. As described by Sun et al. and also presented in detail in the Supporting Information of the current work, the main catalytic cycle in OCM leading to $\text{CH}_3^*$ radicals consists of four steps. Initially, the dissociative adsorption of $\text{O}_2$ leads to the production of the oxidized site $\text{O}^*$, followed by H-atom abstraction from $\text{CH}_4$ by this site leading to $\text{CH}_3^*$ radicals and surface hydroxyl species, $\text{OH}^*$. Two such species recombine to form $\text{O}^*$ and $\text{H}_2\text{O}^*$, the latter desorbing in the gas phase and, thus, liberating again an active site. The majority of the calculated surface coverages is determined by this catalytic cycle.

At the typically high OCM operating temperatures, an equilibrium has been observed among $\text{O}_2$ in the gas phase and the surface oxygen species. This holds also for the current simulations, where reaction C1 is found to be quasi-equilibrated. As evident from the previous section, $\text{O}_2$ does not develop significant concentration gradients in the catalyst pores at the investigated operating conditions and, hence, also the surface coverage by active oxygen species $\text{O}^*$, does not exhibit significant evolutions as a function of the particle diameter, see Figure 4. Along the axial reactor coordinate there is a depletion of gaseous oxygen due to its conversion by the OCM reaction. This depletion is also reflected by the $\text{O}^*$ coverage.

The $\text{OH}^*$ species possesses the highest intraparticle surface coverage together with $\text{O}^*$. The concentration of these two surface species is closely connected via the catalytic cycle.

described above. As discussed by Sinev et al.,21 efficient OCM catalysts exhibit strong oxygen binding leading to a pronounced occurrence of the reverse OH* recombination reaction C5, which directly promotes the coverage by hydroxyl groups at the high operating temperatures in OCM. Across the pellet scale coordinate, a clear enhancement of the OH* is visible in Figure 4. The decreasing concentration of CH3· along this direction, as discussed above, leads to a decreasing participation of the OH* consuming reverse reaction C2 that is responsible for its calculated profile. Regarding the axial coordinate, it should be noted that the major OCM reaction product C2H6 reacts, similarly to CH4, with surface oxygen in an Eley−Rideal type of reaction, leading to C2H5· radicals. The C−H bond strength is weaker in ethane compared to methane, enhancing the generation of OH* surface intermediates as ethane gets produced. Additionally, as was shown by Chen et al.,34 the gradual increase in ethane concentration leads to higher propagation rates in the branched-chain gas-phase reaction mechanism, further increasing the total radical concentration and indirectly the OH* on the surface. As discussed in paragraph 3.2, all gas phase species are able to undergo hydrogen abstraction reactions on the same sites responsible also for CH3· radicals’ generation. Given that the concentration of these species increases in the axial direction of the reactor, the coverage in OH* is further enhanced, explaining its calculated profile in that direction.

Investigating the surface coverage of species related to the heterogeneous deep oxidation of CH3· radicals, it is clear that their shape is also strongly affected by the diffusion limitations of the radical. This is valid for all surface species that participate in the degradation of the methoxy species up to CHO*, with the much higher concentration of the CH3· radicals toward the center of the pellet clearly being reflected in the surface species coverage. Concerning the overall concentration of these species, the very low coverage by CH3O* is qualitatively in line with the IR studies of Lacombe et al.,55 who observed only very weak bands related to methoxy species. Moreover, the considerably higher percentage of the surface being covered by CH3O* compared to the rest of the species related to deep oxidation is explained by reaction C9 being much less exothermic to the rest of the relevant reactions. As described in the Supporting Information, thermodynamic consistency is applied during the calculation of the reaction enthalpies, the much higher formation enthalpy of the equivalent CHO· radical in the thermodynamic cycle leading to a mild exothermicity of reaction C9.

CO2 in the gas phase is in equilibrium with its adsorbed state, explaining its steady rise along the axial coordinate of the catalyst bed. At the studied conditions, reaction C13 is clearly quasi-equilibrated. In the pellet coordinate, the aforementioned mild intraparticle gradients of CO2 are not evident in the coverage of CO2*, due to the much larger change of the variable’s value in the axial direction. Nonetheless, there are differences as high as 3 orders of magnitude from the center of the pellet to its surface in the coverage by CO2*, especially at the start of the catalyst bed. The profile of H2O* is very similar to CO2* for equivalent reasons. It was already discussed that all C2 products have large diffusion lengths and, hence, do not

Figure 3. Concentration profiles at pellet and reactor scale for characteristic molecules and radicals at the conditions of Table 5. The origin of the pellet-coordinate axis corresponds to the center of the catalyst pellet, while the external surface of the catalyst pellet is located at 1.25 × 10−4 m. The remaining distance till 1.95 × 10−4 m corresponds to the interstitial gas phase. (a) C2H6 (b) CH2O, (c) CH3·, (d) HO2·.
develop significant pellet scale concentration gradients. As such, the surface species related to C2H4 oxidation, C2H2O* and C2H3O*, are also not affected by the diffusion limitations of the radicals, while their coverage increases along the axis due to the increasing concentration of C2H4 in the gas phase.

The effect of these observed profiles on calculated selectivity is significant. The production rate of CH3· is uniform along the pellet, given the steady O* and CH4 intraparticle profiles. The consumption of the radical, however, is clearly affected, not only by the decreasing CH3· concentration, which would result mainly in a decreasing rate but also from the intraparticle profile of OH*. Not considering the intraparticle profiles for the surface intermediates at the investigated operating conditions would result in a drop of C2 selectivity from 58.2% to 50.1%, clearly showing the importance of considering the relevant effect during kinetic modeling. The latter statement gains even more importance considering that the goal of such a microkinetic model is to facilitate information extraction from high-throughput experimentation, so as to guide catalyst design, meaning it should be able to guarantee a wide applicability versus operating conditions and catalyst properties.

4.3. Contribution Analysis. A contribution analysis, in combination with information from the surface and gas-phase species profiles, can elucidate the importance of the various reaction pathways, providing valuable insight in the occurring chemistry in relation to process and/or catalyst parameters. Such an analysis is performed in the current work at the outlet of the catalyst bed. The performed contribution analysis is differential with respect to the axial coordinate, while, due to the existence of intraparticle and interstitial gradients, it is
integral with respect to the pellet coordinate. All presented rates and relative contributions over phases are based on the “gas-phase” reactor volume, that is, referring to the gaseous space available in the interstitial phase as well as in the intraparticle phase.

The results of this analysis for the two considered phases are summarized graphically in Figure 5, where the net formation rates of all involved molecules and radicals are presented for the two considered phases (i.e., the intraparticle and interstitial phase). The complexity of the reaction pathways during OCM is more than obvious for both phases. Moreover, the differences in the preferred pathways between the two phases should be noted, noting that it is the intraparticle phase that accounts for the majority of the methane and oxygen consumption and production of the most crucial compounds. The actual magnitude of a reaction rate is represented in this figure via the width of the arrows, such that the relative importance of the two phases can be assessed by comparing the two panels. For example, it is obvious that CH₃· production takes place in the intraparticle phase, while their coupling proceeds in both phases. Also, the importance of direct CO₂ formation routes in the intraparticle phase, either from CH₃· or C₂H₄, is evident.

A more elaborate discussion based on the actual production and consumption rates is given below. In the interstitial phase, the major methane consumption routes relate to its reaction with OH· and H· radicals at a percentage equal to 62.5 and 25.8%, respectively, both leading to CH₃· radicals. In contrast, in the intraparticle phase, hydrogen abstraction via reaction C2 dominates, accounting for 97.8% of the consumption of methane, also leading to the production of CH₃· radicals. In total, the intraparticle phase contributes to more than 95% of the overall methane consumption. The produced CH₃· radicals are consumed via a multitude of reactions in the interstitial phase, the most important one being their coupling at a
percentage equal to 69.6%, leading to the desired product C2H6. Other competitive CH4 consumption pathways are their reaction with HO2· (5.2%), CH2O (5.6%), and C2H4 (7.8%). In the intraparticle phase, coupling in the catalyst pores is still considerable, accounting for 21.9% of CH4 consumption. Reaction C7 leading to the formation of surface methoxy species and eventually to undesired CO2 consumes 12.3% of the radicals, while it is the reverse of reaction C2 that is responsible for the highest percentage of CH4 consumption equal to 64.3%. The pronounced participation of this reaction is in line with the observations of Su et al.14 and can be attributed to the low value of the reaction enthalpy of hydrogen abstraction from methane, ΔH, for the studied catalyst. As observed by these authors and as can also be seen from eq A5 in the Supporting Information, due to thermodynamic consistency the low value of ΔH leads to a strong endothermicity of the hydroxyl recombination reaction C5, which in turn enhances the surface coverage of OH·. From the main catalytic cycle described above, hydroxyl recombination C5 is the most highly activated step for this catalyst. In the previous section, it was seen that multiple other reactions further contribute to the high hydroxyl surface coverage. From Figure 4, it can be seen that more than 70% of the catalyst surface is covered with OH· at these conditions, explaining the high consumption rate of CH4 radicals by the reverse reaction C2. Hence, the recognized high degree of surface hydroxylation16,21 is confirmed also in the results of the current work. The resulting high rate of CH4 radicals’ conversion back to methane was also identified in the simulations by Sinev.20 In all cases though, the net production rate of CH4· remains clearly positive in the intraparticle phase, the radical being produced by surface reactions and consumed at a lower rate in the pores by gas phase reactions, while in the interstitial phase there is clearly a net consumption of the radical.

As expected, in the interstitial phase, CH4· radical coupling accounts for the majority of C2H6 production (98.2%). In the intraparticle phase, the contribution of the CH4· coupling reaction to C2H6 production is still very high and equal to 96.7%. The backward reaction C4, despite the high surface coverage by OH·, contributes only by 3.2% to the produced C2H6, since C2H4· radicals are primarily consumed via reaction C17 toward C2H4, the latter step having a much lower activation barrier. In total, the intraparticle phase accounts for about 53% of the ethane production. Moreover, 92.7% of the produced ethane is consumed via the forward reaction C4, with gas phase reaction with OH· and CH4· toward C2H4·, contributing for the rest of this percentage.

The production of C2H4 in the interstitial phase is mainly attributed to the dehydrogenation and oxy-dehydrogenation of C2H4· radicals with the former reaction contributing by 51.6% and the latter by 27.5%. Decomposition of C2H4· radicals is the only other reaction leading to the production of C2H4 at a relatively high percentage of 20.8%. The intraparticle production of C2H4, though, is dominated, as mentioned previously, by the surface H abstraction from C2H4· (96.9%). In total, about 75% of C2H4 production takes place in the intraparticle phase. On the contrary, a variety of gas phase reactions account for the consumption of C2H4 with its coupling with CH4· radicals (71.0%) being more pronounced, while in the intraparticle phase catalytic oxidation via reaction C14 is the primary C2H4 consumption route at 92.3%. As such, the overall contribution of this phase is very high and amounts to 83.6%.

In the interstitial phase 62.6% of the CO is consumed with HO2· toward the production of CO2, while the rest is converted to CHO· radicals. On the contrary, in the intraparticle phase, CO reacts almost exclusively toward CO2 via adsorption and catalytic oxidation. CO2 in the interstitial phase is produced only via CO oxidation, while in the intraparticle phase, as already commented, the catalytic oxidation of C2H4 and of CH4· radicals also contributes. However, the high concentration of CO at the end of the catalyst bed as compared to that of C2H4 and even more of CH4·, results in a clear domination of the CO oxidation pathway at a percentage of 94.8%.

As already discussed, the catalyst surface contributes significantly to the production of the CH4· radicals. The same holds clearly also for most of the other radicals, where it is seen that in the intraparticle phase the respective H-atom abstraction reactions account for a major part of their production, namely 87.7% for C2H4· via reaction C3, 92.3% for C2H4· via reaction C4 and 48.8% for CHO· via reaction C19. On the other hand, the surface is also responsible for radical quenching. HO2·, which, as already discussed, facilitates to a large extent gas phase deep oxidation, is consumed solely via heterogeneous reactions in the intraparticle phase and more specifically via reaction C26 at a 99.8%.

Given that the experimental conditions are typical for OCM and since O2 is still far from depleted at the end of the catalyst bed, it is believed that the analysis is representative for OCM kinetics of the studied catalyst at any axial position along the reactor. A similar analysis has been conducted at the beginning of the catalyst bed to evaluate the effect of the gas mixture composition. Noted difference is the pronounced role of the homogeneous reaction of CH4 and O2 toward the production CH2· and HO2· radicals, which, given its high activation barrier compared to the reaction of CH4 with radicals, is important only at the onset of the OCM reaction.37 An equally important difference is that CH4· radicals are consumed in the interstitial phase almost exclusively by coupling (94.2%), since numerous OCM products that react with CH4·, namely H2, H2O, HO2·, CH3O, C2H6, and C2H4, do not have yet considerable concentration. Finally, at the inlet, the primary route for catalytic CO2 production is obvious with 36.5% being produced in the intraparticle phase from CH4· total oxidation, in line with former observations.36 Nonetheless, the main consumption and production routes described previously were found to be valid also at this position.

4.4. Effect of Textural Properties. Thybaut et al.25 have discussed the global effect of various textural properties on catalyst performance. In the same respect, a sensitivity analysis would provide additional understanding on their effect but goes beyond the scope of the present manuscript. We have opted to discuss the effects of two important catalyst texture properties, porosity and surface area, in detail in the following two paragraphs by means of a contribution analysis. These simulations are performed by modifying the value of the investigated texture property, while keeping the other properties reported in Table 5 constant.

4.4.1. Pellet Porosity. As reported in Table 6, increasing porosity gives rise to an increase in methane conversion and selectivity toward C2 products.25 On average, the participation of the interstitial phase related to CH4 consumption remains largely unaffected and, as also commented in the previous section, averages 5% of the total CH4 consumption. However, looking at the contribution of the various complex pathways in the intraparticle phase, it can be seen that, as porosity increases,
a relative rise of CH$_4$ consumption via gas phase reactions over catalytic reactions occurs. Nevertheless, the heterogeneous pathways of CH$_4$ consumption are still considerably more important. At the same time though, a significant decrease in CH$_4$ production via the reverse of catalytic reaction C2 can be observed, due to relative suppression of catalytic pathways, explaining the overall increase in CH$_4$ conversion.

As expected, the increase of porosity leads to a considerable increase in the consumption of CH$_3^+$ radicals via gas phase reactions versus catalytic ones. For an increase of porosity from 0.1 to 0.6 a shift of 12.3−87.7% to 34.0−66.0% is observed in the respective contribution of homogeneous versus heterogeneous intraparticle consumption. The total consumption of CH$_3^+$ is higher actually in the lower porosity case; however, the promotion of the gas phase pathways in the high porosity case compensates for this, resulting in an important rise of the coupling versus the deep oxidation route. In parallel, CH$_2^+$ radical production occurs to a larger extent via homogeneous pathways, although catalytic reaction C2 still remains the main production route. The combined effect of these changes in contributions results in a rising net production rate for CH$_2^+$ radicals in the intraparticle phase. Moreover, the increase of porosity at a given surface area essentially corresponds to a larger average pore diameter, increasing from 3.11×10$^{-08}$ to 1.86×10$^{-07}$ m at the investigated range. As a result, the lifetime of CH$_3^+$ radicals increases four times, from 1.78×10$^{-06}$ to 7.22×10$^{-06}$ s. As such, their concentration in the interstitial phase is 21% higher by increasing porosity from 0.1 to 0.6, while the second order of the coupling reaction leads to a more pronounced increase of the CH$_3^+$ coupling rate compared to gas phase oxidation, namely the reaction with HO$_2^+$ radicals.

4.4.2. Internal Surface Area. Increasing the internal surface area from 1 to 6 m$^2$ g$^{-1}$ leads to a sharp rise of CO$_2$ selectivity, accompanied by a corresponding drop in the selectivity of C$_2$ products, mainly affecting C$_2$H$_6$ and, to a lesser extent, also C$_3$H$_4$. At the same time, the CH$_4$ conversion shows a steady rise with increasing surface area. The latter can be attributed to the increase in the rate of CH$_4$ consumption via catalytic reactions due to the higher surface area, as clearly seen in Table 7. Moreover, it is observed that a respective rise in CH$_4$ consumption via gas-phase reactions also occurs in the intraparticle phase with increasing surface area. This is explained via the enhancement of radicals’ production via catalytic pathways that further promotes the gas phase reactions with CH$_4$. For example, for the change of surface area from 1 to 6 m$^2$ g$^{-1}$, the contribution of catalytic reaction C21 in the production of H radicals increases from 21.6% to 53.2%, leading to more than an order of magnitude increase in its net production rate. For similar reasons, OH radicals exhibit an equivalent rise, resulting in a concentration increase of H and OH of four and three times, respectively, the specific radicals being, as discussed, the main reactants with CH$_4$ via homogeneous reactions. The importance of OH-mediated C−H bond activation pathways was also highlighted recently in the work of Takanabe and Iglesia, where it was reported that these are crucial in achieving high C$_2$ yields.

The selectivity shifts can be explained similarly via the increased participation of the heterogeneous network that directly affects the consumption of CH$_3^+$ radicals. As seen in Table 7, there is an evident rise in the rate of radicals consumed via catalytic reactions with increasing surface area. The gas-phase reactions are also enhanced, as commented, due to the increased concentration of radicals in the catalyst pores, leading to a small increase in the consumption of radicals via homogeneous reactions in the intraparticle phase. However, the relative contribution of the heterogeneous reactions in CH$_3^+$ consumption rises steadily from 60.7% to 86.3%.

Considering the analysis of this paragraph, in combination with the findings of the previous one, the textural features of an optimal catalyst can be elucidated. It has been shown via contribution analysis that the intraparticle phase accounts for the majority of the consumption and production of participating compounds, including the gas-phase intermediates. This statement holds not only for the typically considered CH$_3^+$ radicals but for all gas phase species via complex surface−radicals interactions. A high catalyst porosity has been found to be very beneficial to OCM performance leading to an increase of CH$_4$ conversion and of C$_2$ selectivity. Due to the large pores of such a material, CH$_3^+$ coupling is significantly enhanced in
the intraparticle phase, avoiding deep oxidation routes. Of course, this trend cannot extend to extreme porosity values, since in that case the heterogeneous activation of CH₄ would decrease to unacceptable limits. A high surface area on the other hand promotes the heterogeneous consumption routes at a level that becomes unselective for OCM. It can be speculated that a high porosity material with a high concentration of surface defects would represent an optimal OCM catalyst, activating sufficiently CH₄ on one hand but avoiding CH₃⁺ deep oxidation on the other, such that coupling in the pores of the catalyst dominates leading to optimal C₂ yields. Potentially, structured catalyst formulations providing similar textural characteristics should be considered for OCM to achieve maximal C₂ yields.

5. CONCLUSIONS

Intraparticle gradients for reactants, products, radicals, and surface species are now accounted for in a one-dimensional heterogeneous reactor model for simulating oxidative coupling of methane (OCM). Significant gradients develop for radicals as well as for the related surface species, even at an intrinsic kinetics regime for reactants and products. These gradients directly impact conversion and selectivity and, hence, are necessary to take into account for adequate simulation of OCM behavior.

The use of a combined complex microkinetic and reactor model provides unprecedented insight into the occurring phenomena. The majority of the methane is heterogeneously activated by oxidized sites on the catalyst surface in the intraparticle phase. A smaller, but non-negligible, fraction is activated homogeneously in the intraparticle phase, while only minor amounts are consumed in the interstitial phase. The coupling of the formed CH₃⁺ proceeds at significant degree both in the interstitial and in the intraparticle phase. Surface hydroxyl groups are found to affect negatively performance by consuming a considerable part of CH₃⁺ in the intraparticle phase. Optimal C₂ yields can be achieved by maximizing the porosity of catalyst pellets, provided that a sufficient CH₄ activation is achieved, so as to maximize the coupling route over the heterogeneous oxidation of CH₄⁺.

- ASSOCIATED CONTENT
- Supporting Information
  Detailed methodology, additional tables as described in the text. This information is available free of charge via the Internet at http://pubs.acs.org/

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  Notes
  The authors declare no competing financial interest.

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- NOMENCLATURE

  Roman Symbols
  $a_i$: external surface area of the catalyst, m⁻²
  $a_{i,k}$: gas-solid interfacial surface area, m⁻²
  $A_i$: pre-exponential factor of reaction $i$, unit reaction dependent
  $A_r$: reactor cross-sectional surface area, m⁻²
  BDECH₃: bond dissociation energy of O₂, J mol⁻¹
  $C_i$: concentration of component $i$, mol m⁻³
  $d_{i,k}$: average distance between two catalyst pellets, m
  $d_{i}$: catalyst pellet diameter, m
  $d_r$: reactor diameter, m
  $D_{i,k}$: effective diffusivity of component $i$, m² s⁻¹
  $D_m$: molecular diffusivity of component $i$ in a gas mixture, m² s⁻¹
  $D_{i,j}$: binary diffusivity of component $i$ in $j$, m² s⁻¹
  $E_{a,i}$: activation energy of reaction $i$, J mol⁻¹
  $E_{ai}$: intrinsic activation barrier of reaction family $i$, J mol⁻¹
  $F_{i}$: total volumetric flow rate, m³ s⁻¹
  $F_{i,k}$: total molar flow rate, mol s⁻¹
  $G^0$: standard-state Gibbs free energy, J mol⁻¹
  $H^P$: standard-state enthalpy, J mol⁻¹
  $k_i$: rate coefficient of reaction $i$, unit reaction dependent
  $k_{a,i}$: pseudo-first-order rate coefficient, s⁻¹
  $L$: length of catalyst bed, m
  $L_i$: density of active sites, mol m⁻²
  $M_i$: molar mass of component $i$, kg mol⁻¹
  $N_{gas,i}$: total number of gas-phase reactions
  $N_{mol,i}$: total number of molecules
  $N_{rad,i}$: total number of radicals
  $N_{surf,i}$: total number of surface species
  $n$: reaction order
  $P_{tot}$: total pressure, Pa
  $Q_{i-CH₃}$: C–H bond energy of methane, J mol⁻¹
  $Q_{i-X}$: C–H bond energy of X–H compound, J mol⁻¹
  $R$: universal gas constant, 8.314 J mol⁻¹ K⁻¹
  $r_i$: rate of reaction $i$, mol m⁻³ s⁻¹
  $r$: average pore radius, m
  $R_i$: net production rate of component $i$, mol m⁻³ s⁻¹
  $S_i$: standard entropy, J mol⁻¹ K⁻¹
  $S_i$: specific surface area, m² kg⁻¹
  $T$: temperature, K
  $W_i$: stoichiometric coefficient of component $i$ in reaction $j$
  $x_i$: molar fraction of component $i$
  $z$: reactor axial coordinate, m

  Greek Symbols
  $\alpha$: transfer coefficient of Polanyi parameter for reaction family $i$
  $\Delta H$: standard reaction enthalpy, J mol⁻¹
  $\Delta H_i$: standard formation enthalpy, J mol⁻¹
  $\varepsilon_b$: bed porosity, m⁻³
  $\varepsilon_c$: catalyst porosity, m⁻³
  $\theta_i$: fraction of the surface covered by species $i$
  $\xi$: diffusion length of component $i$, m
  $\rho$: catalyst density, kg m⁻³
  $(\Sigma x_i)$: diffusion volume of component $i$, m³ mol⁻¹
  $\tau_c$: catalyst pellet tortuosity, m⁻²
  $\tau$: lifetime, s

  Superscripts
  f: forward reaction step
  b: backward reaction step
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subscripts

c: catalyst pellet
g: gas phase
r: reactor
s: refers to $R_s$ calculated via the global reaction network presented in section 3.4
0: initial conditions

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